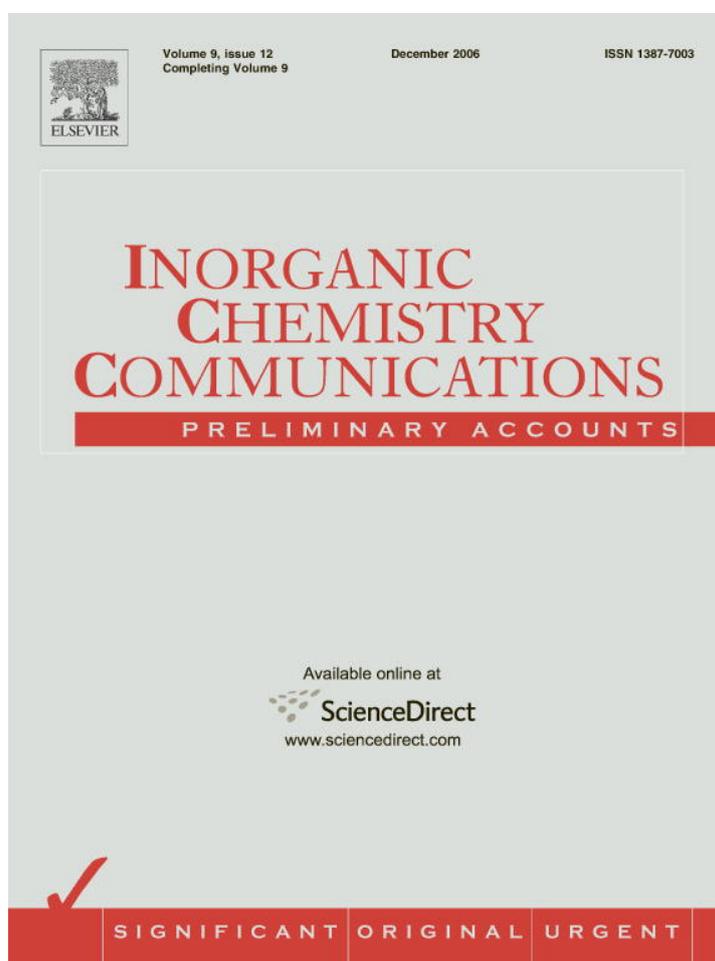


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An unusual dichromium(II,II) compound bearing di-2-pyridyl ketone oximate ligands and prepared by the ligand-assisted reduction of a trichromium(III,III,III) complex in air

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Abstract

The reaction of the oxide-centred triangular, trichromium(III,III,III) complex $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ with di-2-pyridyl ketone oxime, $(\text{py})_2\text{CNOH}$, in MeCN under aerobic and refluxing conditions yields the pivalate-free, dichromium(II,II) complex $[\text{Cr}_2\{(\text{py})_2\text{CNO}\}_4 \cdot 2\text{H}_2\text{O} (\mathbf{1} \cdot 2\text{H}_2\text{O})$. The dinuclear complex can also be prepared by the reaction of $[\text{Cr}(\text{CO})_6]$ with $(\text{py})_2\text{CNOH}$ in refluxing MeCN/H₂O in air. The two high-spin Cr^{II} atoms are doubly bridged by two 2.1110 oximate ligands, while a chelating 1.0110 $(\text{py})_2\text{CNO}^-$ ion completes distorted trigonal bipyramidal coordination at each metal centre. The dimers are stabilized by intramolecular stacking interactions between the terminal $(\text{py})_2\text{CNO}^-$ ligands, and the structural effects of these interactions are discussed.

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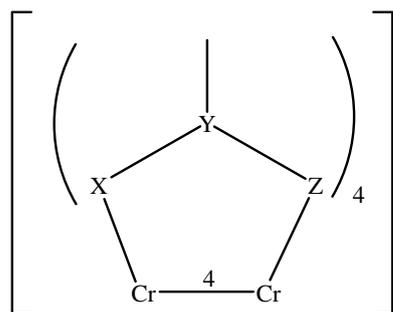
Keywords: Dichromium(II,II) complexes; Di-2-pyridyl ketone oximate complexes; Ligand-assisted reduction of chromium(III); π - π Stacking interactions; Trigonal bipyramidal chromium(II)

The chemistry of the dichromium(II,II) complexes is dominated by the presence of Cr–Cr quadruple bonds [1,2]. The entire range of Cr–Cr distances in isolable compounds, from ca. 1.85 to ca. 2.7 Å, occurs in almost all cases within a common paddlewheel arrangement of three-atom bridging ligands, which are able to form five-membered rings with the two Cr^{II} atoms [1], see Scheme 1. On the contrary, the chemistry of the Cr₂^{II,II} complexes with no metal–metal bonding is limited [3]. In this Communication, we report the unexpected preparation and characterization of a remarkable complex belonging to the latter category of dichromium(II,II) compounds.

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Our results arose from the attempts to introduce di-2-pyridyl ketone oxime [IUPAC name: di-pyridin-2-yl-methanone oxime, $(\text{py})_2\text{CNOH}$, Scheme 2] in the chromium(III) carboxylate chemistry. This ligand occupies a special position amongst 2-pyridyl oximes [4]. One area to which its anion, $(\text{py})_2\text{CNO}^-$ (Scheme 2), is relevant is the chemistry of metallacrowns [5]. Another attractive aspect of $(\text{py})_2\text{CNO}^-$ is its great coordinative flexibility and versatility, characteristics that have led to polynuclear 3d- and 3d/4f-metal complexes with impressive structures and interesting magnetic properties [6]. A last interesting feature is the activation of $(\text{py})_2\text{CNOH}$ by 3d-metal centres [7], which appears to be a fruitful area of contemporary synthetic inorganic chemistry. Although the published coordination chemistry of $(\text{py})_2\text{CNOH}$ and $(\text{py})_2\text{CNO}^-$ is rich [4–6], chromium(III) and chromium(II) complexes bearing $(\text{py})_2\text{CNOH}$ or $(\text{py})_2\text{CNO}^-$ ligands are completely unknown.



Scheme 1. Schematic representation of the paddlewheel structural type commonly observed in dinuclear complexes with quadruply bonded Cr^{II} atoms.

We have been exploring “ligand blend” reactions involving carboxylates (RCO_2^-) and $(\text{py})_2\text{CNO}^-$ as a means to high-nuclearity 3d-metal species. Our results with Fe [8a], Mn [7a,8b], Co [8c] and Cu [8d] have been very encouraging. We have thus decided to extend the exploration of the general $\text{RCO}_2^-/(\text{py})_2\text{CNO}^-$ “ligand blend” to chromium(III), and we can now report that the reaction of a Cr(III) carboxylate source and $(\text{py})_2\text{CNOH}$ has yielded an interesting, carboxylate-free Cr^{II,II}₂ complex.

Reaction of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](\text{O}_2\text{CCMe}_3)$ [9] with three equivalents of $(\text{py})_2\text{CNOH}$ in MeCN under aerobic and refluxing conditions for 12 h gave a dark brown solution, which was layered with Et₂O. Slow mixing during a period of three weeks gave brownish red crystals of the dichromium(II,II) complex $[\text{Cr}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ (**1**·2H₂O) in relatively low yield (~25% based on the available oxime) [10]. It was obvious that a rather unusual reduction of chromium(III) to chromium(II) in air had occurred.

The source of the reducing equivalent is most probably the ligand, with its unidentified oxidation product(s) remaining in the solution. The possibility that the solvent or solvent impurities are responsible for the chromium(III) reduction was ruled out by performing “blind” experiments. Thus, after 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” for 12–24 h, with or without subsequent addition of Et₂O, we obtained no evidence (e.g. dissolution, colour change, etc.) of reduction. In accordance with our belief, 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 nine equivalents of $(\text{py})_2\text{CNOH}$ (i.e., an excess of the ligand) leads to the same product but in higher yield (~50% based on the totally available chromium). A last task was to confirm that the free ligand, $(\text{py})_2\text{CNOH}$, maintains its chemical integrity on dissolution in refluxing MeCN under aerobic condition; if it does not, the reducing agent might be one of the decomposition products of $(\text{py})_2\text{CNOH}$. Careful monitoring of solutions of $(\text{py})_2\text{CNOH}$ in MeCN (after overnight reflux) by NMR spectroscopy at 20 °C revealed the exclusive presence of the free ligand in solution.

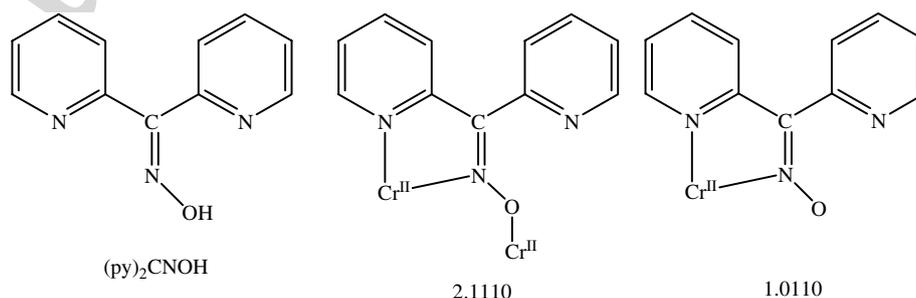
It should be mentioned at this point that metal-ion assisted oxidations of oximes have been reported [11]. Reduction reactions of Cr(III) precursor compounds in air with ligands, which act as reductants and simultaneously appear intact as ligands in the Cr(II) products are extremely rare [12].

As a potentially alternative route to **1**·2H₂O, reactions were investigated between $[\text{Cr}(\text{CO})_6]$ and $(\text{py})_2\text{CNOH}$. Treatment of a white slurry of $[\text{Cr}(\text{CO})_6]$ in MeCN/H₂O (1:1 v/v) with three equivalents of solid $(\text{py})_2\text{CNOH}$ resulted in a pale yellow suspension, which – upon refluxing for 5 days – turned to a brown solution due to slow oxidation of Cr⁰ under aerobic conditions [13]. The brown solution soon deposited brownish red crystals of **1**·2H₂O in 55% yield (based on the available chromium) [10,14].

Since complex **1**·2H₂O is carboxylate-free and contains exclusively Cr^{II} atoms, we wondered if it can be prepared by the reaction of $[\text{Cr}^{\text{II}}\text{Cl}_2(\text{H}_2\text{O})_4]$ and $(\text{py})_2\text{CNOH}$ in the presence of a base (Et₃N, OH⁻). Under aerobic conditions and using a variety of solvents, all our attempts failed; the reactions yield only intractable green precipitates (most probably Cr₂O₃).

While in the mother liquor, crystals of **1**·2H₂O can be kept for weeks. However, once they are isolated from solution and exposed to air, they are slowly oxidized (EPR evidence, vide infra) to a dark green-brown powder. Such air-sensitivity is a common feature for most Cr(II) complexes [15]; only a few examples of air-stable, solid chromium(II) compounds are known at present and this fact has been previously discussed [16].

The crystal structure of **1**·2H₂O [17] reveals the formation of dinuclear molecules (Fig. 1). There is a two-fold crystallographic axis passing through the mid-point of



Scheme 2. The neutral ligand $(\text{py})_2\text{CNOH}$ (left) and its monoanion in the 2.1110 and 1.0110 coordination modes observed in complex **1**·2H₂O.

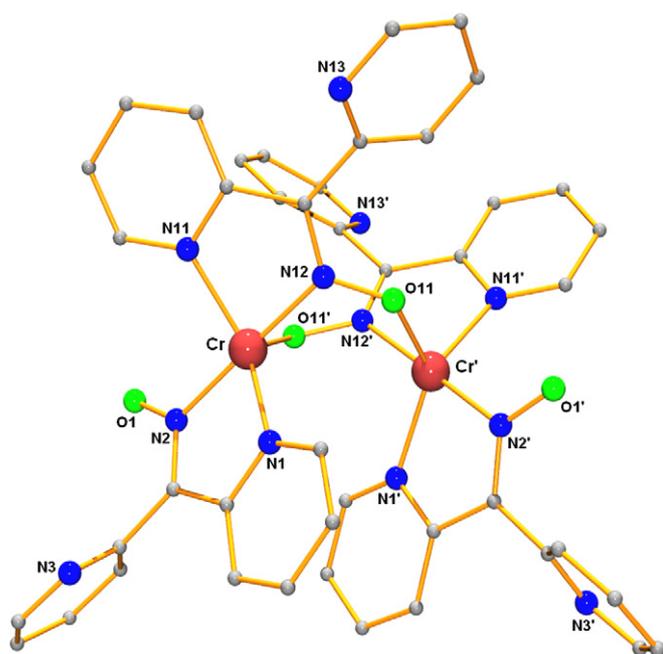


Fig. 1. Partially labelled PovRay representation of complex $1 \cdot 2\text{H}_2\text{O}$. Primes are used for symmetry-related $(-x, y, -z + 1/2)$ atoms. The solvate H_2O molecules and H atoms have been omitted. Selected interatomic distances (Å) and angles ($^\circ$): Cr...Cr' 3.479(2), Cr–N(1) 2.022(4), Cr–N(2) 1.961(4), Cr–N(11) 2.054(4), Cr–N(12) 1.972(4), Cr–O(11) 2.133(3), N(2)–Cr–N(12) 179.0(2), N(2)–Cr–N(1) 81.4(2), N(11)–Cr–O(11') 100.8(2), N(1)–Cr–N(11) 136.1(2).

the $\text{Cr}^{\text{II}} \dots \text{Cr}^{\text{II}}$ axis. The Cr^{II} atoms are doubly bridged by the oximate groups of two $\eta^2:\eta^1:\mu_2$ (or 2.1110 using Harris notation [18]) $(\text{py})_2\text{CNO}^-$ ligands (Scheme 2). A chelating (η^2 or 1.0110 [18], Scheme 2) $(\text{py})_2\text{CNO}^-$ ion completes five coordination at each metal centre. The deprotonated oximate oxygen atoms [O(1), O(1')] of the terminal ligands are unbound to the metal ions. These ligands are in syn arrangement. The metal coordination geometry is described as trigonal bipyramidal with the oximate nitrogens N(2) and N(12) occupying the axial positions for Cr. Analysis of the shape-determining angles using the Reedijk–Addison approach [19] yields a trigonality index τ value of 0.72 for the metal ions, indicating a significantly distorted coordination polyhedron ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively).

The $\text{Cr}^{\text{II}} \dots \text{Cr}^{\text{II}}$ distance of 3.479(2) Å is too long to invoke the existence of a metal–metal bond [3c]. The Cr^{II} atoms seem to be high-spin based on their Cr–O bond distance [2.133(3) Å] and Cr–N bond lengths [1.961(4)–2.054(4) Å]; these bond lengths are similar to Cr–O [15] and Cr–N [3c] distances in structurally characterized 5-coordinate, high-spin chromium(II) complexes with a distorted trigonal bipyramidal coordination geometry. The existence of both terminal and bridging oximate groups results in a difference between the lengths of the two NO bonds, the N(12)–O(11) distance [1.329(5) Å] involving the coordinated oxygen atom being longer than the N(2)–

O(1) distance [1.298(5) Å] involving the free oximate oxygen atom.

The crystal structure of $1 \cdot 2\text{H}_2\text{O}$ 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 (Fig. 2). Their dimensions are: $\text{OW}(1) [x, -y + 1, z + 1/2] \dots \text{O}(1)$ 2.774 Å, $\text{H}_\text{A}\text{OW}(1) [x, -y + 1, z + 1/2] \dots \text{O}(1)$ 1.929 Å, $\text{OW}(1) [x, -y + 1, z + 1/2] - \text{H}_\text{A}\text{OW}(1) \dots \text{O}(1)$ 159.4 $^\circ$ and $\text{OW}(1) [-x, y - 1, -z + 1/2] \dots \text{N}(13)$ 3.004 Å, $\text{H}_\text{B}\text{OW}(1) [-x, y - 1, -z + 1/2] \dots \text{N}(13)$ 2.178 Å, $\text{OW}(1) [-x, y - 1, -z + 1/2] - \text{H}_\text{B}\text{OW}(1) \dots \text{N}(13)$ 157.2 $^\circ$.

The dimers are stabilized by an intramolecular π – π stacking interaction between the terminal $(\text{py})_2\text{CNO}^-$ ligands. The interaction involves the two coordinated 2-pyridyl rings that possess N(1) and N(1') [see Fig. 1], the intercentroid distance ($\text{C}_g \dots \text{C}'_g$) and the dihedral angle being 3.645 Å and 9.5 $^\circ$, 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 of 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).

It should be mentioned at this point that the chromium(II) complex $1 \cdot 2\text{H}_2\text{O}$ is isostructural with the copper(II) complex $[\text{Cu}_2\{(\text{py})_2\text{CNO}\}_4] \cdot 2\text{H}_2\text{O}$ [20], emphasizing the fact that high-spin Cr(II) complexes are often structurally similar to copper(II) complexes [21].

The IR spectrum of $1 \cdot 2\text{H}_2\text{O}$ exhibits a rather strong band at $\sim 3400 \text{ cm}^{-1}$ assignable to the $\nu(\text{OH})$ vibration of the H_2O solvate molecules; its broadness and relatively low frequency are both indicative of the presence of hydrogen bonding. Two bands, one very strong at 1594 cm^{-1} and one medium at 1213 cm^{-1} are assigned [22] to the oximate $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{O})$ modes, respectively, although the higher-wavenumber band should also have an aromatic stretch character. A very freshly prepared sample of $1 \cdot 2\text{H}_2\text{O}$ is EPR silent, as expected. If the solid sample remains in the vial for few hours, the EPR spectrum at 300 K displays a weak to medium intensity isotropic signal (the intensity increases with storage time), with $g = 2.11$, at X-band frequency. Although the g value is slightly higher than normal, the appearance of this signal indicates the presence of Cr(III) [23] produced by the air-oxidation of the sample. Room-temperature magnetic susceptibility measurements, performed 3–4 min after the isolation of solid $1 \cdot 2\text{H}_2\text{O}$ from solution, indicate an effective magnetic moment of 4.70 B.M. per chromium(II), consistent with a high-spin $3d^4$ system [3c,16,24].

In summary, the introduction of di-2-pyridyl ketone oxime in chromium(III) carboxylate cluster chemistry has

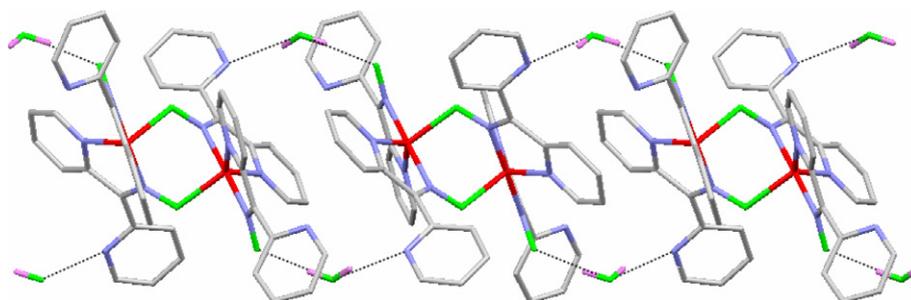


Fig. 2. A perspective view of the crystal structure along the *b* axis showing the hydrogen bonding between solvate H₂O molecules and oximate ligands. Color code: red-brownish, chromium; green, oxygen; blue, nitrogen; grey, carbon. (For interpretation of the figure in colour, the reader is referred to the web version of this article.)

yielded an unusual, carboxylate-free dichromium(II,II) compound via a ligand-assisted reduction of the chromium(III) starting material in air. The complex can also be prepared by the air oxidation of [Cr(CO)₆] in the presence of the ligand. Compound **1**·2H₂O exhibits a series of novelties and interesting aspects. It is the first structurally characterized complex of (py)₂CNOH or (py)₂CNO[−] with chromium at any oxidation state. The structure is remarkable in two respects: First, trigonal–bipyramidal coordination in divalent chromium complexes is extremely rare [3c,15,25]. And second, the isolated syn isomer (considering the positioning of the terminal ligands) seems to be the thermodynamically preferred product due to the existence of intramolecular aromatic ring stacking interactions. An important chemical message from this preliminary work is that the anion of di-2-pyridyl ketone oxime looks an immensely promising candidate ligand for the generation of new, interesting 3d-metal complexes, and it continues to surprise us with its coordination and reactivity versatility. Complex **1**·2H₂O augurs well that it is merely the prototype of a rich new area of chromium(II)/2-pyridyloximates chemistry. Finally, since the initially intended coordination of the second 2-pyridyl nitrogen of (py)₂CNO[−] has not been achieved in **1**·2H₂O, our next synthetic challenge is to realise the μ₃/μ₄ potential of this anionic ligand in chromium(II) or/and chromium(III) chemistry.

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Appendix A. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The

Director, CCDC, 12 Union Road, Cambridge, B2 1EZ, UK, on quoting the deposition number CCDC 609575 for **1**·2H₂O (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.07.030.

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