

Initial use of di-2-pyridyl ketone oxime in chromium carboxylate chemistry: Triangular $\{\text{Cr}^{\text{III}}_3(\mu_3\text{-O})\}^{7+}$ compounds and unexpected formation of a carboxylate-free dichromium(II,II) complex

Konstantina V. Pringouri ^a, Catherine P. Raptopoulou ^b,
Albert Escuer ^c, Theocharis C. Stamatatos ^{a,*}

^a Department of Chemistry, University of Patras, 265 04 Patras, Greece

^b Institute of Materials Science, NCSR “Demokritos”, 153 10 Aghia Paraskevi Attikis, Greece

^c Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, Barcelona 08028, Spain

Received 12 June 2006; received in revised form 24 July 2006; accepted 24 July 2006

Available online 3 August 2006

Inorganic Chemistry – The Next Generation.

Abstract

A systematic investigation of the $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)/(\text{py})_2\text{CNOH}$ [$(\text{py})_2\text{CNOH}$ = di-2-pyridyl ketone oxime] reaction system is described, involving the determination of the influence of the $\text{Cr}^{\text{III}}:(\text{py})_2\text{CNOH}$ ratio, the temperature and the presence of counterions on the identity of the reaction products. As a consequence, complexes $[\text{Cr}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ (**1** · 2H₂O), $[\text{Cr}_3\text{OCl}(\text{O}_2\text{CCMe}_3)_4\{(\text{py})_2\text{CNO}\}_2] \cdot 2\text{Me}_2\text{CO}$ (**2** · 2Me₂CO) and $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_4\{(\text{py})_2\text{CNO}\}_2(\text{H}_2\text{O})](\text{NO}_3) \cdot \text{H}_2\text{O} \cdot 0.5\text{Me}_2\text{CO}$ (**3** · H₂O · 0.5Me₂CO) have been isolated and structurally characterized by single-crystal X-ray studies. $(\text{py})_2\text{CNO}^-$ behaves as a *N,N'*-bidentate chelating and/or *N,N',O*-tridentate bridging ligand binding through one 2-pyridyl and the oximate nitrogen atoms, and/or the oximate oxygen atom. **1** is a relatively stable air-stable dinuclear Cr(II) complex with no metal–metal bonding arising, from the ligand-assisted reduction of the ‘basic carboxylate’ Cr(III) triangle. The structures of **2** and **3** consist of similar neutral and cationic triangles of Cr^{III} ions, respectively, centered by a triply bridging oxo ligand and with two edge-bridging oximate groups from the two 2.1110 $(\text{py})_2\text{CNO}^-$ ligands. Variable-temperature magnetic susceptibility studies and EPR data for **2** reveal an antiferromagnetically-coupled system with an $S_{\text{T}} = 3/2$ ground state. Solid-state IR and ligand field spectra of **2** are briefly discussed in terms of its structure.
© 2006 Elsevier B.V. All rights reserved.

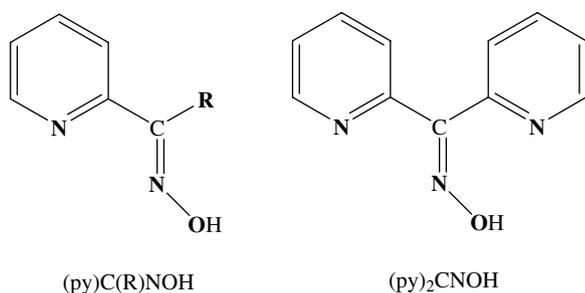
Keywords: Dinuclear chromium(II) complexes; Chromium(III) triangles; Di-2-pyridyl ketone oximate complexes; EPR spectra; Magnetic properties

1. Introduction

There is currently a renewed interest in the coordination chemistry of oximes [1]. The research efforts are driven by a number of considerations. These include the solution of pure chemical problems [2–4], the desire to provide useful

bioinorganic models (oximes may be considered to be reasonable models for the biologically significant imidazole donor group of the amino acid histidine) [5], the design of Ca²⁺- and Ba²⁺-selective receptors based on site-selective transmetallation of multinuclear polyoxime–zinc(II) complexes [6], the development of new oxygen activation catalysts based on nickel(II)–polyoximate complexes [7], the application of metal ion/oxime systems as simple and efficient catalysts for the hydrolysis of organonitriles [8]

* Corresponding author. Tel.: +30 2610 996019; fax: +30 2610 997118.
E-mail address: thstama@chemistry.upatras.gr (T.C. Stamatatos).

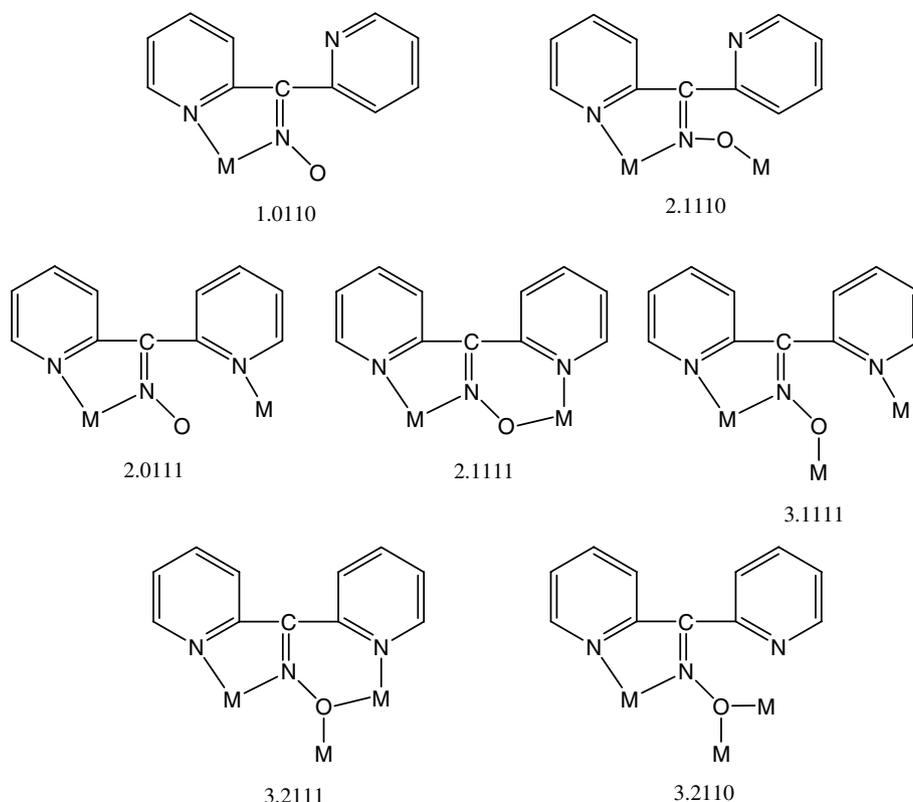


Scheme 1. Structural formulae and abbreviations of the 2-pyridyl oxime ligands discussed in the text (R = H, Me, Ph, etc.).

(metal ions can behave as extremely strong activators of RCN towards nucleophilic attack by $\text{OH}^-/\text{H}_2\text{O}$), the mechanistic study of corrosion inhibition by Acorga P5000 (a modern corrosion inhibitor comprising 5-nonylsalicylaldoxime as a mixture of carbon-chain isomers) on iron surfaces [9] and the employment of oximate ligands in the synthesis of homometallic [1,10–12] and heterometallic [1,12,13] clusters and coordination polymers [14] with interesting magnetic properties, including single-molecule magnetism [11,15] and single-chain magnetism [14,16] behaviours.

Ligands containing one oxime group and one pyridyl group, without other donor atoms, are popular in coordination chemistry. Most of these ligands contain a 2-pyridyl

group and thus are named 2-pyridyl oximes, $(\text{py})\text{C}(\text{R})\text{NOH}$ (Scheme 1). The anionic forms, $(\text{py})\text{C}(\text{R})\text{NO}^-$, of these molecules are versatile ligands for a variety of research objectives, including μ_2 and μ_3 behaviour [1a,12]. Di-2-pyridyl ketone oxime [IUPAC name: di-pyridin-2-ylmethanone oxime, $(\text{py})_2\text{CNOH}$, Scheme 1] occupies a special position amongst the 2-pyridyl oximes because the R group is also a 2-pyridyl group; the compound is thus a bis(2-pyridyl) oxime. One area to which the anionic ligand $(\text{py})_2\text{CNO}^-$ is relevant is the chemistry of metallacrowns (MCs) [17]. Another attractive aspect of $(\text{py})_2\text{CNO}^-$ is its great coordinative flexibility and ability to coordinate to metal ions through either one, or both pyridyl groups, acting as chelating or bridging ligand (Scheme 2), characteristics that have led to polynuclear 3d-metal complexes (clusters) with impressive structures and interesting magnetic properties [12,15,18]. A last interesting chemical feature is the activation of $(\text{py})_2\text{CNOH}$ by 3d-metal centers, which appears to be a fruitful area of contemporary synthetic inorganic chemistry. Examples of this activation are the Mn-assisted transformation of $(\text{py})_2\text{CNOH}$ into the coordinated dianion of the *gem*-diol form of di-2-pyridyl ketone through NO_3^- generation [20a] and the in situ transformation of $(\text{py})_2\text{CNOH}$ into the coordinated ligands di-2-pyridylimine, (amino)di-2-pyridylmethyl ethyl ether and (amino)di-2-pyridylmethyl methyl ether upon its reaction with $[\text{V}^{\text{III}}\text{Cl}_3(\text{THF})_3]$ in various solvents [20b].



Scheme 2. The crystallographically established coordination modes of $(\text{py})_2\text{CNO}^-$ in metal complexes, and the Harris notation [19] that describes these modes.

Although the published coordination chemistry of $(\text{py})_2\text{-CNOH}$ and $(\text{py})_2\text{CNO}^-$ is rich [1a,12], chromium(II) or chromium(III) complexes bearing $(\text{py})_2\text{CNOH}$ or $(\text{py})_2\text{CNO}^-$ ligands have not been reported so far.

We have been exploring “ligand blend” reactions involving carboxylates and the anions of 2-pyridyl oximes (Scheme 1) as a means to high-nuclearity 3d-metal species [12,20a,21–24]. Our results with Mn [20a,21,23b], Co [22], Ni [23] and Cu [24] have been very encouraging. For example, the use of methyl 2-pyridyl ketone oxime (Scheme 1, R = Me) in Mn carboxylate chemistry has yielded a new family of triangular $\{\text{Mn}^{\text{III}}_3(\mu_3\text{-O})\}^{7+}$ core-containing products; the products are very unusual in being ferromagnetically coupled with a resultant $S = 6$ ground-state spin and are the first triangular single-molecule magnets [21e]. We have thus decided to extend the exploration of the general carboxylate/2-pyridyloximate “ligand blend” in chromium(III) chemistry, and we can now report that di-2-pyridyl ketone oxime [$(\text{py})_2\text{CNOH}$, Scheme 1] has yielded new triangular products possessing the $\{\text{Cr}^{\text{III}}_3(\mu_3\text{-O})\}^{7+}$ core and a remarkable carboxylate-free dichromium(II,II) complex with no metal–metal bonding, arising from the reduction of the chromium(III) starting material by the ligand in air. The crystal structure of the latter compound has been very recently communicated [25]. Oxo-centered, triangular chromium(III) complexes are valuable precursors for the synthesis of higher nuclearity clusters exhibiting interesting magnetic and EPR properties [26].

2. Experimental

2.1. Reagents and physical measurements

All manipulations were performed under aerobic conditions using materials as received (Aldrich Co). All chemicals and solvents were of reagent grade. $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ was synthesized as previously described [27].

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. IR spectra ($4000\text{--}500\text{ cm}^{-1}$) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. Solid-state (diffuse reflectance) spectra in the $200\text{--}800\text{ nm}$ range were recorded on a Varian Cary 3 spectrometer, at the in-house facilities of the Chemistry Department of the University of Patras, equipped with an integration sphere. Magnetic susceptibility measurements in the range $2\text{--}300\text{ K}$ and magnetization measurements ($2\text{--}4\text{ K}$) in the field range $0.1\text{--}5\text{ T}$ for complex $2 \cdot 2\text{Me}_2\text{CO}$ were performed with a Quantum Design SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona (Spain). All measurements were performed on polycrystalline samples. Data were corrected for diamagnetic contributions calculated from Pascal’s constants. EPR spectra were recorded with a Bruker ES200 spectrometer at X-band frequency.

2.2. Compound preparation

2.2.1. $[\text{Cr}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ (**1** · $2\text{H}_2\text{O}$)

2.2.1.1. Method A. A green slurry of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ (0.093 g, 0.10 mmol) in MeCN (30 mL) was treated with solid $(\text{py})_2\text{CNOH}$ (0.060 g, 0.30 mmol). The resulting green solution was refluxed for 12 h during which time the colour of the solution turned to dark brown. The solution obtained was further stirred at ambient temperature for 3 h, filtered and layered with Et_2O . After 3 weeks, brownish red crystals of the product were formed which were collected by filtration, washed with MeCN ($2 \times 5\text{ mL}$) and Et_2O ($2 \times 5\text{ mL}$), and dried in air. Yield: 25% (based on the oxime). The air-dried solid was analyzed as **1** · $2\text{H}_2\text{O}$. *Anal. Calc.* for $\text{C}_{44}\text{H}_{36}\text{N}_{12}\text{O}_6\text{Cr}_2$: C, 56.64; H, 3.90; N, 18.02. Found: C, 56.38; H, 3.75; N, 18.24%. IR spectral data (KBr, cm^{-1}): 3388 sb, 3055 w, 1594 vs, 1559 m, 1461 vs, 1380 m, 1270 m, 1213 m, 1130 vs, 1105 w, 1055 w, 1025 m, 975 m, 788 s, 742 s, 705 m, 637 m, 522 m, 495 w.

2.2.1.2. Method B. Treatment of a stirred, white slurry of $[\text{Cr}(\text{CO})_6]$ (0.044 g, 0.20 mmol) in MeCN/ H_2O (30 mL, 1:1 v/v) with solid $(\text{py})_2\text{CNOH}$ (0.120 g, 0.60 mmol) resulted in a pale-yellow suspension, which, upon refluxing for 5 days, gave a brown solution due to slow oxidation of Cr^0 under aerobic conditions. The brown solution soon deposited a brownish red microcrystalline solid, which was collected by filtration, washed with MeCN ($2 \times 5\text{ mL}$) and Et_2O ($2 \times 5\text{ mL}$), and dried in vacuo over silica gel. Yield: 55% (based on the total available chromium). The dried solid analyzed satisfactorily as **1** · $2\text{H}_2\text{O}$. The identity of the product was further confirmed by IR spectroscopic comparison with the authentic sample prepared by method A.

2.2.2. $[\text{Cr}_3\text{OCl}(\text{O}_2\text{CCMe}_3)_4\{(\text{py})_2\text{CNO}\}_2] \cdot 2\text{Me}_2\text{CO}$ (**2** · $2\text{Me}_2\text{CO}$)

Complex **2** · $2\text{Me}_2\text{CO}$ was synthesized under solvothermal techniques. A mixture of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$, $(\text{py})_2\text{CNOH}$ and CH_2Cl_2 at a ratio of 1:2:700 was sealed in a Teflon-lined autoclave, heated to $150\text{ }^\circ\text{C}$ for 3 days, and cooled to room temperature with a rate of $2\text{ }^\circ\text{C h}^{-1}$. The resulting dark brown solution was evaporated to dryness under reduced pressure and the residue was dissolved in Me_2CO (10 mL). The solution was allowed to slowly evaporate at room temperature. After 2 days, dark brown crystals of the product formed which were collected by filtration, washed with Me_2CO ($2 \times 3\text{ mL}$) and Et_2O ($2 \times 5\text{ mL}$), and dried in air. Yield: 72% (based on Cr^{III}). The air-dried solid analyzed as solvate-free. *Anal. Calc.* for $\text{C}_{42}\text{H}_{52}\text{N}_6\text{O}_{11}\text{ClCr}_3$: C, 50.02; H, 5.21; N, 8.34; Cl, 3.52. Found: C, 49.88; H, 5.15; N, 8.44; Cl, 3.50%. IR spectral data (KBr, cm^{-1}): 3400 w, 2962 m, 2930 w, 1588 vs, 1484 m, 1462 m, 1420 vs, 1378 w, 1361 w, 1227 m, 1124 m, 1101 m, 1035 w, 972 w, 797 m, 742 m, 712 w, 660 w, 617 m, 531 w, 477 m.

2.2.3. $[Cr_3O(O_2CCMe_3)_4\{(py)_2CNO\}_2(H_2O)](NO_3) \cdot H_2O \cdot 0.5Me_2CO$ ($3 \cdot H_2O \cdot 0.5Me_2CO$)

2.2.3.1. *Method A.* To a dark brown solution of **2** (0.100 g, 0.10 mmol) in Me_2CO (7 mL) was slowly added a colourless solution of $NaNO_3$ (0.026 g, 0.30 mmol) in H_2O (10 mL). The resulting brownish suspension was kept under stirring for 30 min, filtered and the filtrate was allowed to slowly evaporate at room temperature. After 3 days, pink crystals of the product formed which were collected by filtration, washed with H_2O (1×3 mL), and dried in vacuo over silica gel. Yield: 20% (based on Cr^{III}). The dried solid analyzed as solvate-free. *Anal. Calc.* for $C_{42}H_{54}N_7O_{15}Cr_3$: C, 47.90; H, 5.18; N, 9.31. Found: C, 47.68; H, 5.25; N, 9.34%. IR spectral data (KBr, cm^{-1}): 3370 mb, 2963 m, 2928 w, 1585 vs, 1484 m, 1462 m, 1421 s, 1385 vs, 1227 m, 1124 m, 1101 m, 1031 w, 975 w, 791 m, 742 m, 709 w, 684 s, 659 w, 617 m, 472 m.

2.2.3.2. *Method B.* A green solution of $[Cr_3O(O_2CCMe_3)_6(H_2O)_3](O_2CCMe_3)$ (0.093 g, 0.10 mmol) in Me_2CO (20 mL) was treated with solid $(py)_2CNOH$ (0.040 g, 0.20 mmol). The resulting green solution was refluxed for 30 min during which time the colour of the solution turned to dark brown. A colourless solution of $NaNO_3$ (0.026 g, 0.30 mmol) in H_2O (5 mL) was slowly added to the dark brown solution. The resulting brown slurry was further stirred at ambient temperature for 30 min, filtered and left undisturbed to slowly evaporate at room temperature. After 3 days, pink crystals of the product formed which were collected by filtration, washed with H_2O (1×3 mL)

and cold Me_2CO (2 mL), and dried in vacuo over silica gel. Yield: 34% (based on Cr^{III}). The dried solid analyzed satisfactorily as **3**. The identity of the product was further confirmed by IR spectroscopic comparison with the authentic sample prepared by method A.

2.3. Single-crystal X-ray crystallography

Complete crystal data and parameters for data collection and processing are listed in Table 1. Diffraction measurements for compound **1**· $2H_2O$ were performed on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo $K\alpha$ radiation, while for compounds **2**· $2Me_2CO$ and **3**· $H_2O \cdot 0.5Me_2CO$, the data collection was performed on an Oxford Diffraction CCD instrument using graphite-monochromated Mo $K\alpha$ radiation. Unit cell dimensions for complex **1**· $2H_2O$ were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23^\circ$. Intensity data were recorded using a θ – 2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and Ψ -scan absorption corrections were applied. Unit cell dimensions for complexes **2**· $2Me_2CO$ and **3**· $H_2O \cdot 0.5Me_2CO$ were determined and refined by using 37414 ($3.13 \leq \theta \leq 25.00^\circ$) and 61658 ($3.13 \leq \theta \leq 25.00^\circ$) reflections, respectively. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software [28].

Table 1
Crystallographic data for complexes **1**· $2H_2O$, **2**· $2Me_2CO$ and **3**· $H_2O \cdot 0.5Me_2CO$

Parameter	1 · $2H_2O$	2 · $2Me_2CO$	3 · $H_2O \cdot 0.5Me_2CO$
Empirical formula	$C_{44}H_{36}Cr_2N_{12}O_6$	$C_{48}H_{64}Cr_3N_6ClO_{13}$	$C_{43.5}H_{60.5}Cr_3N_7O_{16.5}$
Formula weight	932.92	1124.63	1101.61
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/a$
<i>a</i> (Å)	23.692(5)	14.2300(10)	19.6419(11)
<i>b</i> (Å)	11.306(3)	21.924(2)	26.3508(13)
<i>c</i> (Å)	19.231(5)	23.0080(10)	20.2109(13)
β (°)	125.308(9)	128.200(2)	93.435(5)
<i>V</i> (Å ³)	4203.7(18)	5640.9(7)	10442.0(10)
<i>Z</i>	4	4	8
<i>D</i> _{calc.} (g cm ⁻³)	1.474	1.324	1.399
<i>T</i> (K)	298	100(2)	100(2)
λ^a (Å)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	0.582	0.677	0.686
θ Range (°)	2.09–25.00	3.51–25.00	3.13–25.00
Collected reflections	3825	36651	61658
Unique reflections (<i>R</i> _{int})	3699 (0.0219)	9560 (0.0483)	18271 (0.0698)
No. of refined parameters	300	751	1319
Observed reflections ^b	2815	6635	10706
<i>R</i> ₁ ^c , <i>wR</i> ₂ ^d [<i>I</i> > 2 σ (<i>I</i>)]	0.0527, 0.1353	0.0523, 0.1329	0.0631, 0.1403
Goodness-of-fit (on <i>F</i> ²)	1.067	1.039	1.031
($\Delta\rho$) _{max.} , ($\Delta\rho$) _{min.} (e Å ⁻³)	0.729, –0.408	0.669, –0.748	0.992, –0.640

^a Mo $K\alpha$ radiation.

^b $I > 2\sigma(I)$.

^c $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$.

^d $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

The structures were solved by direct methods using SHELXS-86 [29] and refined by full-matrix least-squares techniques of F^2 with SHELXL-97 [30]. For complexes $\mathbf{1} \cdot 2\text{H}_2\text{O}$ and $\mathbf{3} \cdot \text{H}_2\text{O} \cdot 0.5\text{Me}_2\text{CO}$, all H atoms were introduced at calculated positions as riding on bonded atoms. For complex $\mathbf{2} \cdot 2\text{Me}_2\text{CO}$, all methyl hydrogen atoms were introduced at calculated positions as riding on bonded atoms, while the H atoms of the $(\text{py})_2\text{CNO}^-$ ligands were located by difference maps and refined isotropically. All non-H atoms were refined with anisotropic thermal parameters.

3. Results and discussion

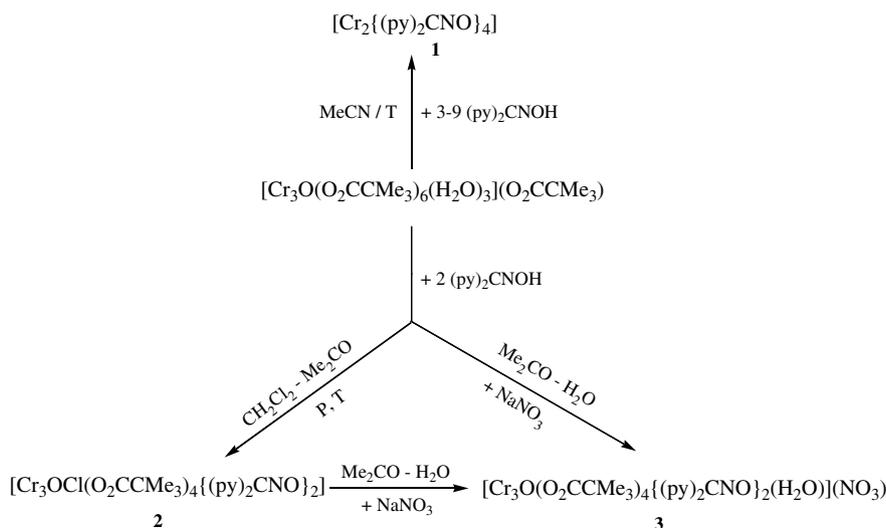
3.1. Syntheses

As stated in Section 1, we have a longstanding interest in the use of anionic 2-pyridyl oximes (Scheme 1) for the preparation of 3d-metal clusters [12]. Although a variety of homometallic 3d-metal 2-pyridyloximate clusters have been reported [1a,12], no Cr(II) and/or Cr(III) complexes have been structurally characterized. As a starting point, we decided to investigate the chromium(III)/carboxylate/di-2-pyridyl ketone oximate $[(\text{py})_2\text{CNO}^-]$, Scheme 1] chemistry. We selected the oxo-centered, triangular chromium(III) carboxylate cluster $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ [27] as the starting material. Obviously $(\text{py})_2\text{CNOH}$ can be deprotonated by O^{2-} or $\text{O}^{2-}/\text{Me}_3\text{CCO}_2^-$; we anticipated that interesting types of $\text{Cr}^{\text{III}}/\text{Me}_3\text{CCO}_2^-/(\text{py})_2\text{CNO}^-$ species might result, as long as the $\text{Me}_3\text{CCO}_2^- : (\text{py})_2\text{CNOH}$ ratio was high enough to leave an amount of non-protonated carboxylate ions in the reaction mixtures, given the fact that both $\text{Me}_3\text{CCO}_2^-$ and $(\text{py})_2\text{CNO}^-$ ligands can potentially adopt a great variety of terminal and bridging modes. As shown in Scheme 3, the chemical and structural identity of the products from the $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)/(\text{py})_2\text{CNOH}$ general reaction system depend on a variety

of synthetic parameters, i.e. the $\text{Cr}^{\text{III}}/(\text{py})_2\text{CNOH}$ ratio, the temperature, the solvent and the presence/absence of counter-anions.

Reaction of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ with three equivalents of $(\text{py})_2\text{CNOH}$ in MeCN under aerobic conditions and reflux for 12 h gave a dark brown solution, from which brownish red crystals of the dichromium(II,II) complex $[\text{Cr}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ ($\mathbf{1} \cdot 2\text{H}_2\text{O}$) were isolated in low ($\sim 25\%$) yield. It was apparent that an unusual reduction of chromium(III) to chromium(II) in air had taken place. The solvent or solvent impurities cannot be responsible for the chromium(III) reduction; upon refluxing green slurries of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ in MeCN at various “concentrations” under aerobic conditions for 12–24 h, with or without Et_2O (the precipitating solvent in the preparation of $\mathbf{1} \cdot 2\text{H}_2\text{O}$), we noticed no obvious (e.g. dissolution or colour change) signs of reduction. The possibility that the reducing agent might be a decomposition product of $(\text{py})_2\text{CNOH}$ was also ruled out, because this ligand maintains its chemical integrity upon dissolution in refluxing MeCN under aerobic conditions (NMR evidence). Thus, we do believe that the reducing reagent is an amount of the ligand itself, with its unidentified oxidation product(s) remaining in the solution. In accordance with our proposal, the reaction of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ with an excess of the ligand, i.e. $\text{Cr}^{\text{III}}_3 : (\text{py})_2\text{CNOH} = 1:9$, gives the same $\text{Cr}^{\text{II,II}}_2$ product but in higher yield ($>45\%$). Metal-ion assisted oxidations of oximes have been reported [31]. Reduction reactions of Cr(III) starting materials in air with ligands which act as reductants – and simultaneously appear intact in the Cr(II) products – are very rare [32].

Complex $\mathbf{1} \cdot 2\text{H}_2\text{O}$ was also prepared by the reaction of $[\text{Cr}(\text{CO})_6]$ with an excess of the ligand in MeCN/ H_2O under refluxing aerobic conditions; the yield is satisfactory, higher than 50%, based on the totally available chromium.

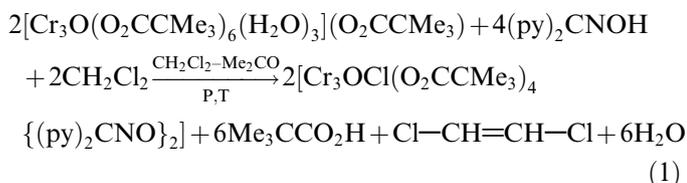


Scheme 3. Reaction scheme summarizing the synthesis of compounds **1**, **2**, and **3**.

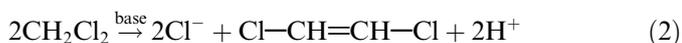
Since complex **1** is carboxylate-free and contains exclusively Cr^{II} atoms, our next goal was its preparation using simpler reaction systems, i.e. CrCl₂ · 4H₂O/(py)₂CNOH at different pH values. Under the reaction conditions employed (a variety of solvents, Et₃N or NaOH, etc.), no evidence of the formation of complex **1** was observed. Instead, green insoluble, non-crystalline precipitates of Cr^{III}₂O₃ were seen as the main products of the reactions.

Crystals of **1** · 2H₂O can be kept for weeks in the mother liquor. Once they are isolated from solution and exposed to air, they are slowly oxidized to a dark green-brown powder containing Cr(III) as revealed by EPR spectroscopy. While a very freshly prepared sample of the complex is EPR silent, the room-temperature spectrum of the dark green-brown powder displays an isotropic signal, whose intensity increases with storage time, with *g* ≈ 2.1 at X-band frequency, indicative of a Cr(III) percentage.

The preparation of complex [Cr₃OCl(O₂CCMe₃)₄{(py)₂CNO} ₂] · 2Me₂CO (**2** · 2Me₂CO) can be achieved *exclusively* by solvothermal techniques. Hydrothermal and/or solvothermal methods can favour the formation of metastable compounds [33] that are difficult or impossible to be obtained by the conventional coordination chemistry techniques, i.e., solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of common solvents. Solvothermal techniques allow not only the application of high temperatures to reactions in low boiling solvents, but they also offer excellent crystallization conditions [34]. The possible formation of **2** *under solvothermal conditions* can be summarized in the balanced Eq. (1).

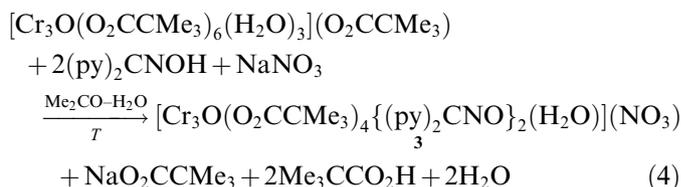
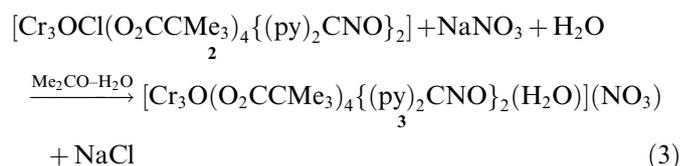


The presence of the terminally-coordinated Cl[−] ligand is intriguing, and can be attributed to the decomposition of the dichloromethane solvent (Eq. (2)). This transformation is presumably favoured by a combination of the presence of the metal ion [35] and the high-temperature/pressure conditions during the solvothermal procedure. Alkyl halides are known to undergo elimination reactions in the presence of Lewis bases (e.g. RCO₂[−]). Elimination occurs under special circumstances and depends on the structure of the alkyl halide and the basicity of the anion. When (Me)₃CCO₂[−] reacts with CH₂Cl₂, a proton from the carbon of the latter is abstracted by the Lewis base, the carbon atom that bears the leaving group is somewhat sterically hindered, and elimination (E2) predominates over substitution [36].



The preparation of the trinuclear complex **3** was achieved by two methods represented by the balanced Eqs. (3) and (4). Three features of the reactions represented

by Eqs. (3) and (4) deserve brief comments. First, the metathesis reaction that leads to **3** (Eq. (3)) is accompanied by the substitution of the terminal Cl[−] ligand of **2** by a terminally-coordinated H₂O molecule. Second, this reaction needs also to be carried out in a solvent mixture containing H₂O to ensure non-contamination of the solid product with NaCl. And third, the coordination of H₂O instead of a nitrate ligand in **3** may be due to the large excess of H₂O in the reaction mixture and to the satisfaction of crystal lattice requirements.



Under the reaction conditions employed for the isolation of complexes **2** and **3**, the propensity of the second pyridyl nitrogen atom of (py)₂CNO[−] towards coordination has not been realized, whereas – under the same conditions – the deprotonated oximate oxygen atom is coordinated (vide infra). An excess of the metal ion in the reaction mixtures may favour the synthesis of higher nuclearity metal clusters with both pyridyl nitrogens coordinated, a possibility that is currently under investigation in our laboratories.

3.2. Description of structures

Selected interatomic distances and angles for complexes **1** · 2H₂O, **2** · 2Me₂CO, and **3** · H₂O · 0.5Me₂CO are listed in Tables 2–4, respectively. Partially labelled ORTEP plots of these complexes are shown in Figs. 1–3.

Complex **1** · 2H₂O crystallizes in monoclinic space group C2/c. Its structure consists of isolated dinuclear [Cr₂{(py)₂CNO} ₄] molecules and two solvate H₂O molecules; the latter will not be further discussed. There is a twofold crystallographic axis passing through the midpoint of the Cr^{II}...Cr^{II} axis. The Cr^{II} atoms are doubly bridged by two η¹:η¹:η¹:μ₂ (or 2.1110 using Harris notation [19]); each of these ligands chelates one Cr^{II} atom forming a five-membered CrNCCN chelating ring, while its oximate oxygen atom is terminally bound to the other metal center. A chelating (η² or 1.0110 [19]) (py)₂CNO[−] ligand (Scheme 2) completes five-coordination at each metal with the deprotonated oxime oxygen [O(1) and its symmetry-related partner] being unbound to a Cr^{II} atom. These ligands are in *syn* arrangement. Each oximate ligand has an unbound 2-pyridyl nitrogen atom [N(3), N(13) and their symmetry-related partners]. The bridging CrN(12)-O(11)Cr' unit is not planar. The deviations of atoms Cr,

Table 2
Selected interatomic distances (Å) and bond angles (°) for complex **1** · 2H₂O

Cr–O(11')	2.133(3)	Cr–N(11)	2.054(4)
Cr–N(1)	2.022(4)	Cr–N(12)	1.972(4)
Cr–N(2)	1.961(4)	Cr···Cr'	3.479(2)
O(11')–Cr–N(1)	123.02(15)	N(1)–Cr–N(11)	136.13(16)
O(11')–Cr–N(2)	90.97(14)	N(1)–Cr–N(12)	98.08(15)
O(11')–Cr–N(11)	100.80(15)	N(2)–Cr–N(11)	101.39(16)
O(11')–Cr–N(12)	88.61(14)	N(2)–Cr–N(12)	178.98(16)
N(1)–Cr–N(2)	81.37(15)	N(11)–Cr–N(12)	79.60(15)

Symmetry code: ' = $-x, y, -z + 1/2$.

Table 3
Selected interatomic distances (Å) and bond angles (°) for complex **2** · 2Me₂CO

Cr(1)–O(21)	1.984(2)	Cr(2)–N(12)	2.020(3)
Cr(1)–O(31)	1.986(3)	Cr(3)–O(1)	1.981(2)
Cr(1)–O(41)	1.966(2)	Cr(3)–O(11)	2.002(2)
Cr(1)–O(61)	1.853(2)	Cr(3)–O(42)	2.028(2)
Cr(1)–N(1)	2.061(3)	Cr(3)–O(52)	2.020(2)
Cr(1)–N(2)	2.023(3)	Cr(3)–O(61)	1.895(2)
Cr(2)–O(22)	1.994(2)	Cr(3)–Cl(1)	2.328(1)
Cr(2)–O(32)	1.976(3)	Cr(1)···Cr(2)	3.248(5)
Cr(2)–O(51)	1.964(2)	Cr(1)···Cr(3)	3.199(2)
Cr(2)–O(61)	1.858(2)	Cr(2)···Cr(3)	3.192(4)
Cr(2)–N(11)	2.076(3)		

Cr(1)–O(61)–Cr(2)	122.11(12)	O(32)–Cr(2)–O(61)	95.61(10)
Cr(1)–O(61)–Cr(3)	117.17(12)	O(32)–Cr(2)–N(11)	97.63(11)
Cr(2)–O(61)–Cr(3)	116.51(12)	O(32)–Cr(2)–N(12)	174.97(12)
O(21)–Cr(1)–O(31)	89.20(10)	O(51)–Cr(2)–O(61)	90.77(10)
O(21)–Cr(1)–O(41)	172.36(10)	O(51)–Cr(2)–N(11)	87.83(11)
O(21)–Cr(1)–O(61)	96.00(10)	O(51)–Cr(2)–N(12)	90.79(11)
O(21)–Cr(1)–N(1)	84.18(11)	O(61)–Cr(2)–N(11)	166.72(11)
O(21)–Cr(1)–N(2)	88.05(11)	O(61)–Cr(2)–N(12)	88.87(11)
O(31)–Cr(1)–O(41)	90.32(10)	N(11)–Cr(2)–N(12)	77.94(12)
O(31)–Cr(1)–O(61)	95.38(10)	O(1)–Cr(3)–O(11)	92.25(10)
O(31)–Cr(1)–N(1)	98.78(11)	O(1)–Cr(3)–O(42)	90.41(10)
O(31)–Cr(1)–N(2)	175.76(11)	O(1)–Cr(3)–O(52)	176.59(10)
O(41)–Cr(1)–O(61)	91.64(10)	O(1)–Cr(3)–O(61)	89.48(10)
O(41)–Cr(1)–N(1)	88.36(11)	O(1)–Cr(3)–Cl(1)	89.11(8)
O(41)–Cr(1)–N(2)	91.97(11)	O(11)–Cr(3)–O(42)	177.34(10)
O(61)–Cr(1)–N(1)	165.84(12)	O(11)–Cr(3)–O(52)	90.94(10)
O(61)–Cr(1)–N(2)	88.12(11)	O(11)–Cr(3)–O(61)	91.03(10)
N(1)–Cr(1)–N(2)	77.73(12)	O(11)–Cr(3)–Cl(1)	90.82(7)
O(22)–Cr(2)–O(32)	89.10(10)	O(42)–Cr(3)–O(52)	86.40(10)
O(22)–Cr(2)–O(51)	173.02(11)	O(42)–Cr(3)–O(61)	89.02(10)
O(22)–Cr(2)–O(61)	96.10(10)	O(42)–Cr(3)–Cl(1)	89.19(7)
O(22)–Cr(2)–N(11)	85.21(11)	O(52)–Cr(3)–O(61)	89.25(10)
O(22)–Cr(2)–N(12)	88.15(10)	O(52)–Cr(3)–Cl(1)	92.07(7)
O(32)–Cr(2)–O(51)	91.43(10)	O(61)–Cr(3)–Cl(1)	177.71(8)

O(11), N(12) and Cr' from the CrN(12)O(11)Cr' best mean plane are 0.085, 0.210 Å below, and 0.224, 0.072 Å above the plane, respectively. Analysis of the shape-determining bond angles using the approach of Reedijk and co-workers [37] yields a value for the trigonality index, τ , of 0.72 for chromium(II) ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively). Thus, the geometry about each Cr^{II} center can be described as slightly distorted trigonal bipyramidal (tbp), with the api-

Table 4
Selected interatomic distances (Å) and bond angles (°) for one of the two crystallographically independent trinuclear cations present in the complex **3** · H₂O · 0.5Me₂CO

Cr(1)–Ox(1)	1.856(3)	Cr(2)–N(12)	2.026(4)
Cr(1)–O(21)	1.974(3)	Cr(3)–Ox(1)	1.880(3)
Cr(1)–O(23)	1.958(3)	Cr(3)–O(1)	1.982(3)
Cr(1)–O(25)	1.970(3)	Cr(3)–OW(1)	1.999(3)
Cr(1)–N(1)	2.071(4)	Cr(3)–O(11)	1.971(3)
Cr(1)–N(2)	2.023(4)	Cr(3)–O(26)	1.990(3)
Cr(2)–Ox(1)	1.859(3)	Cr(3)–O(28)	2.008(3)
Cr(2)–O(22)	1.987(3)	Cr(1)···Cr(2)	3.264(6)
Cr(2)–O(24)	1.971(3)	Cr(1)···Cr(3)	3.180(5)
Cr(2)–O(27)	1.965(3)	Cr(2)···Cr(3)	3.170(1)
Cr(2)–N(11)	2.060(4)		
Cr(1)–Ox(1)–Cr(2)	122.98(16)	Ox(1)–Cr(2)–O(27)	90.52(13)
Cr(1)–Ox(1)–Cr(3)	116.67(16)	Ox(1)–Cr(2)–N(11)	166.59(16)
Cr(2)–Ox(1)–Cr(3)	115.95(16)	O(22)–Cr(2)–N(12)	177.38(15)
Ox(1)–Cr(1)–O(21)	93.89(13)	O(24)–Cr(2)–O(27)	173.47(13)
Ox(1)–Cr(1)–O(23)	96.27(13)	Ox(1)–Cr(3)–O(1)	90.65(13)
Ox(1)–Cr(1)–O(25)	92.13(13)	Ox(1)–Cr(3)–OW(1)	178.17(14)
Ox(1)–Cr(1)–N(1)	166.31(15)	Ox(1)–Cr(3)–O(11)	92.44(14)
O(21)–Cr(1)–N(2)	176.92(15)	Ox(1)–Cr(3)–O(26)	92.38(13)
O(23)–Cr(1)–O(25)	171.42(14)	O(1)–Cr(3)–O(28)	173.87(13)
Ox(1)–Cr(2)–O(22)	91.90(13)	O(11)–Cr(3)–O(26)	174.85(14)
Ox(1)–Cr(2)–O(24)	95.99(14)		

cal sites of Cr occupied by an oximate nitrogen atom of a bridging (py)₂CNO[−] ligand [N(12)] and an oximate nitrogen atom of a chelating (py)₂CNO[−] group [N(2)]. Two 2-pyridyl nitrogen atoms [N(1), N(11)] arising from the chelating and bridging (py)₂CNO[−] ligands and one oxygen atom [O(11')] form the equatorial plane for Cr. Cr lies 0.025 Å out of the equatorial plane towards N(2). The rather small N(1)–Cr–N(2) and N(11)–Cr–N(12) angles [81.37(15) and 79.60(15), respectively] reflect the small bite of the (py)₂CNO[−] ligands. The Cr···Cr' distance of 3.479(2) Å is essentially too long to invoke the existence of a metal–metal bond [38].

The Cr^{II} atoms seem to be high-spin based on the Cr–O bond length [2.133(3) Å] and Cr–N bond distances [1.961(4)–2.054(4) Å]. These bond lengths are similar to Cr–O [39] and Cr–N [40] distances in structurally characterized five-coordinate, high-spin chromium(II) complexes with a distorted tbp coordination geometry.

The crystal structure of **1** · 2H₂O is stabilized by two crystallographically independent hydrogen bonds with the solvate water oxygen atom as donor, and the uncoordinated oximate oxygen atom and the uncoordinated pyridyl nitrogen atom N(13) as acceptors. Their dimensions are: OW(1) [x, −y + 1, z + 1/2]···O(1) 2.774 Å, H_AOW(1) [x, −y + 1, z + 1/2]···O(1) 1.929 Å, OW(1) [x, −y + 1, z + 1/2]···H_AOW(1)···O(1) 159.4° and OW(1) [−x, y − 1, −z + 1/2]···N(13) 3.004 Å, H_BOW(1) [−x, y − 1, −z + 1/2]···N(13) 2.178 Å, OW(1) [−x, y − 1, −z + 1/2]···H_BOW(1)···N(13) 157.2°.

The dimers are stabilized by an intramolecular π – π stacking interaction between the terminal (py)₂CNO[−] ligands. The interaction involves the two coordinated

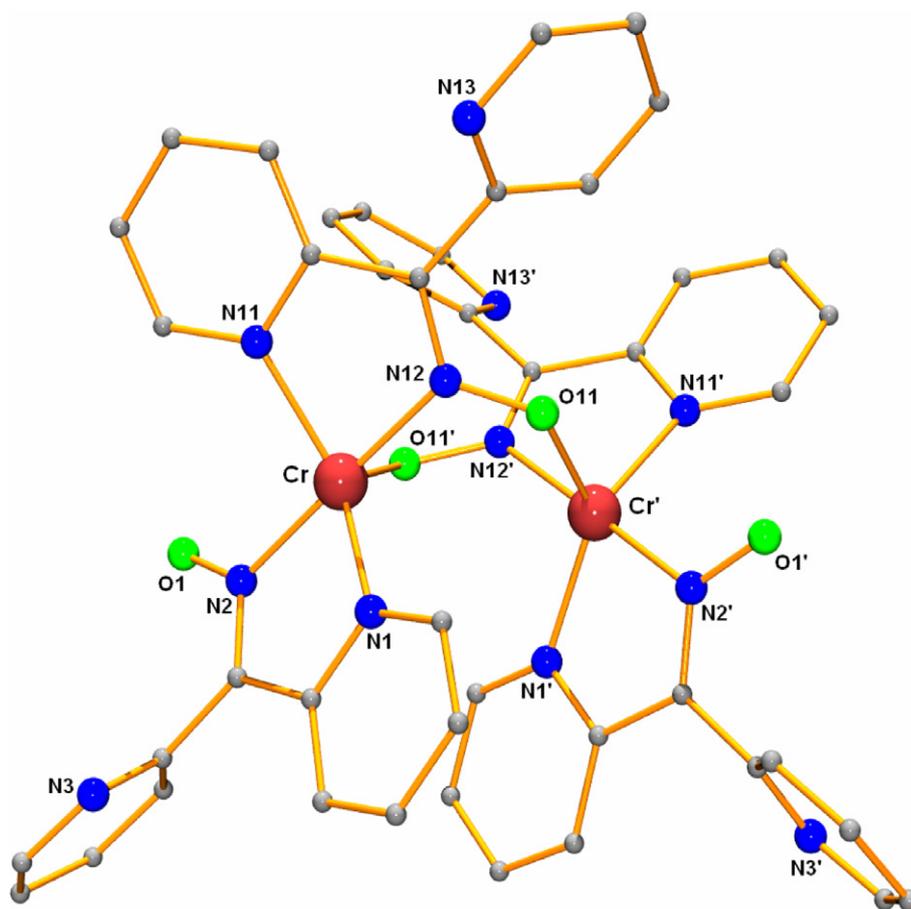


Fig. 1. Partially labelled PovRay representation of complex **1**. H atoms have been omitted for clarity. Primes are used for symmetry-related atoms.

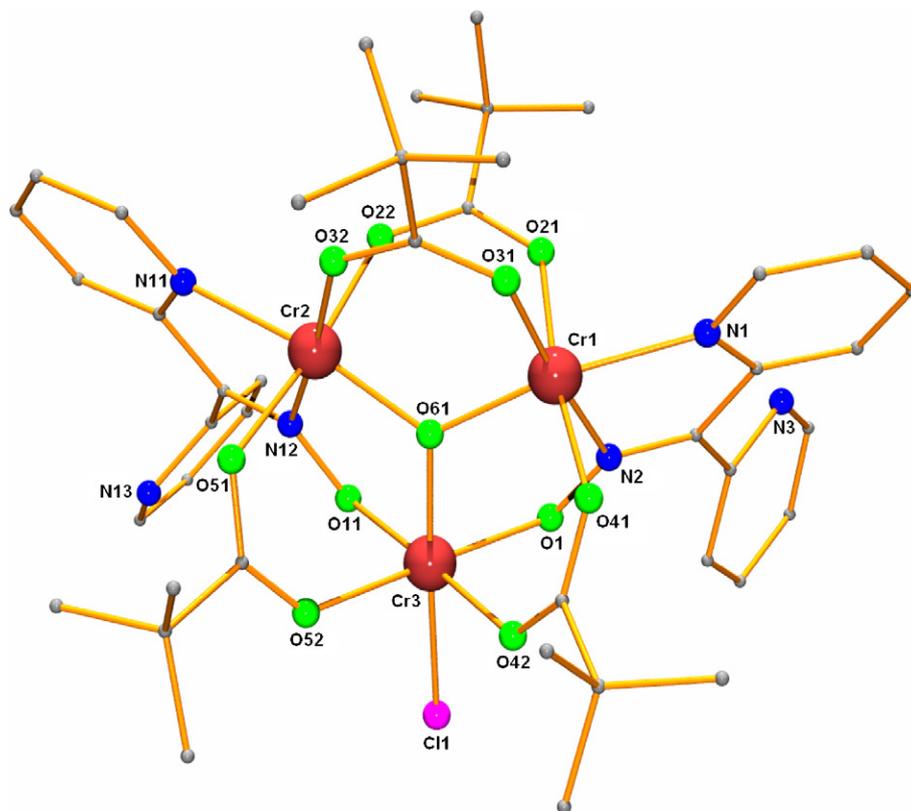


Fig. 2. Partially labelled PovRay representation of complex **2**. H atoms have been omitted for clarity.

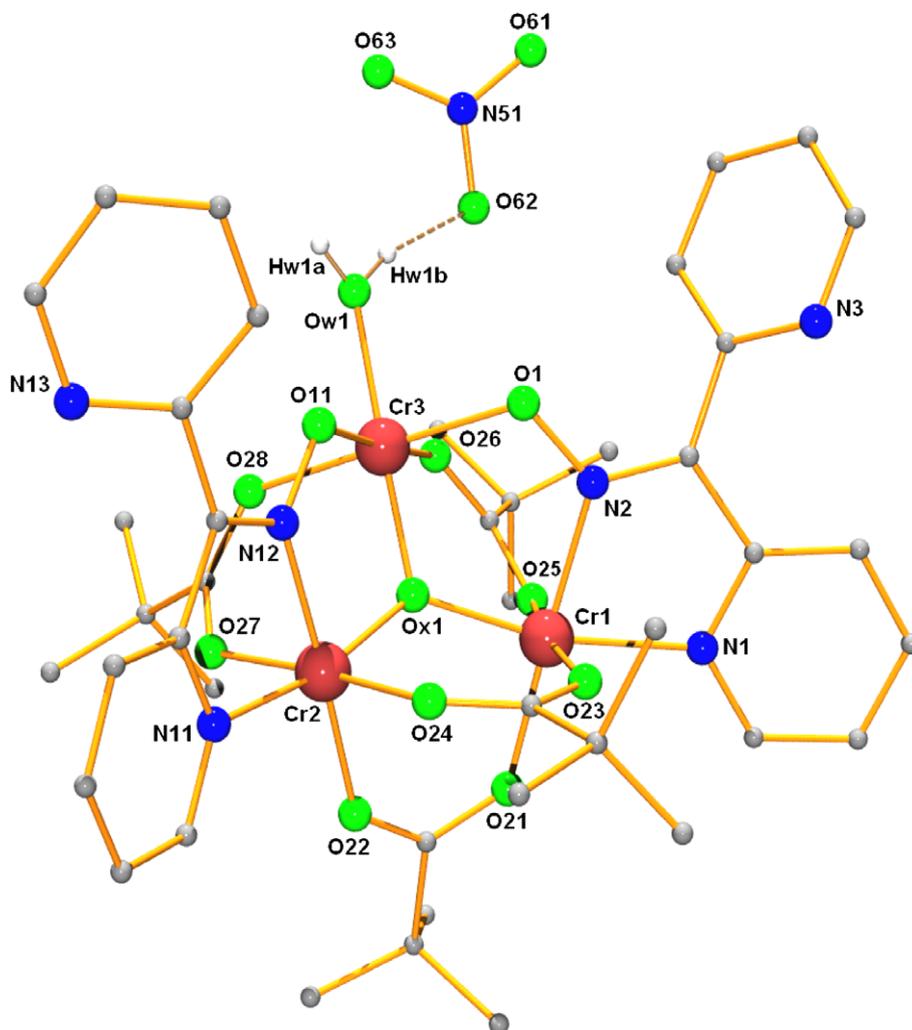


Fig. 3. A view of one of the crystallographically independent trinuclear cations present in complex $3 \cdot \text{H}_2\text{O} \cdot 0.5\text{Me}_2\text{CO}$. H atoms of the $(\text{py})_2\text{CNO}^-$ and $\text{Me}_3\text{CCO}_2^-$ have been omitted for clarity. The hydrogen between the aquo ligand and the nitrate counterion is also shown.

2-pyridyl rings that possess N(1) and N(1') (see Fig. 1), the intercentroid distance ($C_g \cdots C'_g$) and the dihedral angle being 3.645 Å and 9.5°, respectively. The corresponding perpendicular distance from C_g and C'_g to the best least-squares ring planes of the other stacking moieties is 3.540 Å. Given that there are only two bridging $(\text{py})_2\text{CNO}^-$ ligands and no metal–metal bonding, we believe that the molecular structure of **1** is maintained by the attractive aromatic ring stacking interaction. Furthermore, this interaction is most probably the reason for the isolation of the isomer with the *syn* terminal $(\text{py})_2\text{CNO}^-$ ligands, and not of the isomer with the *anti* arrangement (or a mixture of the two isomeric forms).

Compound $1 \cdot 2\text{H}_2\text{O}$ is the first structurally characterized complex of chromium (at any oxidation state) with $(\text{py})_2\text{CNOH}$ or $(\text{py})_2\text{CNO}^-$ ligands. The observed trigonal-bipyramidal coordination is extremely rare in divalent chromium chemistry [39–41]; most five-coordinate Cr(II) complexes that have been structurally characterized have a square pyramidal geometry at the metal ion [38,42]. Complex $1 \cdot 2\text{H}_2\text{O}$ joins a very small family of structurally char-

acterized dichromium(II,II) complexes with no metal–metal bonding [40,43]; it is well known that the chemistry of the $\text{Cr}^{\text{II,II}}_2$ complexes is dominated by the presence of Cr–Cr quadruple bonds [38,42].

The dichromium(II,II) complex $1 \cdot 2\text{H}_2\text{O}$ is isostructural with the dicopper(II,II) analogue $[\text{Cu}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ [44], in accordance with the general belief that high-spin Cr(II) compounds are often structurally very similar to copper(II) complexes [45].

Complex $2 \cdot 2\text{Me}_2\text{CO}$ crystallizes in the monoclinic space group $P2_1/c$. Its structure consists of trinuclear $[\text{Cr}_3\text{OCl}(\text{O}_2\text{CCMe}_3)_4\{(\text{py})_2\text{CNO}\}_2]$ molecules and acetone solvate molecules; the latter will not be further discussed. The complex does not possess any imposed symmetry element. The core of the complex consists of a near-equilateral Cr^{III}_3 triangle capped by a central $\mu_3\text{-O}^{2-}$ ion [O(61)]. The μ_3 -oxide atom is 0.223 Å above the Cr_3 plane and occupies the common vertex of the coordination octahedra around the three Cr^{III} atoms. Each of the Cr(1)···Cr(3) and Cr(2)···Cr(3) edges is further bridged by one *syn,syn*- $\eta^1:\eta^1:\mu_2$ (2.11 [19]) $\text{Me}_3\text{CCO}_2^-$ group and

one oximate group of a $\eta^1:\eta^1:\eta^1:\mu_2$ (or 2.1110 using Harris notation [19]) $(\text{py})_2\text{CNO}^-$ ligand, while the $\text{Cr}(1)\cdots\text{Cr}(2)$ edge is further bridged by two *syn,syn*- $\eta^1:\eta^1:\mu_2$ (2.11 [19]) $\text{Me}_3\text{CCO}_2^-$ groups. A terminal chloro ligand completes six coordination at $\text{Cr}(3)$. The bridging oximate groups and the carboxylate ligands deviate significantly from planarity. As a representative example, the distances of $\text{Cr}(1)$, $\text{O}(1)$, $\text{N}(2)$ and $\text{Cr}(3)$ from the $\text{Cr}(1)\text{O}(1)\text{N}(2)\text{Cr}(3)$ best mean plane are 0.048, 0.113 Å above, and 0.115, 0.046 Å below the plane, respectively. The presence of two diatomic oximate bridges [$\text{O}(1)\text{N}(2)$, $\text{O}(11)\text{N}(12)$] between $\text{Cr}(1)\cdots\text{Cr}(3)$ and $\text{Cr}(2)\cdots\text{Cr}(3)$ instead of the two “triatomic” carboxylate bridges [$\text{O}(21)\text{C}(41)\text{O}(22)$, $\text{O}(31)\text{C}(51)\text{O}(32)$] between $\text{Cr}(1)\cdots\text{Cr}(2)$ causes the Cr_3 triangle to be virtually isosceles, with the $\text{Cr}(1)\cdots\text{Cr}(2)$ separation

(3.248 Å) being longer than the $\text{Cr}(1)\cdots\text{Cr}(3)$ (3.199 Å) and $\text{Cr}(2)\cdots\text{Cr}(3)$ (3.192 Å) distances.

The coordination geometry at $\text{Cr}(1)$, $\text{Cr}(2)$ and $\text{Cr}(3)$ is distorted octahedral. The three chromophores are of the $\text{Cr}(1,2)(\text{O}_{\text{oxo}})(\text{O}_{\text{pivalate}})_3(\text{N}_{\text{oximate}})(\text{N}_{2\text{-pyridyl}})$ and $\text{Cr}(3)-(\text{O}_{\text{oxo}})(\text{O}_{\text{pivalate}})_2(\text{O}_{\text{oximate}})_2\text{Cl}$ types. The main distortions around the polyhedra of $\text{Cr}(1)$ and $\text{Cr}(2)$ arise from the five-membered chelating rings of the $(\text{py})_2\text{CNO}^-$ groups with the narrow $\text{N}(1)\text{--Cr}(1)\text{--N}(2)$ [$77.73(12)^\circ$] and $\text{N}(11)\text{--Cr}(2)\text{--N}(12)$ [$77.94(12)^\circ$] angles. The $\text{Cr}\text{--O}(61)\text{--Cr}$ angles are in the $116.51(12)\text{--}122.11(12)^\circ$ range. The Cr^{III} atoms have similar distances to the central oxygen atom, with an average 1.869(2) Å. The $\text{Cr}(1,2)\text{--N}_{2\text{-pyridyl}}$ and $\text{Cr}(3)\text{--Cl}(1)$ bonds are all *trans* to the oxo bridge; they are all relatively long [$2.061(3)\text{--}2.328(1)$ Å] as a result of the *trans*

Table 5
Comparison of selected structural parameters for symmetric and asymmetric complexes containing the $[\text{Cr}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ core

Complex ^a	Cr···Cr (Å)	Cr–O ²⁻ (Å)	Cr–O ²⁻ –Cr (°)	Ref.
[Cr ₃ O(O ₂ CMe) ₆ (H ₂ O) ₃]Cl	3.279(1)	1.885(3)	119.78(18)	[46h]
	3.281(1)	1.899(4)	120.05(18)	
	3.288(1)	1.902(4)	120.13(18)	
[Cr ₃ O(O ₂ CMe) ₆ (na) ₃](PF ₆)	3.297(2)	1.889(6)	118.9(3)	[46j]
	3.300(2)	1.912(6)	120.3(3)	
	3.306(2)	1.917(6)	120.9(3)	
[Cr ₃ O(O ₂ CMe) ₆ (py) ₃](ClO ₄)	3.313 ^b	1.913(3) ^b	120.00(6) ^b	[27]
	3.313 ^b	1.913(3) ^b	120.00(6) ^b	
	3.313 ^b	1.913(3) ^b	120.00(6) ^b	
[C(NH ₂) ₂] ₂ [Cr ₃ O(O ₂ CC ₂ H ₅) ₆ F ₃]	3.302(1)	1.908(4)	119.6(2)	[46d]
	3.308(1) ^b	1.909(2) ^b	120.2(1) ^b	
	3.308(1) ^b	1.909(2) ^b	120.2(1) ^b	
[Cr ₃ O(O ₂ CCMe ₃) ₆ (H ₂ O) ₃](O ₂ CCMe ₃)	3.290 ^b	1.900(4) ^b	120.0 ^b	[27]
	3.290 ^b	1.900(4) ^b	120.0 ^b	
	3.290 ^b	1.900(4) ^b	120.0 ^b	
[Cr ₃ O(O ₂ CPh) ₆ (MeOH) ₃](NO ₃)	3.266(1)	1.888(2)	119.5(1)	[46a]
	3.277(1)	1.893(2)	120.1(1)	
	3.287(1)	1.895(3)	120.4(1)	
Na[Cr ₃ O(O ₂ CPh) ₆ (py) ₃](ClO ₄)	3.263(8) ^b	1.883(4) ^b	120.0 ^b	[46e]
	3.263(8) ^b	1.883(4) ^b	120.0 ^b	
	3.263(8) ^b	1.883(4) ^b	120.0 ^b	
Na[Cr ₃ O(nicH) ₆ (H ₂ O) ₃](ClO ₄) ₈	not reported	1.906(6)	120.0	[46b]
		1.906(6)	120.0	
		1.906(6)	120.0	
Na[Cr ₃ O(picH) ₆ (H ₂ O) ₃](ClO ₄) ₈	not reported	1.918(2) ^b	120.0(6) ^b	[46c]
		1.918(2) ^b	120.0(6) ^b	
		1.918(2) ^b	120.0(6) ^b	
[Cr ₃ O(O ₂ CPh) ₄ (8-hqn) ₃]	2.909(1)	1.882(4)	98.9(2)	[46f]
	3.235(1)	1.890(4)	118.1(2)	
	3.466(2)	1.939(4)	130.2(2)	
[Cr ₃ OCl(O ₂ CCMe ₃) ₄ {(py) ₂ CNO ₂ }] ₂	3.192(4)	1.853(2)	116.51(12)	this work
	3.199(2)	1.858(2)	117.17(12)	
	3.248(5)	1.895(2)	122.11(12)	
[Cr ₃ O(O ₂ CCMe ₃) ₄ {(py) ₂ CNO ₂ }(H ₂ O)](NO ₃)	3.170(1)	1.856(3)	115.95(16)	this work
	3.180(5)	1.859(3)	116.67(16)	
	3.264(6)	1.880(3)	122.98(16)	

Abbreviations: na, nicotinamide; py, pyridine; nicH, nicotinic acid; picH, picolinic acid; 8-hqn, 8-hydroxyquinolate(–1).

^a Solvate molecules have been omitted.

^b Symmetry imposed.

influence of the relatively short Cr–(μ_3 -O) bond. The Cr–N, Cr–O and Cr–Cl bond lengths lie in the expected range for this metal and oxidation state [46,47].

The structure of complex **3** · H₂O · 0.5Me₂CO consists of trinuclear [Cr₃O(O₂CCMe₃)₄{(py)₂CNO}₂(H₂O)]⁺ cations, nitrate counterions, and water and acetone solvate molecules; the latter two will not be further discussed. There are two crystallographically independent trinuclear clusters in the asymmetric unit with completely similar structural characteristics. The molecular structures of the cations of complex **3** are very similar to the structure of complex **2**, with the only difference being the presence of a terminal aquo ligand in the former instead of the chloro ligand in the latter. The resulting cationic units of **3** are counterbalanced by NO₃[−] counterions. The anion acts also as acceptor of a strong hydrogen bond (Fig. 3), with the coordinated aquo ligand acting as donor; the dimensions are: OW(1)–Hw(1b)··O(62) = 2.645 Å, Hw(1b)··O(62) = 1.790 Å, OW(1)–Hw(1b)··O(62) = 165.06° [symmetry operator of acceptor: *x*, *y*, *z*].

Complexes **2** · 2Me₂CO and **3** · H₂O · 0.5Me₂CO are the first structurally characterized Cr(III)/(py)₂CNO[−] complexes. They also join a family of complexes containing the (μ_3 -oxo)trichromium(III) core, {Cr^{III,III,III}(μ_3 -O)}⁷⁺. Most of these complexes have the general formula [Cr₃O(O₂CR)₆L₃]^{*n*+/0}, where L is a monodentate ligand and RCO₂ is an anionic or neutral zwitterionic carboxylate ligand. Remarkably, complexes **2** and **3** are the second and the third, respectively, members of this family that contain two types of μ_2 ligands, i.e. a mixed peripheral bridging ligation, the first reported example being complex [Cr₃O(O₂CPh)₄(8-hqn)₃] [46f]. In Table 5 are compared selected structural parameters for representative complexes containing the {Cr₃(μ_3 -O)}⁷⁺ core. The existence of the mixed μ_2 -ligation affects the Cr··Cr distances. Thus, the distances spanned by a bridging carboxylate ligand and a monoatomic ([Cr₃O(O₂CPh)₄(8-hqn)₃]/diatomic (**2**, **3**) ligand are the shortest, i.e. 2.909(1) Å in [Cr₃O(O₂CPh)₄(8-hqn)₃] [46f], 3.192(4) and 3.199(2) Å in **2**, and 3.170(1) and 3.180(5) Å in **3**. The unsymmetric nature of the just mentioned three complexes is also emphasized by the wide ranges (compared to the “symmetric” complexes) of the Cr^{III}–(μ_3 -O)–Cr^{III} angles [98.9(2)–130.2(2)° in [Cr₃O(O₂CPh)₄(8-hqn)₃], 116.5(1)–122.1(1)° in **2**, 116.0(2)–123.0(2)° in **3**]. It should be also pointed out that two Cr^{III}–(μ_3 -O) bond lengths in both **2** and **3** [1.853(2), 1.858(2) Å in **2** and 1.856(3), 1.859(3) in **3**] are the shortest observed in the family of “basic chromium(III) carboxylate” complexes; the Cr^{III} atoms that form these very strong bonds are bridged by two carboxylate groups and have 2-pyridyl nitrogen donor atoms *trans* to the oxo group.

3.3. IR spectroscopy

The IR spectra of complexes **1** · 2H₂O and **3** · H₂O · 0.5Me₂CO (dried samples) exhibit a medium to strong band at ~3380 cm^{−1} assignable to the ν (OH) vibration

of the solvate/coordinated water molecules [48]. The broadness and the relatively low frequency of this band are both indicative of strong hydrogen bonding [48].

Two bands, one very strong at about 1590 cm^{−1} and one of medium intensity at about 1220 cm^{−1}, are common in the spectra of **1–3**; these bands are tentatively assigned to the oximate ν (C=N) and ν (N–O) vibrational modes [49], respectively, although the higher-wavenumber band should also have aromatic and carboxylate stretch characters.

The ν_{as} (CO₂) and ν_s (CO₂) strong bands are at 1588 (**2**), 1585 (**3**) and 1420 (**2**), 1421 (**3**) cm^{−1}, respectively. The difference Δ [$\Delta = \nu_{as}(\text{CO}_2) - \nu_s(\text{CO}_2)$] is 168 cm^{−1} for **2** and 164 cm^{−1} for **3**; these values are less than the Δ value for NaO₂CCMe₃ · H₂O (210 cm^{−1}), as expected for the bidentate bridging ligation of the four carboxylates [50]. The medium intensity bands at about 2965 and 1460 cm^{−1} are assigned to the ν_{as} (CH₃) and δ_d (CH₃) vibrational modes of the Me₃CCO₂[−] ligands [51]. The presence of ionic NO₃[−] in **3** (established by crystallography) follows from the spectrum of this compound through the appearance of the ν_3 (E′)[ν_d (NO)] mode of the D_{3h} ionic nitrate at ~1385 cm^{−1} [52].

A medium intensity band at 617 cm^{−1} appears in the spectra of **2** · 2Me₂CO and **3** · H₂O · 0.5Me₂CO. This band is absent from the spectrum of **1** · 2H₂O and can be assigned to the ν_{as} (Cr₃O) vibration [46d,46e,53].

3.4. Electronic spectroscopy

From the solution electronic spectra, it is difficult to decide if the structures seen in the solid state persist in solution; structural changes are possible in solvents of high donor capacity (MeOH, DMF). The solid-state (diffuse reflectance) electronic spectra of the trinuclear complexes **2** and **3** are almost identical, as expected. The visible spectra of pseudo-octahedral Cr(III) complexes are expected to display two dominant d–d bands, corresponding to the spin-allowed ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g}(F) transitions [54]; these bands appear at ~585 and ~435 nm, respectively, in the spectra of **2** and **3** [46c,46e,46g,54]. The third spin-allowed d–d transition ⁴A_{2g} → ⁴T_{1g}(P) is expected well in the UV region, but it cannot be resolved from the (py)₂CNO[−] ligand transitions [46e]. A series of 3–4 weaker transitions at longer wavelengths, corresponding to formally spin-forbidden transitions, result in weak bands in the 640–720 nm range [46c,46e,54]. Of remarkable interest are two shoulders for both complexes, appeared at 348 and 361 nm; such features have been assigned [46e] to simultaneous pair excitations, where a d → d excitation occurs simultaneously at two Cr^{III} atoms.

3.5. Magnetic and EPR studies of complex **2**

Solid-state direct current (dc) magnetic susceptibility (χ_M) data for the representative complex **2** were collected

in the temperature range 2.0–300 K in an applied field of 3 kG (0.3 T).

The $\chi_M T$ versus T plot is shown in Fig. 4. The $\chi_M T$ product gradually decreases from $4.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature to $1.74 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 25.0 K and then increases reaching a value of $1.91 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 8.0 K before dropping further to $1.71 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K. The value of $\chi_M T$ at room temperature is lower than that expected for a cluster of three non-interacting Cr^{III} ions ($5.625 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for $g = 2.0$), indicative of antiferromagnetic exchange interactions even at 300 K. The drop of $\chi_M T$ with decreasing temperature reflects the presence of antiferromagnetic interactions within the cluster leading to a small, but non-zero ground state. The 25.0 K value of $1.74 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is consistent with an $S_T = 3/2$ ground state and a g value slightly less than 2.0, as expected for a $\text{Cr}(\text{III})$ complex; the spin-only ($g = 2.0$) value for an $S_T = 3/2$ state is $1.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$.

In order to confirm the ground state of complex **2**, magnetization data were collected in the magnetic field and temperature ranges 0.5–50 KG and 2.0–4.0 K, respectively. These measurements are plotted as $M/N\beta$ versus H in Fig. 5. The magnetization at high fields tends to a saturation value consistent with three unpaired electrons, indicating an $S_T = 3/2$ ground state.

This magnetic behaviour is in good agreement with the response of an isosceles triangle of Cr^{III} ions (equilateral Cr^{III} triangles are frustrated systems with $S_T = 1/2$ ground state exhibiting a lower $\chi_M T$ value close to $0.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). On the basis of the structural information, fit of the experimental data was performed by means of the CLUMAG program [55] applying the Hamiltonian:

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3) - J_2(S_2 \cdot S_3) \quad (5)$$

where the J_1 coupling constant corresponds to the two interactions involving the oximato/carboxylato ligands and the J_2 one to the interaction involving the two carboxylato bridges, in addition to the interactions through the common central oxo bridge. Best fit parameters were

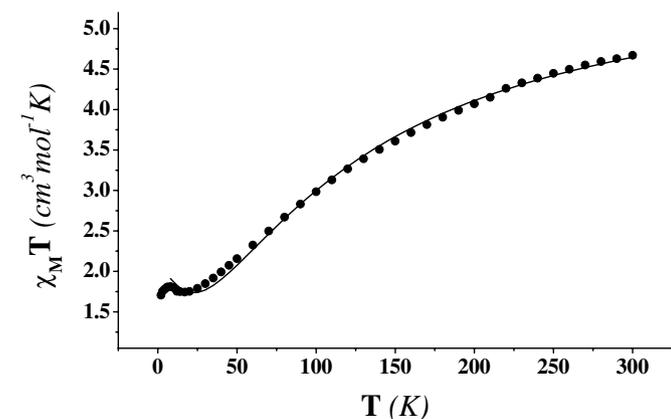


Fig. 4. $\chi_M T$ vs. T plot for a polycrystalline sample of complex **2** in a 3 kG field. The solid, black line is the fit of the experimental data to the appropriate 2- J model; see the text for the fitting parameters.

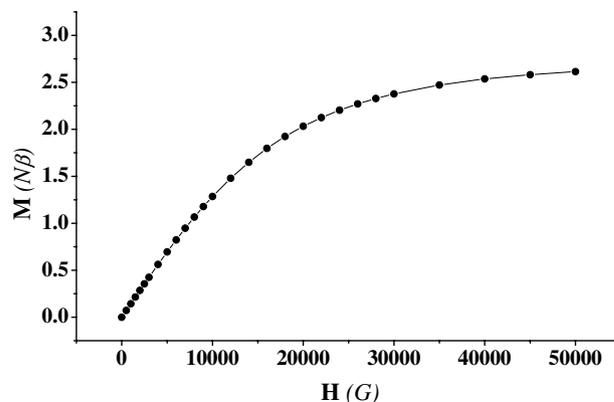


Fig. 5. Magnetization M vs. applied magnetic field H plot at 2 K for complex **2**. The solid, black line represents the theoretical Brillouin function for an $S = 3/2$ system with $g = 2.0$.

$J_1 = -26.5 \text{ cm}^{-1}$, $J_2 = -9.1 \text{ cm}^{-1}$ and $g = 2.06$, $R = 3.2 \times 10^{-3}$.

The μ_3 -oxo centered chromium(III) triangles of the $[\text{Cr}_3(\mu_3\text{-O})(\text{RCOO})_6\text{L}_3]^+$ general type are well known from the structural point of view, but their magnetic properties have been measured only in few cases in spite of the fact that $[\text{Cr}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]\text{Cl} \cdot 6\text{H}_2\text{O}$ was one of the earlier studied trinuclear systems [56]. Regular oxo-centered chromium(III) triangles with a variety of bridging carboxylates and $\text{Cr}-\text{O}-\text{Cr}$ bond angles very close to 120° and the oxo ligand coplanar with the Cr^{III} atoms give J values typically around -20 cm^{-1} [46a,46i,56]. The only example with a distorted triangle in which the oxo ligand is strongly displaced from the plane defined by the Cr^{III} atoms gives a J coupling constant of only -4.6 cm^{-1} [46f]. Despite the fact that this system is not fully comparable because the bridges contain other ligands in addition to the carboxylates, the resulting loss of overlap between the chromium atoms and the out-of-plane μ_3 -oxo ligand should play an important role in the decrease of the superexchange interaction. In complex **2**, the oximato ligands introduce a

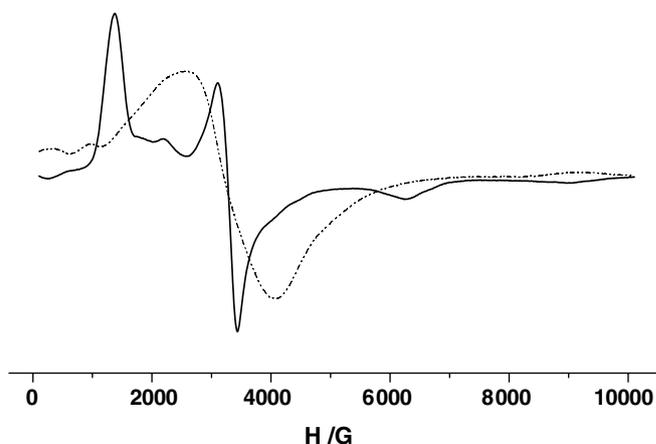


Fig. 6. X-band EPR spectra of complex **2** recorded at room temperature (dashed line) and 20 K (solid line).

moderate distortion in the triangular $\{\text{Cr}_3(\mu_3\text{-O})\}^{7+}$ core with the Cr–O–Cr bond angles deviating few degrees from 120° and the oxo ligand lying out of the plane defined by the three Cr^{III} atoms. The distortion is intermediate between the above mentioned regular and highly distorted cores, and the intermediate J_2 value of -9.1 cm^{-1} for **2** is in full agreement with the structural features. On the other hand, there is only one example of an oxo-centered chromium(III) triangle with additional oximate bridges and a comparable out-of-plane position of the μ_3 -oxo ligand, for which the reported J value is -28.4 cm^{-1} [57]. Comparison of those previously reported coupling constants with these calculated for compound **2** are in excellent agreement with the expected values for these kind of bridges.

EPR spectra recorded at various temperatures (Fig. 6) are consistent with a moderately anisotropic Cr^{III} environment. The room-temperature spectrum displays a broad band centered at g 2.06 which overlaps signals due to several populated spin levels. At temperatures lower than 20 K, the complex exhibits a more complicated spectrum with intense bands at $g = 4.88/2.07$ and several broad and weaker absorptions at $g = 11, 3.0$ and 1.08 attributable to an anisotropic $3/2$ spin level.

4. Conclusions and perspectives

The present work extends the body of results that emphasize the ability of the monoanionic ligand $(\text{py})_2\text{CNO}^-$ to form interesting structural types in 3d-metal chemistry. The use of di-2-pyridyl ketone oxime in reactions with $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ has provided access to three new complexes, one carboxylate-free dichromium(II,II) (**1**) and two mixed-ligand triangular (**2** and **3**) containing the $\{\text{Cr}_3(\mu_3\text{-O})\}^{7+}$ core. In the case of the dinuclear $[\text{Cr}^{\text{II}}_2\{(\text{py})_2\text{CNO}\}_4]$ compound, an intriguing oximate-assisted $\text{Cr}(\text{III}) \rightarrow \text{Cr}(\text{II})$ reduction in air has taken place. The triangular complex **2** possesses a terminally ligated Cl^- anion which arises from an elimination reaction of the dichloromethane solvent in the presence of the metal ion under solvothermal conditions. Complex **2** exhibits interesting magnetic and EPR features; the cluster has an $S_{\text{T}} = 3/2$ ground state and its magnetic behaviour can successfully be modeled using a realistic $2\text{-}J$ model. Complexes **1–3** are the first structurally characterized chromium complexes with $(\text{py})_2\text{CNOH}$ or $(\text{py})_2\text{CNO}^-$ ligands.

The terminal chloro and aquo ligands present in **2** and **3**, respectively, could have future utility as sites for facile incorporation of other anionic or neutral monodentate ligands by metathesis reactions or as means of accessing higher-nuclearity species by using bis(monodentate) bridging inorganic ligands (e.g. $\mu_{1,3}\text{-N}_3^-$, $\mu_{1,3}\text{-N}(\text{CN})_2^-$) or aromatic heterocycles (e.g. 4,4'-bipyridine, pyrazine). One of our future synthetic goals is to try to realize the μ_3/μ_4 potential of $(\text{py})_2\text{CNO}^-$ (not achieved in **1–3**) in chromium(III) or/and chromium(II) chemistry by “forcing” the free 2-pyridyl nitrogen to bind a metal ion. Work in

progress at the time of writing reveals that replacement of $(\text{py})_2\text{CNOH}$ by other, seemingly similar, 2-pyridyl oxime ligands in otherwise analogous reaction systems has a dramatic effect on the structural identity of the obtained dinuclear $[\text{Cr}^{\text{II}}_2(\text{oximate})_4]$ complexes in terms of the $\text{Cr}^{\text{II}} \cdots \text{Cr}^{\text{II}}$ distance and the formation or not of a metal–metal bond. In addition, the free coordination sites of the $(\text{py})_2\text{CNO}^-$ ligands of **1–3** makes these complexes very useful precursors for the synthesis of heterometallic $3d/3d'$ and $3d/4f$ clusters using the “complexes as ligands” synthetic strategy.

Acknowledgements

Th.C.S. thanks European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and particularly the Program PYTHAGORAS I (Grant b. 365.037), for funding the above work. We thank Professor Spyros P. Perlepes for helpful comments and stimulating discussions.

Appendix A. Supplementary material

Crystallographic data for complexes **1**·2H₂O, **2**·2Me₂CO and **3**·H₂O·0.5Me₂CO (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 609575, 609576 and 609577, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.07.063.

References

- [1] (a) For an excellent review see: P. Chaudhuri, *Coord. Chem. Rev.* 243 (2003) 143; (b) A.J.L. Pombeiro, V.Yu. Kukushkin, in: J.A. McCleverty, T.J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, vol. 1, Elsevier, Amsterdam, 2004, p. 631.
- [2] D. Burdinski, F. Birkelbach, T. Weyhermüller, U. Flörke, H.-J. Haupt, M. Lengen, A.X. Trautwein, E. Bill, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* 37 (1998) 1009.
- [3] V.V. Pavlishchuk, S.V. Kolotilov, A.W. Addison, M.J. Prushan, D. Schollmeyer, L.K. Thompson, T. Weyhermüller, E.A. Gorshnik, *Dalton Trans.* (2003) 1587.
- [4] V.Yu. Kukushkin, A.J.L. Pombeiro, *Coord. Chem. Rev.* 181 (1999) 147.
- [5] D.T. Rosa, J.A. Krause Bauer, M.J. Baldwin, *Inorg. Chem.* 40 (2001) 1606.
- [6] S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima, *J. Am. Chem. Soc.* 127 (2005) 540.
- [7] M.J. Goldcamp, S.E. Robison, J.A. Krause Bauer, M.J. Baldwin, *Inorg. Chem.* 41 (2002) 2307.
- [8] M.N. Kopylovich, V.Yu. Kukushkin, M. Haukka, J.J.R.F. da Silva, A.J.L. Pombeiro, *Inorg. Chem.* 41 (2002) 4798.
- [9] J.M. Thorpe, R.L. Beddoes, D. Collison, C.D. Garner, M. Helliwell, J.M. Holmes, P.A. Tasker, *Angew. Chem., Int. Ed.* 38 (1999) 1119.
- [10] R.J. Butcher, C.J. O'Connor, E. Sinn, *Inorg. Chem.* 20 (1981) 537.

- [11] C.J. Milios, C.P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S.P. Perlepes, A. Escuer, *Angew. Chem., Int. Ed.* 43 (2004) 210.
- [12] For a comprehensive review see: C.J. Milios, Th.C. Stamatatos, S.P. Perlepes, *Polyhedron* 25 (2006) 134 (Polyhedron Report).
- [13] (a) P. Chaudhuri, M. Winter, F. Birkelbach, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *Inorg. Chem.* 30 (1991) 4291;
(b) S. Ross, T. Weyhermüller, E. Bill, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* 40 (2001) 6656.
- [14] See, for example: R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* 124 (2002) 12837.
- [15] F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, *J. Am. Chem. Soc.* 128 (2006) 1440.
- [16] For an excellent review see: H. Miyasaka, R. Clérac, *Bull. Chem. Soc. Jpn.* 78 (2005) 1725.
- [17] For an excellent review see: V.L. Pecoraro, A.J. Stemmler, B.R. Gibney, J.J. Bodwin, H. Wang, J.W. Kampf, A. Barwinski, *Prog. Inorg. Chem.* 45 (1997) 83.
- [18] T. Afrati, C. Dendrinou-Samara, C.P. Raptopoulou, A. Terzis, V. Tangoulis, D.P. Kessissoglou, *Angew. Chem., Int. Ed.* 41 (2002) 2148.
- [19] R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny, *J. Chem. Soc., Dalton Trans.* (2000) 2349.
- [20] (a) C.J. Milios, P. Kyritsis, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, *Dalton Trans.* (2005) 501;
(b) H. Kumagai, M. Endo, M. Kondo, S. Kawata, S. Kitagawa, *Coord. Chem. Rev.* 237 (2003) 197.
- [21] (a) C.J. Milios, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, *Inorg. Chem. Commun.* 6 (2003) 1056;
(b) C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, R. Vicente, N. Lalioti, A. Escuer, S.P. Perlepes, *Chem. Commun.* (2003) 819;
(c) C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S.P. Perlepes, *Polyhedron* 23 (2004) 83;
(d) C.J. Milios, Th.C. Stamatatos, P. Kyritsis, A. Terzis, C.P. Raptopoulou, R. Vicente, A. Escuer, S.P. Perlepes, *Eur. J. Inorg. Chem.* (2004) 2885;
(e) Th.C. Stamatatos, D. Foguet-Albiol, C.C. Stoumpos, C.P. Raptopoulou, A. Terzis, W. Wernsdorfer, S.P. Perlepes, G. Christou, *J. Am. Chem. Soc.* 127 (2005) 15380.
- [22] (a) Th.C. Stamatatos, S. Dionyssopoulou, G. Efthymiou, P. Kyritsis, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, *Inorg. Chem.* 44 (2005) 3374;
(b) Th.C. Stamatatos, A. Bell, P. Cooper, A. Terzis, C.P. Raptopoulou, S.L. Heath, R.E.P. Winpenny, S.P. Perlepes, *Inorg. Chem. Commun.* 8 (2005) 533.
- [23] (a) Th.C. Stamatatos, E. Diamantopoulou, A. Tasiopoulos, V. Psycharis, R. Vicente, C.P. Raptopoulou, V. Nastopoulos, A. Escuer, S.P. Perlepes, *Inorg. Chim. Acta* 359 (2006) 4149;
(b) Th.C. Stamatatos, Ph.D. Thesis, University of Patras, 2006.
- [24] Th.C. Stamatatos, J.C. Vlahopoulou, Y. Sanakis, C.P. Raptopoulou, V. Psycharis, A.K. Boudalis, S.P. Perlepes, *Inorg. Chem. Commun.* 9 (2006) 814.
- [25] Th.C. Stamatatos, K.V. Pringouri, C.P. Raptopoulou, R. Vicente, V. Psycharis, A. Escuer, S.P. Perlepes, *Inorg. Chem. Commun.*, in press.
- [26] (a) I.M. Atkinson, C. Benelli, M. Murrie, S. Parsons, R.E.P. Winpenny, *Chem. Commun.* (1999) 285;
(b) E.J.L. McInnes, C. Anson, A.K. Powell, A.J. Thomson, S. Poussereau, R. Sessoli, *Chem. Commun.* (2001) 89.
- [27] Y. Simonov, P. Bourosh, G. Timco, S. Grebenko, M. Mazus, C. Indrichan, N. Gerbelev, *Chem. Bull.* 43 (1998) 128.
- [28] Oxford Diffraction, CrysAlis CCD and CrysAlis RED, version 1.171.27p20, Oxford Diffraction Ltd., Abingdon, Oxford, England, 2005.
- [29] G.M. Sheldrick, *SHELXS-86*, Structure Solving Program, University of Göttingen, Göttingen, Germany, 1986.
- [30] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.
- [31] V.Yu. Kukushkin, D. Tudela, A.J.L. Pombeiro, *Coord. Chem. Rev.* 156 (1996) 333.
- [32] (a) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.* (1999) 827;
(b) P.J. Toscano, P.T. DiMauro, S. Geremia, L. Randaccio, E. Zangrando, *Inorg. Chim. Acta* 217 (1994) 195.
- [33] R.H. Laye, E.J.L. McInnes, *Eur. J. Inorg. Chem.* 14 (2004) 2811.
- [34] For a comprehensive review see: D.J. Chesnut, D. Hagman, P.J. Zapf, R.P. Hammond, R. LaDuca Jr., R.C. Haushalter, J. Zubietta, *Coord. Chem. Rev.* 737 (1999), and references therein.
- [35] E.C. Constable, *Metals and Ligand Reactivity*, VCH Publishers, New York, 1996.
- [36] F.A. Carey, *Organic Chemistry*, fourth ed., 2001, p. 302.
- [37] A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349.
- [38] F.A. Cotton, in: F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), *Multiple Bonds Between Metal Atoms*, third ed., Springer Science, 2005, pp. 35–68.
- [39] F.A. Cotton, C.A. Murillo, I. Pascual, *Inorg. Chem.* 38 (1999) 2746.
- [40] M.D. Fryzuk, D.B. Leznoff, S.J. Rettig, R.C. Thompson, *Inorg. Chem.* 33 (1994) 5528.
- [41] N.M. Alfaro, F.A. Cotton, L.M. Daniels, C.A. Murillo, *Inorg. Chem.* 31 (1992) 2718.
- [42] J.L. Eglin, in: J.A. McCleverty, T.J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, vol. 4, Elsevier, Amsterdam, 2004, pp. 599–603.
- [43] (a) B.D. Murray, H. Hope, P.P. Power, *J. Am. Chem. Soc.* 107 (1985) 169;
(b) A.R. Hermes, G.S. Girolami, *Inorg. Chem.* 27 (1988) 1775;
(c) J.J.H. Edema, S. Gambarotta, F. van Bolhuis, A.L. Spek, *J. Am. Chem. Soc.* 111 (1989) 2142;
(d) F.A. Cotton, R.L. Luck, K.-A. Son, *Inorg. Chim. Acta* 168 (1990) 3;
(e) J.J.H. Edema, S. Gambarotta, A. Meetsma, A.L. Spek, W.J.J. Smeets, M.Y. Chiang, *J. Chem. Soc., Dalton Trans.* (1993) 789.
- [44] E.O. Schlemper, J. Stunker, C. Patterson, *Acta Crystallogr., Sect. C* 46 (1990) 1226.
- [45] M.A. Babar, L.F. Larkworthy, B.W. Fitzsimmons, *Inorg. Chim. Acta* 148 (1988) 25.
- [46] (a) A. Vlachos, V. Psycharis, C.P. Raptopoulou, N. Lalioti, Y. Sanakis, G. Diamantopoulos, M. Fardis, M. Karayanni, G. Papavassiliou, A. Terzis, *Inorg. Chim. Acta* 357 (2004) 3162, and references therein;
(b) E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat, J.A. Ibers, *Inorg. Chim. Acta* 66 (1982) 115;
(c) J.E. Bradshaw, D.A. Grossie, D.F. Mullica, D.E. Pennington, *Inorg. Chim. Acta* 141 (1988) 41;
(d) C.E. Anson, N. Chai-Sa'ard, J.P. Bourke, R.D. Cannon, U.A. Jayasooriya, A.K. Powell, *Inorg. Chem.* 32 (1993) 1502;
(e) A. Harton, M.K. Nagi, M.M. Miriam, M. Glass, P.C. Junk, J.L. Atwood, J.B. Vincent, *Inorg. Chim. Acta* 217 (1994) 171;
(f) M.K. Nagi, A. Harton, S. Donald, Y.-S. Lee, M. Sabat, C.J. O'Connor, J.B. Vincent, *Inorg. Chem.* 34 (1995) 3813;
(g) T. Glowiak, H. Kozłowski, L. Strinna Erre, G. Micera, *Inorg. Chim. Acta* 248 (1996) 99;
(h) C.E. Anson, J.P. Bourke, R.D. Cannon, U.A. Jayasooriya, M. Molinier, A.K. Powell, *Inorg. Chem.* 36 (1997) 1265;
(i) R.L. Lieberman, A. Bino, N. Mirsky, D.A. Summers, R.C. Thompson, *Inorg. Chim. Acta* 297 (2000) 1;
(j) R.A. Coxall, A. Parkin, S. Parsons, A.A. Smith, G.A. Timco, R.E.P. Winpenny, *J. Solid State Chem.* 159 (2001) 321.
- [47] (a) P.A. Lay, A. Levina, in: J.A. McCleverty, T.C. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, vol. 4, Elsevier, Amsterdam, 2003, p. 357;
(b) M. Sassmannshausen, H.D. Lutz, *Z. Anorg. Allg. Chem.* 627 (2001) 1071.
- [48] I. Chadjistamatis, A. Terzis, C.P. Raptopoulou, S.P. Perlepes, *Inorg. Chem. Commun.* 6 (2003) 1365.

- [49] M. Alexiou, E. Katsoulakou, C. Dendrinou-Samara, C.P. Raptopoulou, V. Psycharis, E. Manessi-Zoupa, S.P. Perlepes, D.P. Kessissoglou, *Eur. J. Inorg. Chem.* (2005) 1964.
- [50] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.
- [51] K. Nakamoto, *Infrared and Raman Spectra of Inorganic Chemistry and Coordination Compounds*, fourth ed., Wiley, New York, 1986, pp. 231–233, 375–377.
- [52] U. Casellato, P.A. Vigato, M. Vidali, *Coord. Chem. Rev.* 36(1981) 183.
- [53] R.D. Cannon, R.P. White, *Prog. Inorg. Chem.* 36 (1988) 195.
- [54] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, second ed., Elsevier, Amsterdam, 1984, pp. 417–429.
- [55] D. Gatteschi, P. Luca, *Gazz. Chim. Ital.* 123 (1993) 231.
- [56] B.N. Figgis, G.B. Robertson, *Nature* 205 (1965) 694.
- [57] P. Chaudhuri, M. Hess, E. Rentschler, T. Weyhermüller, U. Flörke, *New. J. Chem.* (1998) 553.