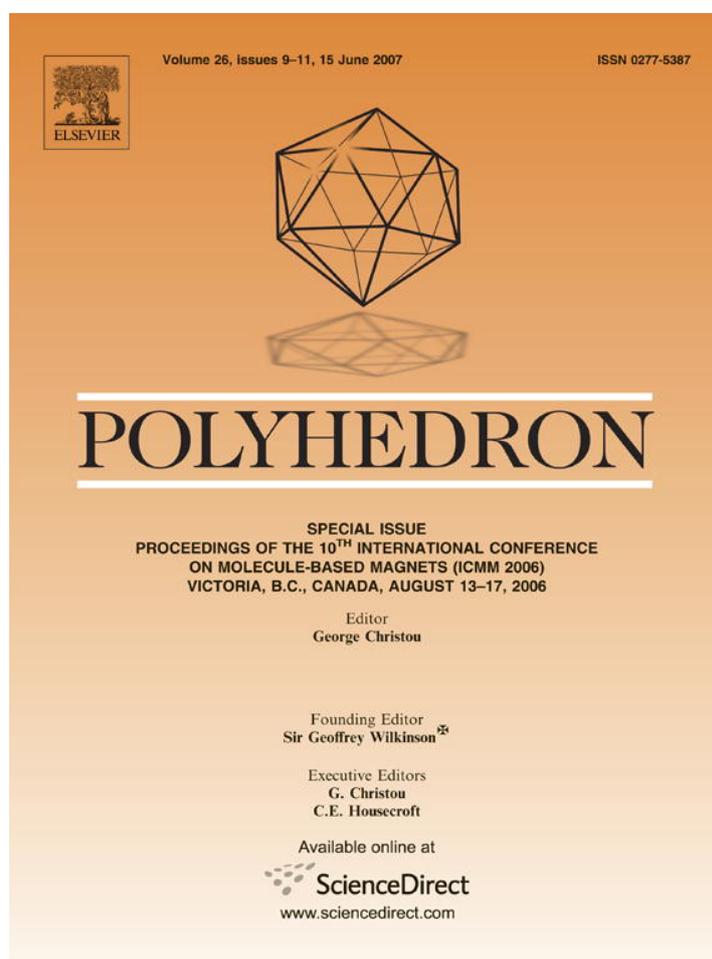


Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>



2-Pyridyloximate clusters of cobalt and nickel

Theocharis C. Stamatatos^a, Constantina Papatriantafyllopoulou^a, Eugenia Katsoulakou^a,
Catherine P. Raptopoulou^b, Spyros P. Perlepes^{a,*}

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

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

Received 29 August 2006; accepted 19 September 2006

Available online 29 September 2006

Abstract

The use of 2-pyridyloximate(-1) ligands, (py)C(R)NO⁻ [R = H, Ph, 2-pyridyl (py)] in cobalt and nickel(II) chemistry has been investigated and led to four families of clusters. A representative member of each family, namely [Co^{II}Co^{III}{(py)C(ph)NO}₆](PF₆)₂ (**1**), [Co^{II}Co^{III}(OH)₂(O₂CMe)₂{(py)₂CNO}₄(MeOH)₂](ClO₄)₂ (**2**), [Ni₉(OH)₄{(py)CHNO}₁₀(H₂O)₈]{N(CN)₂}₃(ClO₄) [**3**{N(CN)₂}₃(ClO₄)] and [Ni₄(O₂CMe)₄{(py)C(ph)NO}₄(MeOH)₂] (**4**) is briefly structurally and magnetically described.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Cobalt clusters; Crystal structures; Magnetic properties; Mixed-valent cobalt complexes; Nickel(II) clusters; 2-Pyridyloximate ligands

One major reason for the current interest by groups around the world in the preparation and magnetic characterization of high-nuclearity, molecular 3d-metal clusters is the search for high-spin molecules [1] and single-molecule magnets [2]. Important to such efforts is the continuing development of new synthetic procedures to high-nuclearity species. The organic ligands play a central role in successful cluster synthesis. The monoanions of 2-pyridyl oximes, (py)C(R)NOH (Fig. 1), are excellent sources of high-nuclearity, homo- and heterometallic clusters with interesting structures and magnetic properties [3]. We herein report the preparation, structural characterization and preliminary magnetic study of some tri-, tetra- and enneanuclear complexes arising from the use of 2-pyridyloximate ligands shown in Fig. 1 in Co and Ni chemistry.

Complex [Co₃{(py)C(ph)NO}₆](PF₆)₂ (**1**) was isolated in good yield (>50%) from the CoX₂ · xH₂O/(py)C(ph)NOH/Me₄NOH/NH₄PF₆ (1:2:2:1) reaction mixtures in MeCN

(X = Cl, NO₃, MeCO₂) in the presence of atmospheric oxygen.¹ The crystal structure of **1** · 6MeCN² reveals the formation of a linear, valence-trapped Co^{III}Co^{II}Co^{III} cation (Fig. 2). The central Co^{II} ion, Co(2), is octahedrally coordinated by six oxygen atoms belonging to six η¹:η¹:η¹:μ₂

¹ The complexes described in this Short Communication gave very good analytical results.

² Crystallographic data in brief: For complex **1** · 6MeCN: C₈₄H₇₂N₁₈O₆P₂F₁₂Co₃, 1896.32 g mol⁻¹, triclinic, *P* $\bar{1}$, *a* = 13.909(8), *b* = 15.61(1), *c* = 10.793(7) Å, α = 89.98(2), β = 82.71(2), γ = 73.31(2)°, *Z* = 1, *V* = 2225(2) Å³, ρ_{calc} = 1.415 g cm⁻³, *T* = 298(2) K, *R*₁(on *F*) = 0.0620, *wR*₂(on *F*²) = 0.1650. For complex **2** · 4 MeOH · 3.08H₂O: C₅₄H_{70.16}N₁₂O_{27.08}Cl₂Co₄, 1627.28 g mol⁻¹, triclinic, *P* $\bar{1}$, *a* = 10.523(5), *b* = 13.556(5), *c* = 12.465(5) Å, α = 110.15(1), β = 95.25(2), γ = 92.05(2)°, *Z* = 1, *V* = 1658(2) Å³, ρ_{calc} = 1.630 g cm⁻³, *T* = 293(2) K, *R*₁(on *F*) = 0.0545, *wR*₂(on *F*²) = 0.1379. For complex **3**{N(CN)₂}₃(ClO₄) · 11.11H₂O: C₆₆H_{92.21}N₂₉O_{37.11}ClNi₉, 2449.46 g mol⁻¹, triclinic, *P* $\bar{1}$, *a* = 15.228(1), *b* = 16.799(1), *c* = 22.326(1) Å, α = 106.76(1), β = 98.03(1), γ = 96.18(1)°, *Z* = 2, *V* = 5348.6(6) Å³, ρ_{calc} = 1.521 g cm⁻³, *T* = 100(2) K, *R*₁(on *F*) = 0.0712, *wR*₂(on *F*²) = 0.1695. For complex **4** · 2MeOH: C₆₀H₆₄N₈O₁₆Ni₄, 1388.08 g mol⁻¹, orthorhombic, *C*2/*c*, *a* = 22.422(15), *b* = 16.699(10), *c* = 16.848(10) Å, *Z* = 4, *V* = 6308(7) Å³, ρ_{calc} = 1.478 g cm⁻³, *T* = 298(2) K, *R*₁(on *F*) = 0.0288, *wR*₂(on *F*²) = 0.0747.

* Corresponding author. Tel.: +30 2610 997146; fax: +30 2610 997118.
E-mail address: perlepes@patreas.upatras.gr (S.P. Perlepes).

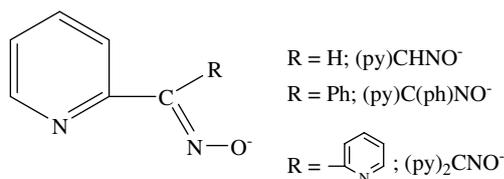


Fig. 1. Formulae and abbreviations of the 2-pyridyloximate(-1) ligands used in this work. The neutral ligands are abbreviated as (py)C(R)NOH.

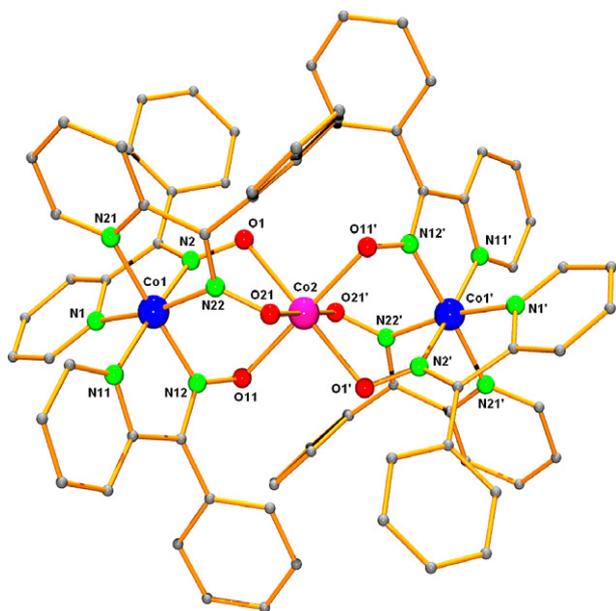
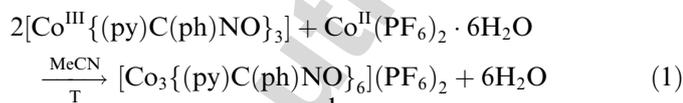


Fig. 2. Molecular structure of the cation $[\text{Co}_3^{\text{III,III,III}}\{(\text{py})\text{C}(\text{Ph})\text{NO}\}_6]^{2+}$ present in $1 \cdot 6\text{MeCN}$. Primes are used for the symmetry-related ($-x, -y, -z$) atoms.

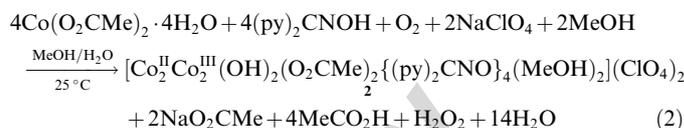
(py)C(Ph)NO⁻ ligands. The six sites on each of the distorted octahedral low-spin, terminal Co^{III} ions are occupied by the nitrogen atoms that belong to the “chelating” part of three (py)C(Ph)NO⁻ ligands, with the three oximate N atoms in the *fac* configuration. Complex 1 can also be obtained by the 2:1 reaction between *mer*-[Co^{III}-(py)C(Ph)NO]₃ [4] and Co(PF₆)₂ · 6H₂O in MeCN (“metal complexes as ligands” strategy), see Eq. (1). Magnetically, complex 1



behaves as a monomeric octahedral, high-spin Co(II) complex ($\mu_{\text{eff}} = 5.01$ BM per trimer at 22 °C). The Co/(py)CHNOH chemistry [4] is very similar to the Co/(py)C(Ph)NOH chemistry.

In order to investigate to what extent the presence of a donor atom on the substituent R of the oxime group of 2-pyridyl oximes might affect the identity of isolated Co products, we studied the Co/(py)₂CNOH chemistry. Aerobic reaction of Co(O₂CMe)₂ · 4H₂O with (py)₂CNOH, in the presence of NaClO₄(1:1:1 reaction ratio), in MeOH/H₂O

(5:1, v/v) led to the red cluster $[\text{Co}_2^{\text{II}}\text{Co}_2^{\text{III}}(\text{OH})_2(\text{O}_2\text{CMe})_2\{(\text{py})_2\text{CNO}\}_4(\text{MeOH})_2](\text{ClO}_4)_2$ (**2**) in very good yield (>65%), see Eq. (2). The tetranuclear, mixed-valent cation of $2 \cdot 4\text{MeOH} \cdot 3.08\text{H}_2\text{O}$ (Fig. 3)²



has the four metal ions in a rectangular arrangement. Based on Co-donor atom bond lengths, Co(1) and its symmetry-related Co(1') are assigned as the Co^{III} ions. The cobalt centers are bridged along each short edge of the rectangle [Co(1) ··· Co(2) = 3.213(1) Å] by one hydroxide [O(21), O(21')], one syn,syn $\eta^1:\eta^1:\mu_2$ -MeCO₂⁻ group and one oximate group. The bridging along each long side [Co(1) ··· Co(2') = 4.441(1) Å] occurs through one oximate group only. Short edge (py)₂CNO⁻ ligands adopt the $\eta^1:\eta^1:\eta^1:\mu_2$ coordination mode, while long edge (py)₂CNO⁻ ions function as $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$ ligands. Complex 2 has a novel inverse 12-metallacrown-4 structural motif [5]. Since the paramagnetic, high-spin d⁷ Co^{II} ions alternate with the diamagnetic Co^{III} ones in the ring of **2**, superexchange between the former is negligible. The observed decrease of $\chi_{\text{M}}T$ as *T* is lowered (Fig. S1) can be attributed to the spitting of the ⁴T_{1g} ground state by low symmetry ligand fields and spin-orbit coupling [6].

Use of 2-pyridyloximate(-1) ligands in nickel(II) chemistry gives different clusters, as expected. The synthetic investigation of the Ni^{II}/(py)CHNOH/OH⁻ reaction systems in H₂O, H₂O/MeOH or H₂O/MeCN in the presence of coun-

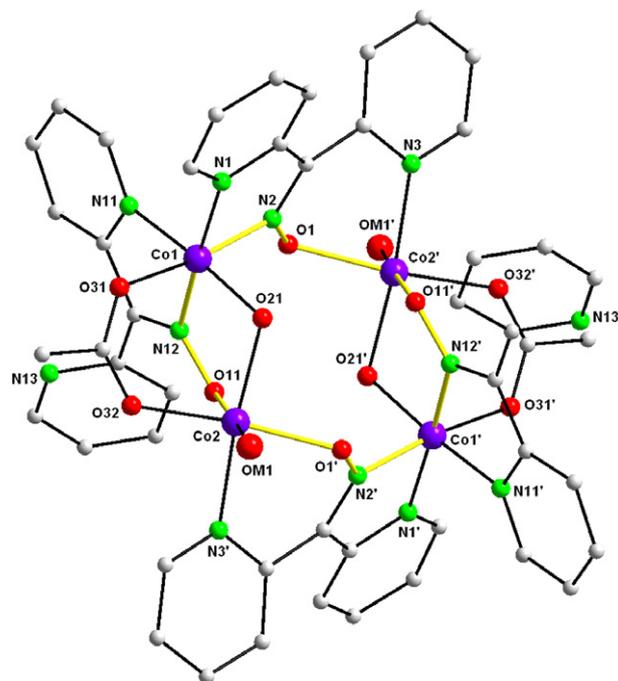
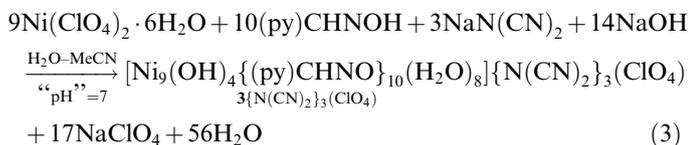


Fig. 3. The molecular structure of the $\text{Co}_2^{\text{II}}\text{Co}_2^{\text{III}}$ cation present in complex $2 \cdot 4\text{MeOH} \cdot 3.08\text{H}_2\text{O}$. Primed and unprimed atoms are related by the crystallographic inversion center.

terions has led to a variety of salts possessing the thermodynamically stable enneanuclear cation $[\text{Ni}_9(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2\{\mu_3\text{-(py)CHNO}\}_4\{\mu_2\text{-(py)CHNO}\}_6(\mu_2\text{-OH}_2)_2(\text{H}_2\text{O})_6]^{4+}$ (3^{4+}) [7,8]. The preparation of the representative salt **3** $\{\text{N}(\text{CN})_2\}_3(\text{ClO}_4)$ is summarized in Eq. (3). The cation (Fig. 4)² can be described as consisting of two



$[\text{Ni}_4(\mu_2\text{-OH})_2\{\mu_2\text{-(py)CHNO}\}_5(\mu_2\text{-OH}_2)(\text{H}_2\text{O})_3]^{+}$ subunits linked to the central Ni(1) ion through four oximate oxygens and two *trans* disposed bridging OH^- groups; as a result of this association, one OH^- group of each subunit becomes μ_3 , and two oximate oxygens of each subunit become μ_2 . Six of the $(\text{py})\text{CHNO}^-$ ions behave as $\eta^1:\eta^1:\eta^1:\mu_2$ ligands and the remaining four as $\eta^1:\eta^1:\eta^2:\mu_3$ ligands. All the salts of 3^{4+} exhibit a very similar magnetic behaviour. The $\chi_M T$ vs. T plot for the representative cluster $3(\text{ClO}_4)_4 \cdot 7.85\text{H}_2\text{O} \cdot 1.4\text{MeOH}$ (2–300 K, 0.1 T), shown in Fig. 5, is indicative of strong antiferromagnetic coupling.

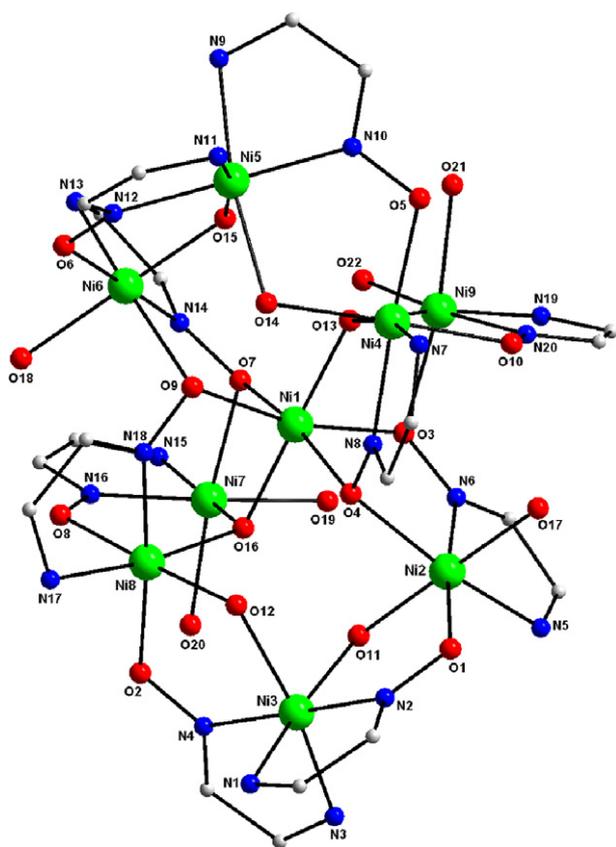


Fig. 4. A plot of the enneanuclear cation present in $3\{\text{N}(\text{CN})_2\}_3(\text{ClO}_4) \cdot 11.11\text{H}_2\text{O}$. Most carbon atoms of the 10 $(\text{py})\text{CHNO}^-$ ligands have been omitted. Atoms O(13), O(16) belong to the $\mu_3\text{-OH}^-$ ligands, while atoms O(11) and O(15) to the $\mu_2\text{-OH}^-$ ligands. The $\mu_2\text{-H}_2\text{O}$ oxygen atoms are O(12) and O(14), while O(17)–O(22) are the oxygen atoms of the terminal aqua ligands. The rest oxygen atoms belong to the $(\text{py})\text{CHNO}^-$ ligands.

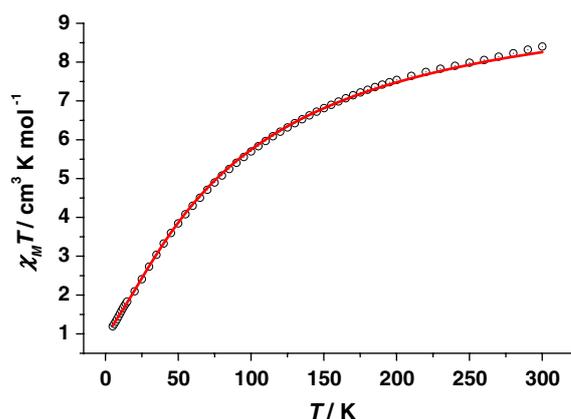
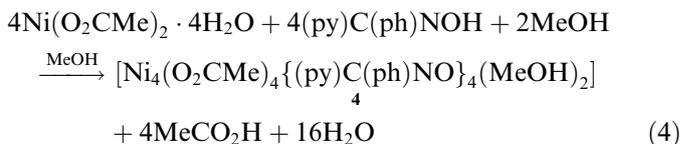


Fig. 5. Plot of the $\chi_M T$ product vs. T for an analytically pure sample of complex $3(\text{ClO}_4)_4 \cdot 7.85\text{H}_2\text{O} \cdot 1.4\text{MeOH}$ [6,7]. The solid line is the fit of the data to the appropriate 3- J model (see text).

Magnetization experiments at 2 K (Fig. S2) up to a field of 5 T show a saturation value equivalent to two electrons, indicating an $S_T = 1$ ground state. The susceptibility data were fit to a 3- J model. Best-fit parameters, obtained by means of the program CLUMAG [9], are $J_1 = -16.4 \text{ cm}^{-1}$, $J_2 = -8.7 \text{ cm}^{-1}$, $J_3 = -27.1 \text{ cm}^{-1}$ and $g = 2.079$. The J_1 coupling constant is assigned to $\text{Ni} \cdots \text{Ni}$ interactions involving a diatomic oximate group and a single O atom that belongs to a $\mu_3\text{-OH}^-$, a $\mu_2\text{-OH}^-$ or to a μ_3 -oximate group. The J_2 coupling constant is assigned to $\text{Ni} \cdots \text{Ni}$ interactions involving two single oxygen atoms, one from a μ_3 -oximate group and the second from a $\mu_3\text{-OH}^-$ group, while the J_3 coupling constant is assigned to $\text{Ni} \cdots \text{Ni}$ interactions through a diatomic oximate group.

Reaction of $\text{Ni}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ with one equivalent of $(\text{py})\text{C}(\text{ph})\text{NOH}$ in MeOH and layering of Et_2O onto the resulting red solution gave violet crystals of $[\text{Ni}_4(\text{O}_2\text{CMe})_4\{(\text{py})\text{C}(\text{ph})\text{NO}\}_4(\text{MeOH})_2]$ (**4**), see Eq. (4); the yield was 65%.



The crystal structure of **4** $\cdot 2\text{MeOH}^2$ reveals the presence of tetranuclear molecules (Fig. 6). The core consists of a tetrahedron of Ni^{II} ions to form a distorted $[\text{Ni}_4(\text{NO})_4]^{4+}$ ‘cube’ (the term ‘*cubane*’ is avoided since it implies the existence of only monoatomic bridges between the metal ions) comprising single (O) and double (N–O) atom edges. Each molecule is held together by two *syn,syn* $\eta^1:\eta^1:\mu_2\text{-MeCO}_2^-$ groups and four $\eta^1:\eta^1:\eta^2:\mu_3$ $(\text{py})\text{C}(\text{ph})\text{NO}^-$ ligands; the remaining two acetates are monodentate, while one terminal MeOH molecule completes octahedral coordination at Ni(2) and Ni(2′). The terminal acetates can easily be replaced by other monoanionic monodentate ligands providing a family of structurally similar $[\text{Ni}_4(\text{O}_2\text{CMe})_2\text{-X}_2\{(\text{py})\text{C}(\text{ph})\text{NO}\}_4(\text{ROH})_2]$ clusters ($X = \text{Cl}, \text{Br}, \text{NCS}, \text{N}(\text{CN})_2^-, \dots$; $R = \text{Me}, \text{Et}, \text{}^n\text{Pr}, \dots$). Preliminary variable-

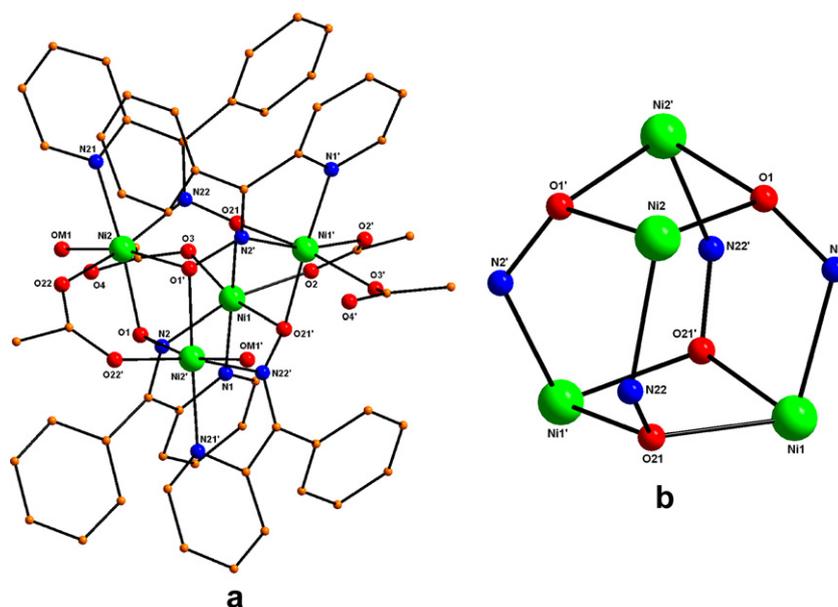


Fig. 6. (a) The molecular structure of the tetranuclear molecule present in complex **4** · 2MeOH, and (b) its core. Primed and unprimed atoms are related by the symmetry operator $x, -y, 1 - z$.

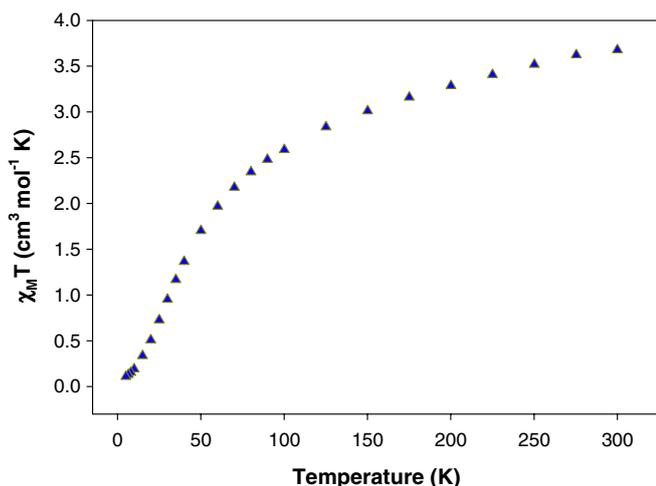


Fig. 7. Plot of the $\chi_M T$ product vs. T for a polycrystalline sample of **4**.

temperature magnetic susceptibility data (Fig. 7) are indicative of antiferromagnetic coupling within the cluster with a resultant $S_T = 0$ ground state.³

In conclusion, the present work emphasizes the ability of 2-pyridyloximate ligands to form interesting structural types in 3d-metal cluster chemistry. The great structural diversity of the complexes described stems in part from the ability of the (py)C(R)NO⁻ ligands to exhibit a variety of distinct coordination modes. Results at the time of writing show that employment of β -diketonates or sulfates in the (py)C(R)NO⁻ cobalt and nickel chemistry give an extraordinary structural flexibility in the resulting ligand “blends”. Reactions are also in progress for the substitu-

tion of the hydroxo bridges that are present in **2** and salts of 3^{4+} by end-on azido ligands, in an effort to specifically introduce ferromagnetic components in the superexchange scheme of these clusters.

Acknowledgements

We thank European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and particularly the Program PYTHAGORAS (Grant b. 365.037), for funding the above work. We also thank Profs. Albert Escuer and Ramon Vicente (Departament de Química Inorgànica, Universitat de Barcelona, Spain) for the magnetic study of the compounds reported in this communication.

Appendix A. Supplementary material

Variable-temperature magnetic susceptibility data for **2** (Fig. S1) and magnetization data at 2 K for **3**(ClO₄)₄ (Fig. S2).

CCDC 264165, 249267, 602391 and 619211 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] (a) A.M. Ako, I.J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C.E. Anson, A.K. Powell, *Angew. Chem., Int. Ed.* 45 (2006) 4926; (b) M. Murugesu, M. Habrych, W. Wernsdorfer, K.A. Abboud, G. Christou, *J. Am. Chem. Soc.* 126 (2004) 4766.

³ Details will be provided in the full paper.

- [2] (a) For reviews, see: G. Aromi, E.K. Brechin, *Struct. Bond.* 122 (2006) 1;
(b) D. Gatteschi, R. Sessoli, *Angew. Chem., Int. Ed.* 42 (2003) 268;
(c) G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, *MRS Bull.* 25 (2000) 66.
- [3] For a review, see: C.J. Milios, Th. C. Stamatatos, S.P. Perlepes, *Polyhedron* 25 (2006) 134, *Polyhedron Report*.
- [4] 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.
- [5] 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.
- [6] O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, 1993, p. 38.
- [7] S. Khanra, T. Weyhermüller, E. Rentschler, P. Chaudhuri, *Inorg. Chem.* 44 (2005) 8176.
- [8] 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.
- [9] D. Gatteschi, L. Pardi, *Gazz. Chim. Ital.* 123 (1993) 231.

Author's personal copy