A Ni^{II} cubane with a ligand derived from a unique metal ion-promoted, crossed-aldol reaction of acetone with di-2-pyridyl ketone

Constantinos G. Efthymiou [a,b], Constantina Papatriantafyllopoulou [b], Guillem Aromi [c], Simon J. Teat [d], George Christou [b,*], Spyros P. Perlepes [a,*]

[a] Department of Chemistry, University of Patras, 265 04 Patras, Greece
[b] Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA
[c] Department de Quimica Inorganica, Universitat de Barcelona, Marti Franqués 1-11, Barcelona 08028, Spain
[d] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

ABSTRACT

Nucleophilic attack by the carbanion $\bar{C}H_2COCH_3$ at the carbonyl atom of di-2-pyridyl ketone, $(py)_2CO$, in the presence of Ni^{II} under basic conditions has yielded the cationic cluster $[Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4]$ $(ClO_4)_4$ (1). The cluster cation possesses a distorted cubane $\{Ni_4(\mu_3\text{-}OR')_4\}^{4+}$ core resulting from the $\eta^1:\eta^3:\eta^1:\eta^1:\mu_3$ coordination mode of the in situ formed ligand and has a diamagnetic ground state.

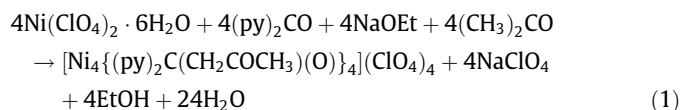© 2011 Elsevier Ltd. All rights reserved.

Polynuclear complexes (clusters [1]) of 3d metals at intermediate oxidation states have become of intense interest in recent times [2], mainly due to their relevance to bioinorganic chemistry [3] and to the special class of molecular magnetic materials known as single-molecule magnets (SMMs) [4]. In the development of new synthetic routes to 3d-metal clusters, the choice of the ligands is always a key issue. A popular ligand is di-2-pyridyl ketone, $(py)_2CO$ (Scheme 1). Water and alcohols (ROH) have been shown to add to the carbonyl group upon coordination of the carbonyl oxygen and/or the 2-pyridyl nitrogen atoms, forming the ligands $(py)_2C(OH)_2$ [the gem-diol form of $(py)_2CO$] and $(py)_2C(OR)(OH)$ [the hemiketal form of $(py)_2CO$], respectively (Scheme 1). The impressive structural chemistry of the $(py)_2CO$-based metal clusters [5] stems from the ability of the anionic ligands $(py)_2CO_2^{2-}$, $(py)_2C(OH)(O)^-$ and $(py)_2C(OR)(O)^-$ to exhibit no less than 16 distinct bridging coordination modes ranging from μ_2 to μ_5 [5].

Recent studies have shown that attack by nucleophiles other than H_2O and alcohols on the carbonyl C atom of $(py)_2CO$ in the presence of metal ions generates the ligands shown in Scheme 2, which can be deprotonated to yield structurally interesting metal

clusters [5–9]. The molecules in Scheme 2 can be considered as a second generation family of ligands derived from $(py)_2CO$.

Since the a-hydrogens of acetone are weakly acidic (pK_a ~20) [10], we have been interested in investigating whether $(py)_2CO$ would be capable of undergoing reactivity towards $^-$:CH_2COCH_3 in the presence of metal ions. The present work describes the realization of this goal.

The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, $(py)_2CO$, and NaOEt in an 1:1:1 molar ratio in Me_2CO gave a dark green microcrystalline solid after storage of the initially formed solution at room temperature for one week. The solid was isolated by filtration and recrystallized from MeCN to give dark green, block-shaped crystals of $[Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4](ClO_4)_4 \cdot 2.55H_2O$ (1·2.55H$_2$O) in 40% yield,[1] where $(py)_2C(CH_2COCH_3)(O)^-$ is the anion of bis(2-pyridine-2-yl)butane-1-ol-3-one (Scheme 2, bottom right). Assuming that the only product from this reaction system is the Ni$_4^{II}$ cluster, the formation of 1 can be summarized in Eq. (1).

$$4Ni(ClO_4)_2 \cdot 6H_2O + 4(py)_2CO + 4NaOEt + 4(CH_3)_2CO$$
$$\rightarrow [Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4](ClO_4)_4 + 4NaClO_4$$
$$+ 4EtOH + 24H_2O \qquad (1)$$

* Corresponding authors. Tel.: +1 352 3928314; fax: +1 352 3928757 (G. Christou), tel.: +30 2610 997146; fax: +30 2610 997118 (S.P. Perlepes).

E-mail addresses: christou@chem.ufl.edu (G. Christou), perlepes@patras. upatras.gr (S.P. Perlepes).

---

1 The dried solid analyzed as 1·H$_2$O. Anal. Calc. for $C_{56}H_{54}Ni_4N_8O_{25}Cl_4$: C, 41.62; H, 3.38; N, 6.94. Found: C, 42.03; H, 3.68; N, 7.14%. IR (KBr, cm^{-1}): 1675s [ν(C=O)].
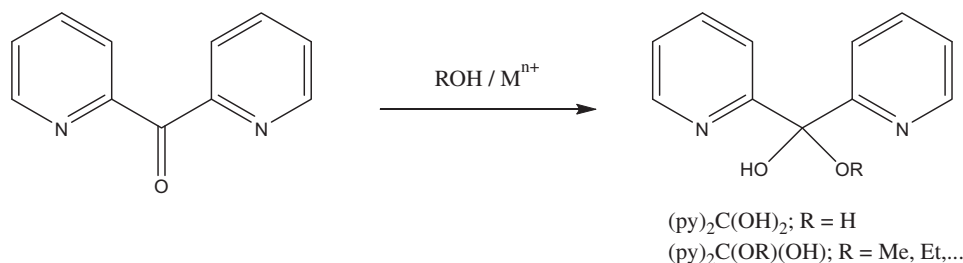
Scheme 1. Di-2-pyridyl ketone and its neutral *gem*-diol and hemiketal forms. Note that $(py)_2C(OH)_2$, $(py)_2C(OR)(OH)$ and their anions do not exist as free species but exist only in their respective metal complexes. M^{n+} is a metal ion (n = 2, 3).
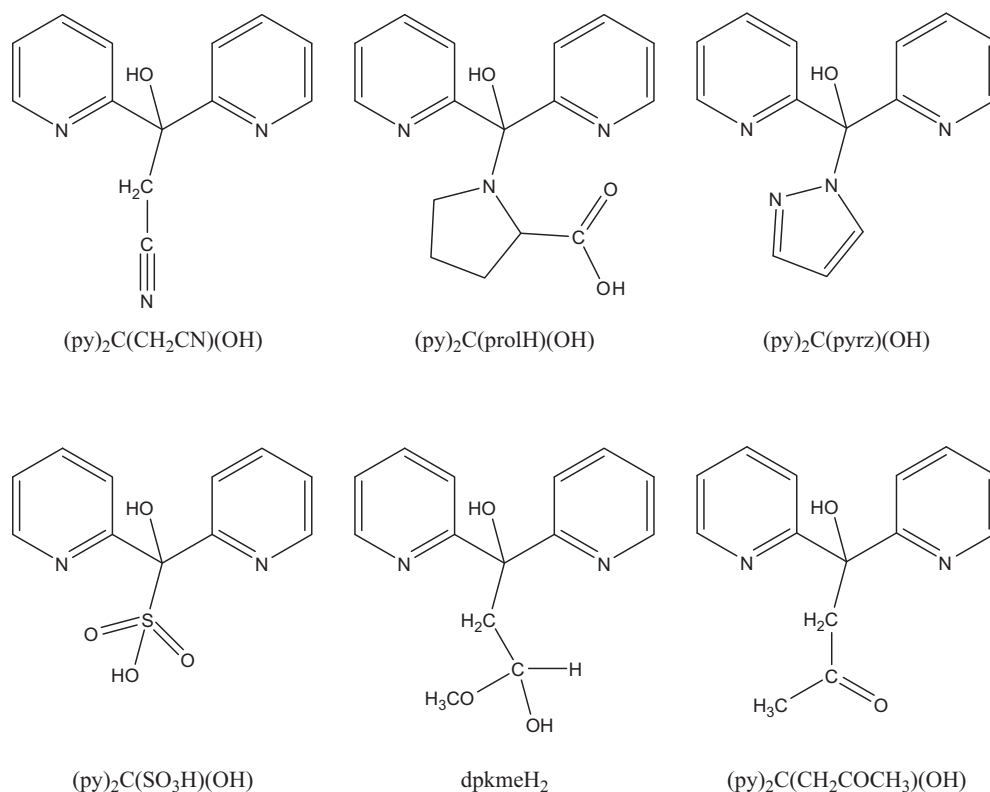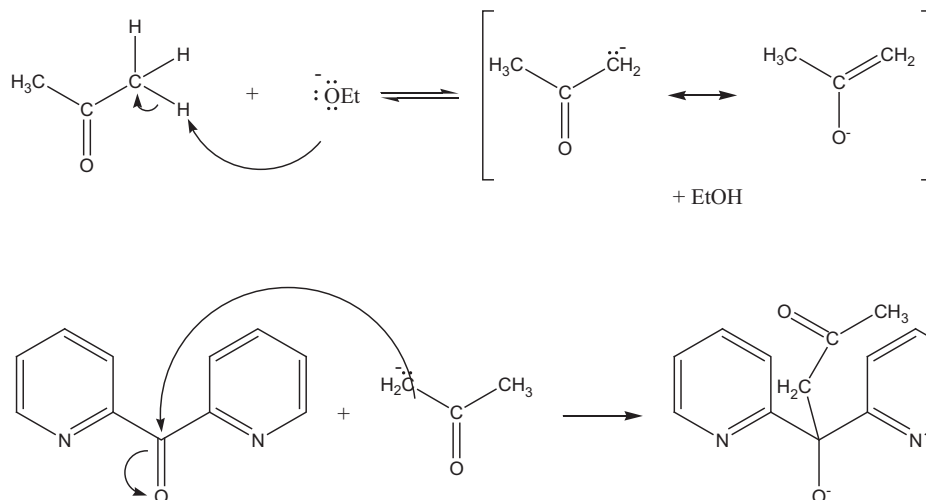

Scheme 2. The second generation family of ligands derived from $(py)_2CO$. Note that none of them exist as free species but are found only in their respective metal complexes. The new ligand that is present in complex **1**·2.55H$_2$O is $(py)_2C(CH_2COCH_3)(O)^-$.

A simplified mechanism for the formation of $(py)_2C(CH_2COCH_3)(O)^-$ is proposed in Scheme 3. The strong base EtO$^-$ abstracts an a-hydrogen from acetone which is in equilibrium with the corresponding, resonance-stabilized carbanion [10,11]. Once the carbanion $CH_3COCH_2^-$ is formed, it attacks the positively carbonyl carbon of $(py)_2CO$. As the carbanion forms the C–C bond, the π electrons of the carbonyl group of $(py)_2CO$ are transferred completely to the oxygen, forming an alkoxide ion. The reaction that leads to $(py)_2C(CH_2COCH_3)(O)^-$ is not an aldol condensation, because the product is not further dehydrated to form a double carbon–carbon bond [10,11]. Possible reasons for the non-condensation of $(py)_2C(CH_2COCH_3)(O)^-$ are the strongly basic medium which does not permit the existence of a neutral alcohol function and/or its stabilization by the Ni^{II} center. The formation of $(py)_2C(CH_2COCH_3)(O)^-$ is most probably metal-ion promoted (or assisted). We have failed to date to synthesize the free neutral ligand (this compound is not known in organic chemistry) by the reaction of $(py)_2CO$ and acetone in the presence of strong bases under several reaction conditions.

Complex **1**·2.55H$_2$O crystallizes in the monoclinic space group $P2_1/n$. The structure[2] consists of tetranuclear [Ni$_4${$(py)_2C(CH_2CO-CH_3)(O)$}$_4$]$^{4+}$ cations, ClO$_4^-$ counterions and solvate H$_2$O molecules. The tetranuclear cluster cation (Fig. 1) has a distorted cubane {Ni$_4(\mu_3$-OR')$_4$}$^{4+}$ core with Ni^{II} and oxygen atoms occupying alternate vertices of the cube [R'O$^-$ = $(py)_2C(CH_2COCH_3)(O)^-$]. Thus, the cation consists of two interpenetrating cocentric tetrahedra, one of four Ni^{II} atoms and one of the four μ_3-oxygen atoms originating from the ligands. In addition to the three μ_3-oxygen atoms, each Ni^{II} center is coordinated to two N atoms belonging to two different $(py)_2C(CH_2COCH_3)(O)^-$ ligands and to the ketone oxygen atom of one ligand to complete a distorted octahedral N$_2$O$_4$ coordination. One octahedral face of each Ni^{II} atom is occupied by the three alkox-

Scheme 3. The proposed simplified mechanism that leads to $(py)_2C(CH_2COCH_3)(O)^-$ that is present as ligand in cluster **1**; the Ni^{II} ion stabilizes the resonance-stabilized enolate intermediate and the final ketone/alkoxo product.
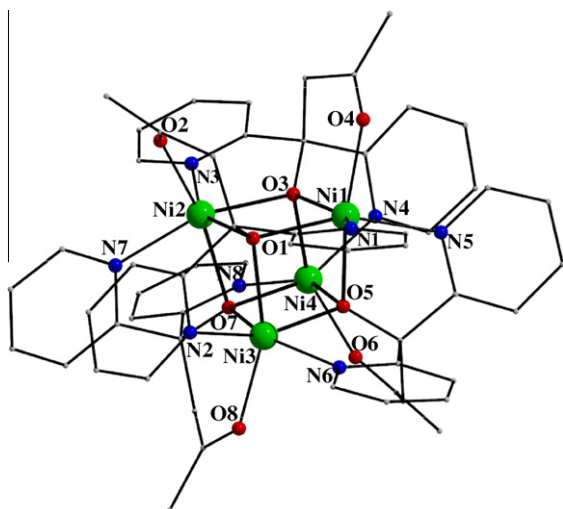

Fig. 1. Partially labeled plot of the cation present in **1**·2.55H$_2$O.
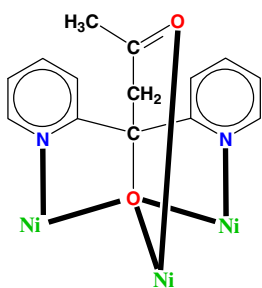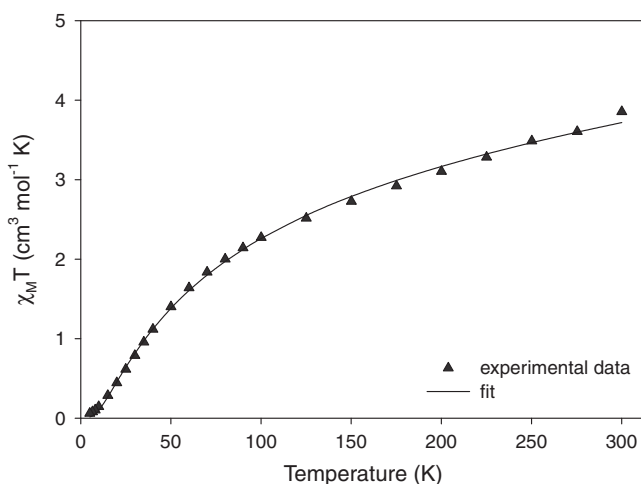

Fig. 3. $\chi_M T$ versus T plot for **1** in a 0.1 T dc field. The solid line is the fit of the data to the theoretical expression for the $2 - J$ model shown in Fig. 4; see the text for the fit parameters.

(Ni–OR′–Ni) are larger averaging 99.3(1)°. The Ni^{II}···Ni^{II} distances are in the 3.018(1)–3.243(1) Å range. Distinguishable C–O single [C–O(1, 3, 5, 7) = 1.401(3)–1.404(4) Å] and C=O double bonds [C–O(2, 4, 6, 8) = 1.223(4)–1.229(4) Å] are evident, confirming the description of $(py)_2C(CH_2COCH_3)(O)^-$ as containing one single and one double carbon–oxygen bond (Scheme 2). Complex **1** joins a large family of Ni$_4^{II}$ cubanes with a $\{Ni_4(\mu_3\text{-}OR')_4\}^{4+}$ core [12,13].

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data were collected on a powdered sample of dried **1** in the 5.0–300 K range in a 0.1 T field. The $\chi_M T$ value steadily decreases from 3.86 cm^3 mol^{-1} K at 300 K to 0.06 cm^3 mol^{-1} K at 5.0 K (Fig. 3). The room temperature $\chi_M T$ value is slightly lower than the expected value of 4.00 cm^3 mol^{-1} K for four $S = 1$ uncoupled spins with $g = 2$. The temperature dependence of the $\chi_M T$ product is indicative of an overall antiferromagnetic behaviour that leads to a diamagnetic ground state. The structural parameters of **1** suggest a lower symmetry than T_d. The magnetic analysis was carried out using a $2 - J$ model, see Fig. 4. The corresponding isotropic spin Hamiltonian is given by Eq. (2).

$$H = -2J_1(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) - 2J_2(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4)$$

(2)

Fig. 2. The coordination mode of the anion $(py)_2C(CH_2COCH_3)(O)^-$ in cluster **1**.

ide-type oxygen atoms and the other contains the remaining donor atoms. Each $(py)_2C(CH_2COCH_3)(O)^-$ ion functions as a η^1:η^3:η^1:η^1:μ_3 ligand (Fig. 2) forming two five-membered NiNCCO chelate rings with two different metal ions and one six-membered NiOCCCO chelate ring with a third metal ion; the three rings share a common C–O edge. The cube deviates from the ideal geometry. The internal cube angles at the Ni^{II} cube vertices (OR′–Ni–OR′) average 79.4(1)°, whereas the corresponding angles for the alkoxide corners
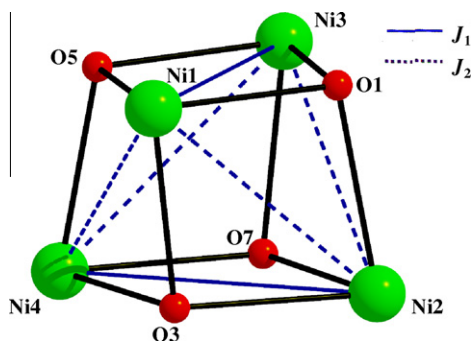
Fig. 4. Magnetic exchange interactions in complex **1**. The Ni^{II} and μ_3-O numbering schemes are the same with those employed in the real structure, see Fig. 1.

The eigenvalue of this spin Hamiltonian can be determined analytically with the Kambe vector coupling method and the substitutions $\hat{S}_A = \hat{S}_1 + \hat{S}_3$, $\hat{S}_B = \hat{S}_2 + \hat{S}_4$ and $\hat{S}_T = \hat{S}_A + \hat{S}_B$, where S_T is the total spin of the cation. The spin Hamiltonian is transformed into the equivalent operator form and its eigenvalues are given by Eq. (3). For complex **1** there are 19 different spin states involving S_T values of 4, 3, 2, 1 and 0 with degeneracies of 1, 3, 6, 6 and 3, respectively.

$$E(S_T, S_A, S_B) = -J_1[S_A(S_A + 1) + S_B(S_B + 1)] - J_2[S_T(S_T + 1) \\ - S_A(S_A + 1) - S_B(S_B + 1)] \qquad (3)$$

These were used to derive the appropriate van Vleck equation, which was used to fit the $\chi_M T$ versus T data, giving fit parameters of $J_1 = +2.21$ cm^{-1}, $J_2 = -13.16$ cm^{-1} and $g = 2.03$ (solid line in Fig. 3). A temperature-independent paramagnetism (TIP) term was included and held constant at 600×10^{-6} cm^3 mol^{-1}. The exchange interactions thus indicate the complex to have the $|S_T, S_A, S_B> = |0, 2, 2>$ ground state, with the $|1, 2, 2>$ first excited state at 26.32 cm^{-1} above the ground state. The $S_T = 0$ ground state was confirmed by the alternating-current (ac) magnetic susceptibility data (Fig. S1).

The values and the signs of the J_1 and J_2 parameters are in line with the previously established magnetostructural correlation [12–14] for clusters possessing the {Ni$_4$(μ_3-OR′)$_4$}$^{4+}$ core. The mean Ni–O–Ni angle for the four Ni$_2^{II}$ pairs (faces of the cube) described by J_2 is 101.6°, larger than the critical value of ~99°; the coupling is thus predicted to be weakly antiferromagnetic and, indeed, it is. The mean Ni–O–Ni value of 94.6° for the remaining two faces [Ni(1)O(1)Ni(3)O(5), Ni(2)O(3)Ni(4)O(7)] justifies the ferromagnetic value of J_1 (+2.21 cm^{-1}).

In summary, it has been shown that coordinated (py)$_2$CO is capable of undergoing a unique reactivity in acetone under basic conditions which is due to the presence of a weakly acidic a-hydrogen in the solvent and to the δ+ character of the carbonyl carbon atom of the ligand; the anion of the β-hydroxy ketone that is formed bridges three Ni^{II} atoms through its alkoxide group facilitating the formation of the cubane core. We are now (i)

investigating the incorporation of carboxylates in the general Ni^{II}/(py)$_2$CO/base/acetone reaction system, and (ii) targeting clusters of other 3d-metal ions that will contain the (py)$_2$C (CH$_2$COCH$_3$)(O)$^-$ ligand [15].

Acknowledgements

Appendix A. Supplementary data

CCDC 806902 contains the supplementary crystallographic data for **1**·2.55H$_2$O. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.02.024.

References

[1] For a discussion on the various meanings of the term "cluster" in several areas of inorganic chemistry, see: M.H. Chisholm, Polyhedron 17 (1998) 2773.
[2] R.E.P. Winpenny, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 7, Elsevier, Amsterdam, 2004, pp. 125–175 (Chapter 7.3).
[3] J. Barber, J.W. Murray, Coord. Chem. Rev. 252 (2008) 233.
[4] (a) For reviews, see: R. Bagai, G. Christou, Chem. Soc. Rev. 38 (2009) 1011;
(b) G. Aromi, E.K. Brechin, Struct. Bonding (Berlin) 122 (2006) 1.
[5] For a recent microreview, see: Th.C. Stamatatos, C.G. Efthymiou, C.C. Stoumpos, S.P. Perlepes, Eur. J. Inorg. Chem. (2009) 2261.
[6] M.-L. Tong, M. Monfort, J.M. Clemente Juan, X.-M. Chen, X.-H. Bu, M. Ohba, S. Kitagawa, Chem. Commun. (2005) 233.
[7] Y. Li, S. Xiang, T. Sheng, J. Zhang, S. Hu, R. Hu, R. Fu, X. Huang, X. Wu, Inorg. Chem. 45 (2006) 6577.
[8] B.F. Abrahams, T.A. Hudson, R. Robson, Chem. Eur. J. 12 (2006) 7095.
[9] Th.C. Stamatatos, K.A. Abboud, W. Wernsdorfer, G. Christou, Inorg. Chem. 48 (2009) 807.
[10] P.S. Bailey Jr., C.A. Bailey, Organic Chemistry, fifth ed., Prentice Hall, Upper Saddle River, New Jersey, USA, 1995. pp. 359–365.
[11] A.A. Kitos, C.G. Efthymiou, C. Papatriantafyllopoulou, V. Nastopoulos, A.J. Tasiopoulos, M.J. Manos, W. Wernsdorfer, G. Christou, S.P. Perlepes, Polyhedron, in press, doi:10.1016/j.poly.2011.02.013.
[12] C.G. Efthymiou, C. Papatriantafyllopoulou, N.I. Alexopoulou, C.P. Raptopoulou, R. Boča, J. Mrozinski, E.G. Bakalbassis, S.P. Perlepes, Polyhedron 28 (2009) 373 (and references cited therein).
[13] For a tabulation and a critical structural/magnetic analysis of Ni$_4$ cubanes, see: K. Isele, F. Gigon, A.F. Williams, G. Bernardinelly, P. Franz, S. Decurtins, Dalton Trans. (2007) 332.
[14] M.A. Halcrow, J.-S. Sun, J.C. Huffman, G. Christou, Inorg. Chem. 34 (1995) 4167.
[15] Few days before the submission of this Communication, Latham and coworkers reported [16] the X-ray structure of the dinuclear complex [Cu$_2$(NCS)$_2${(py)$_2$C(CH$_2$COCH$_3$)(O)}$_2$] in which the *in situ* formed ligand behaves in the η^1:η^2:η^1:μ_2 fashion.
[16] K.B. Szpakolski, K. Latham, C.J. Rix, J.M. White, Eur. J. Inorg. Chem. (2010) 5660.