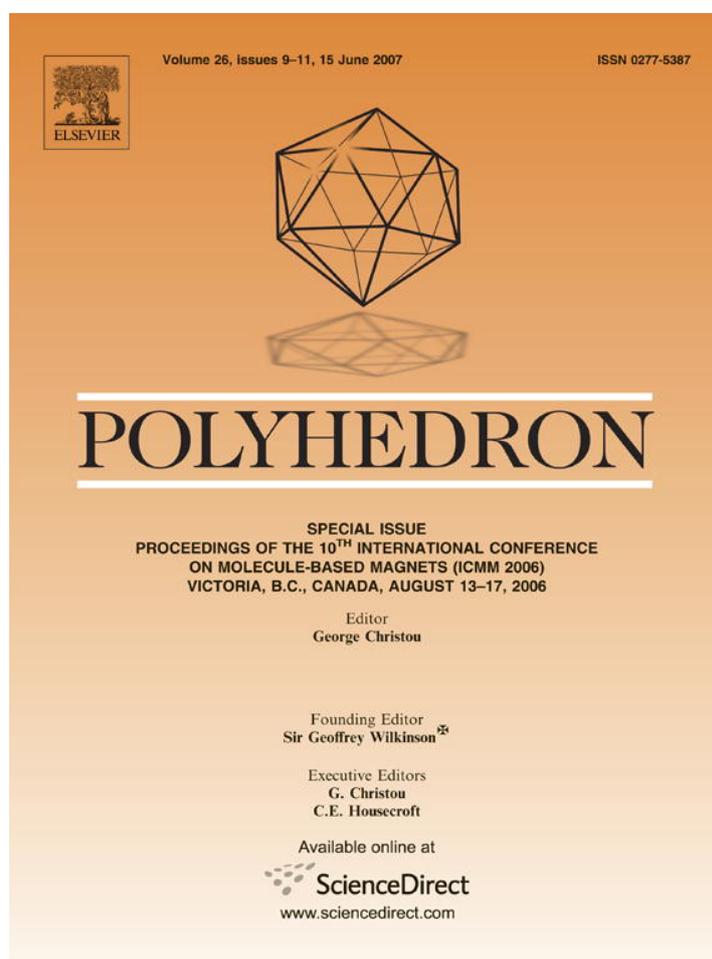


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A general synthetic route for the preparation of high-spin molecules: Replacement of bridging hydroxo ligands in molecular clusters by end-on azido ligands

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Abstract

A general method of increasing the ground-state total spin value of a polynuclear 3d-metal complex is illustrated through selected examples from cobalt(II) and nickel(II) cluster chemistry that involves the dianion of the *gem*-diol form of di-2-pyridyl ketone and carboxylate ions as organic ligands. The approach is based on the replacement of hydroxo bridges, that most often propagate antiferromagnetic exchange interactions, by the end-on azido ligand, which is a ferromagnetic coupler.

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1. Introduction

The study of molecules or ions possessing large number of unpaired electrons in their ground state is a sub-area of transition-metal cluster chemistry of intense current interest. One reason for this interest is that a large spin (S) value is a necessary (but not sufficient) requirement for molecules or ions to exhibit the exciting phenomenon of single-molecule magnetism [1]. Large S values arise from ferromagnetic (or ferrimagnetic) and/or competing antifer-

romagnetic exchange interactions of comparable strength (spin-frustration effects) [2]. The highest total spin values for molecular clusters that have been reported are $S = 83/2$ for a recently described $\text{Mn}_{12}^{\text{III}}\text{Mn}_7^{\text{II}}$ complex [3], and $S = 51/2$ for a $\text{Mn}^{\text{IV}}\text{Mn}_{18}^{\text{III}}\text{Mn}_6^{\text{II}}$ cluster [4] and a $\text{Mn}_9^{\text{II}}\text{Mo}_6^{\text{V}}$ cyano-bridged species [5].

The importance of high S values in cluster chemistry has stimulated efforts for the synthesis of new examples of high-spin molecules/ions [6] and for the development of strategies that will permit chemists to isolate species with this property at will. The latter is an extremely difficult task because synthetic chemists cannot predict in advance the structural types and metal topologies that will lead to high-spin clusters. We have been trying to develop a general synthetic approach for the increase in the ground-state

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total spin value of 3d-metal clusters [7–9]. We herein report examples of this approach.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. IR spectra (4000–500 cm^{-1}) were recorded on Perkin–Elmer 16 PC and Nicolet 520 FTIR spectrometers with samples prepared as KBr pellets. Magnetic susceptibility measurements under magnetic fields of approximately 0.1 T in the range 2–300 K and magnetisation measurements (only for complexes **2** and **4**) in the field range of 1–5 T were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were performed on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic corrections which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities.

2.2. Compound preparation

2.2.1. $[Co_9(OH)_2(O_2CMe)_8\{(py)_2CO_2\}_4] \cdot 14.6H_2O$ (**1** · 14.6 H_2O)

MeCN (45 mL) was added to a mixture of $Co(O_2CMe)_2 \cdot 4H_2O$ (0.27 g, 1.08 mmol) and $(py)_2CO$ (0.10 g, 0.54 mmol). The solids dissolved on stirring under reflux for 2 h to give a pale purple solution, which was allowed to stand undisturbed at room temperature overnight. Well-formed, X-ray quality crystals of **1** · 14.6 H_2O appeared slowly. The purple crystals were collected by filtration, washed with a little cold EtOH, and dried in air. Yield: 30%. *Anal.* Calc. for $C_{60}H_{87.2}Co_9N_8O_{40.6}$: C, 34.31; H, 4.18; N, 5.33; Co, 25.25. Found: C, 34.42; H, 4.13; N, 5.51; Co, 25.74%. IR (KBr, cm^{-1}): 3589s, 3434s, 2927w, 1675s, 1584s, 1476m, 1431s, 1352w, 1293w, 1232m, 1155w, 1123m, 1097m, 1031s, 976m, 890w, 805m, 784m, 754m, 690m, 675m, 646m, 621m, 542w, 485w, 445w, 416w.

2.2.2. $[Co_9(N_3)_2(O_2CMe)_8\{(py)_2CO_2\}_4] \cdot 4DMF \cdot 2.5H_2O$ (**2** · 4DMF · 2.5 H_2O)

DMF (25 mL) was added to a mixture of $Co(O_2CMe)_2 \cdot 4H_2O$ (0.17 g, 0.60 mmol), $(py)_2CO$ (0.06 g, 0.32 mmol) and NaN_3 (0.02 g, 0.30 mmol). The solids dissolved on stirring under heating to give a dark blue solution, which was allowed to stand undisturbed at room temperature for 3 days. Well-formed, X-ray quality pink-red crystals of **2** · 4DMF · 2.5 H_2O appeared, which were isolated by filtration, washed with DMF and Et_2O , and dried in air. Yield: 60%. *Anal.* Calc. for $C_{72}H_{89}Co_9N_{18}O_{30.5}$: C, 38.87; H, 4.03; N, 11.33. Found:

C, 38.24; H, 4.05; N, 11.65%. IR (KBr, cm^{-1}): 3446m, 3070w, 3025w, 2928w, 2802w, 2504w, 2073s, 1669s, 1583s, 1475m, 1430s, 1346w, 1294w, 1254w, 1229m, 1155w, 1119m, 1092m, 1057s, 1041s, 1020m, 973m, 962m, 890w, 806m, 780m, 757m, 686m, 664m, 617w, 529w, 475w, 442w, 421w.

2.2.3. $[Ni_9(OH)_2(O_2CMe)_8\{(py)_2CO_2\}_4] \cdot 19H_2O$ (**3** · 19 H_2O)

DMF (25 mL) was added to a mixture of $Ni(O_2CMe)_2 \cdot 4H_2O$ (0.15 g, 0.60 mmol) and $(py)_2CO$ (0.06 g, 0.32 mmol). The solids dissolved on stirring under heating to give a green solution, which was allowed to stand undisturbed at room temperature for 4 days. Well-formed, X-ray quality green crystals of **3** · 19 H_2O appeared, which were isolated by filtration, washed with DMF and Et_2O , and dried in air. Yield: 60%. *Anal.* Calc. for $C_{60}H_{96}Ni_9N_8O_{45}$: C, 33.09; H, 4.44; N, 5.15. Found: C, 33.41; H, 4.48; N, 5.03%. IR (KBr, cm^{-1}): 3591s, 3441s, 2930w, 1678s, 1588s, 1477m, 1431s, 1353w, 1293w, 1232m, 1157w, 1125m, 1098m, 1030s, 975m, 891w, 807m, 782m, 756m, 691m, 676m, 648m, 620m, 540w, 484w, 445w, 416w.

2.2.4. $[Ni_9(N_3)_2(O_2CMe)_8\{(py)_2CO_2\}_4] \cdot 4DMF \cdot 4.5H_2O$ (**4** · 4DMF · 4.5 H_2O)

Method A. DMF (25 mL) was added to a mixture of $Ni(O_2CMe)_2 \cdot 4H_2O$ (0.15 g, 0.6 mmol), $(py)_2CO$ (0.06 g, 0.32 mmol) and NaN_3 (0.02 g, 0.30 mmol). The solids dissolved on stirring under heating to give a green solution, which was allowed to stand undisturbed at room temperature for 7 days. Well-formed, X-ray quality green crystals of **4** · 4DMF · 4.5 H_2O appeared, which were isolated by filtration, washed with DMF and Et_2O , and dried in air. Yield: 60%. *Anal.* Calc. for $C_{72}H_{93}Ni_9N_{18}O_{32.5}$: C, 38.28; H, 4.15; N, 11.16. Found: C, 38.50; H, 4.19; N, 11.25%. IR (KBr, cm^{-1}): 3436s, 3070w, 2929w, 2085s, 1652s, 1587s, 1477m, 1431s, 1348w, 1293w, 1232m, 1156w, 1123m, 1099m, 1039s, 976m, 891w, 807m, 782m, 757m, 691m, 675m, 648m, 620w, 537w, 486w, 445w, 420w.

Method B. DMF (15 mL) and MeOH (10 mL) were added to a mixture of **3** · 19 H_2O (0.15 g, 0.6 mmol) and NaN_3 (0.08 g, 1.20 mmol). The solids dissolved on stirring under heating to give a green solution, which was allowed to stand undisturbed at room temperature for 5 days. Well-formed, X-ray quality green crystals of **4** · 4DMF · 4.5 H_2O appeared, which were isolated by filtration, washed with DMF and Et_2O , and dried in air. Yield: 80%. IR data and elemental analyses (C, H, N) were similar to the data obtained for the product prepared by Method A.

2.3. Single-crystal X-ray crystallography

Crystals of **2** · 4DMF · 2.5 H_2O , **3** · 19 H_2O and **4** · 4DMF · 4.5 H_2O were mounted in air, while crystals of **1** · 14.6 H_2O were mounted in capillary. Diffraction measurements for **1** · 14.6 H_2O were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo

Table 1

Brief crystallographic data for complexes **1** · 14.6H₂O, **2** · 4DMF · 2.5H₂O, **3** · 19H₂O and **4** · 4DMF · 4.5H₂O

Parameter	1 · 14.6H ₂ O	2 · 4DMF · 2.5H ₂ O	3 · 19H ₂ O	4 · 4DMF · 4.5H ₂ O
Formula	C ₆₀ H _{87.2} Co ₉ N ₈ O _{40.6}	C ₇₂ H ₈₉ Co ₉ N ₁₈ O _{30.5}	C ₆₀ H ₉₆ Ni ₉ N ₈ O ₄₅	C ₇₂ H ₉₃ Ni ₉ N ₁₈ O _{32.5}
Formula weight	2114.58	2224.99	2177.67	2258.75
Crystal system	monoclinic	tetragonal	tetragonal	tetragonal
Space group	C2/c	P4/n	P4/ncc (no.130)	P4/n (no. 85)
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	14.37(1)	17.762(1)	17.785(8)	17.841(8)
<i>b</i> (Å)	39.28(3)	17.762(1)	17.785(8)	17.841(8)
<i>c</i> (Å)	16.62(1)	14.203(1)	27.313(3)	14.008(3)
β (°)	115.69(3)			
<i>V</i> (Å ³)	8451(1)	4480.9(5)	8639(6)	4459(3)
<i>Z</i>	4	2	4	2
ρ_{calc} (g cm ⁻³)	1.651	1.652	1.643	1.676
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71069	Mo K α , 0.71069	Mo K α , 0.71069
Temperature (K)	298	298	293	293
μ (mm ⁻¹)	1.814	1.710	2.013	1.947
Reflections collected/unique (<i>R</i> _{int})	7637/7369 (0.0384)	18191/4761 (0.0531)	37752/7038 (0.082)	24451/5241 (0.038)
Data with <i>I</i> > 2 σ (<i>I</i>)	5734	2950	4166	3417
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0642	0.0365	0.0630	0.0375
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^b	0.1712	0.1037	0.1703	0.1052

^a $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$.^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

radiation. Analyses on **2** · 4DMF · 2.5H₂O, **3** · 19H₂O and **4** · 4DMF · 4.5H₂O were carried out with a MAR345 diffractometer with an image plate detector; intensities were collected with graphite-monochromated Mo radiation. Crystal data and parameters for data collection and processing are reported in Table 1.

The structures were solved by direct methods (SHELXS-86, SHELXS-97) and refined by full-matrix least squares techniques on *F*² (SHELXL-97). For the four structures, almost all non-hydrogen atoms were refined using anisotropic thermal parameters. Almost all hydrogen atoms were introduced at calculated positions as riding on their respective bonded atoms.

3. Results and discussion

The reaction of an excess of Co(O₂CMe)₂ · 4H₂O with di-2-pyridyl ketone, (py)₂CO (Fig. 1), in MeCN under reflux for 2 h gave the enneanuclear cluster [Co₉(OH)₂(O₂CMe)₈{(py)₂CO₂}₄] (**1**), see Eq. (1). The complex contains the doubly deprotonated form, (py)₂CO₂²⁻, of the *gem*-diol form of di-2-pyridyl ketone, (py)₂C(OH)₂ (Fig. 1) [10]; this is a consequence of the excess of acetates in the reaction mixture. The structure of **1** · 14.6H₂O consists of

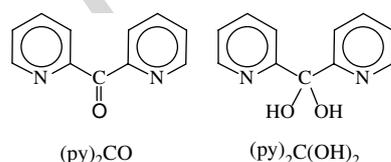
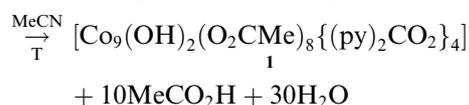
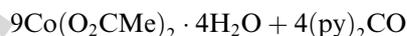


Fig. 1. Structural formulae and abbreviations of di-2-pyridyl ketone (left) and its *gem*-diol form (right). The ligand (py)₂C(OH)₂ does not exist as a free species, but only in the presence of metal ions.

enneanuclear molecules (Fig. 2, top). The complex has a crystallographic twofold axis passing through Co(1) and bisecting the angles around this metal ion, i.e. O(1)–Co(1)–O(1), O(2)–Co(1)–O(2), O(3)–Co(1)–O(3) and O(4)–Co(1)–O(4),



which is the shared apex of two square pyramids. The most characteristic feature of the structure is the coordination number 8 for Co(1), which is extremely rare in cobalt(II) chemistry. The dianion (py)₂CO₂²⁻ bridges five metal ions (Fig. 3) with the simultaneous formation of three chelate rings per ligand (coordination mode $\eta^1:\eta^3:\eta^3:\eta^1:\mu_5$). Each of the two hydroxides bridges four metal ions and all MeCO₂⁻ groups are in the familiar *syn,syn*- $\eta^1:\eta^1:\mu_2$ mode. The complex has an overall antiferromagnetic behaviour; the antiferromagnetic interactions are due to the $\eta^4:\mu_4$ OH⁻ ligands [11]. It is self-evident that we could not predict the structure of **1**; clearly it was obtained by serendipity [12].

At this point we started thinking in a more rational way. We decided to perform the same reaction that leads to **1**, but in the presence of N₃⁻ ions. The choice of the latter was based on established magnetostructural correlations which had shown that the end-on N₃⁻ ligand is an effective ferromagnetic coupler [13]. We hoped that the end-on azido ligands would be incorporated into the enneanuclear skeleton, instead of the hydroxo ligands which mediate a strong antiferromagnetic interaction. This substitution would lead to an increase of the total spin in the ground state.

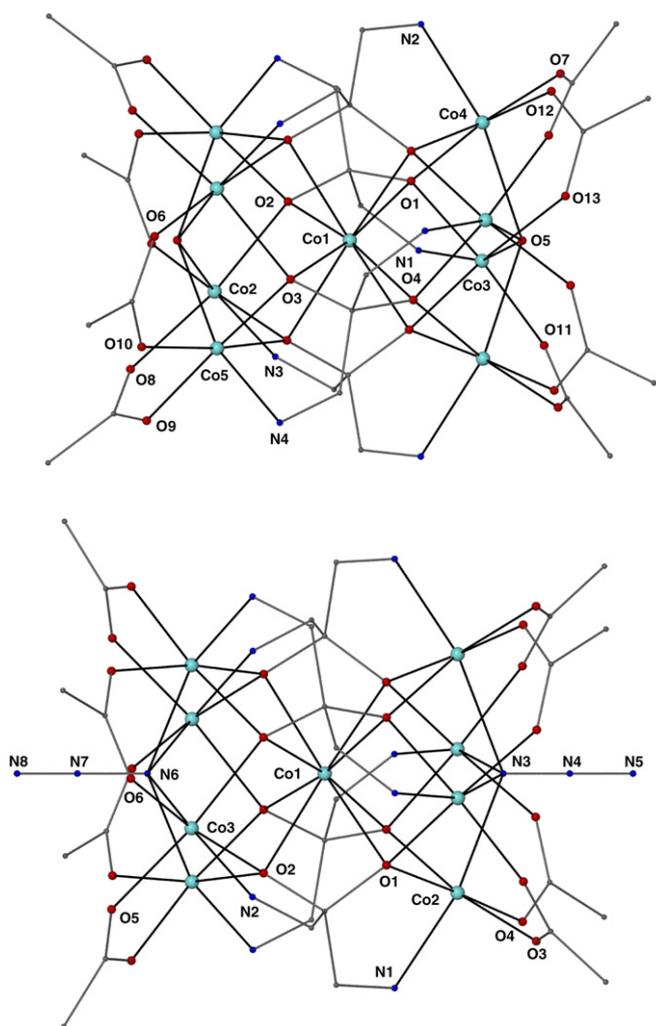


Fig. 2. Partially labeled plots of $[\text{Co}_9(\text{OH})_2(\text{O}_2\text{CMe})_8\{(\text{py})_2\text{CO}_2\}_4]$ (**1**, top) and $[\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8\{(\text{py})_2\text{CO}_2\}_4]$ (**2**, bottom). All H atoms and most C atoms of the $(\text{py})_2\text{CO}_2^{2-}$ ligands have been omitted for clarity.

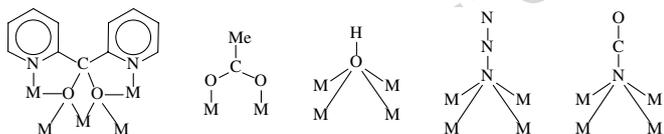


Fig. 3. The crystallographically established coordination modes of the ligands present in the complexes discussed in this work.

This has, indeed, turned out to be the case. The reaction represented by Eq. (2) in hot DMF (to keep the produced NaO_2CMe soluble) gave a dark blue solution from which the enneanuclear cage $[\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8\{(\text{py})_2\text{CO}_2\}_4]$ (**2**) was isolated in 60% yield. Complex **2** · 4DMF · 2.5 H_2O (Fig. 2, bottom) bears striking structural similarity

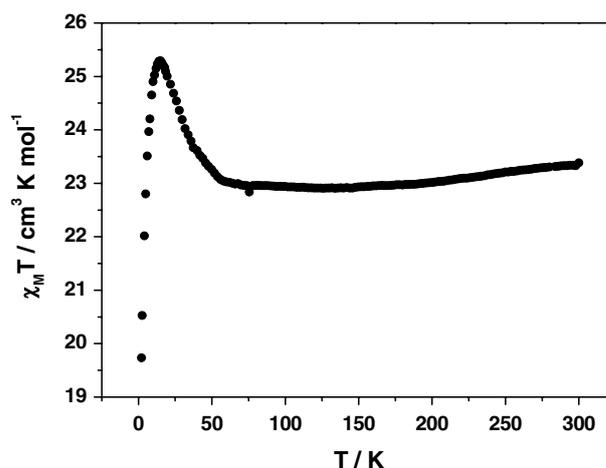
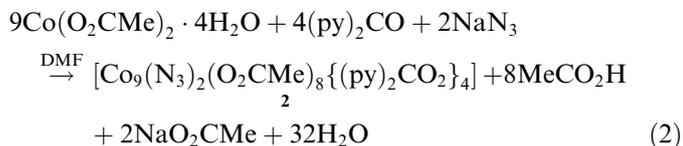


Fig. 4. Plot of the $\chi_M T$ vs. T product for **2**.

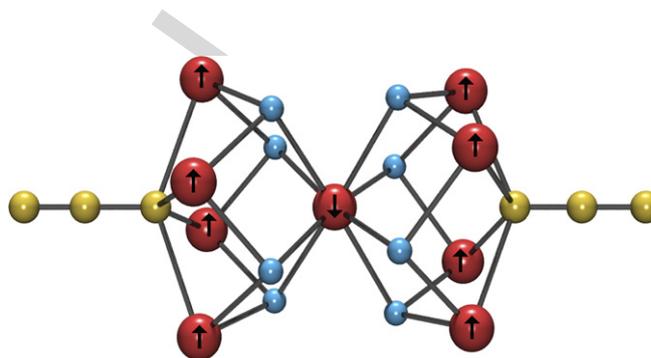


Fig. 5. The ferrimagnetic "structure" of complex **2**.

with the hydroxo cluster, the only difference being the presence of the novel quadruply bridging end-on azido ligands ($\eta^4:\mu_4$, Fig. 3) instead of the quadruply bridging hydroxo ligands. The complex has a crystallographic fourfold axis passing through Co(1) and the azido nitrogen atoms N(3), N(4), N(5), N(6), N(7) and N(8), thus bisecting the angles around this metal ion, i.e. O(1)–Co(1)–O(1') [$1.5 - x, 1.5 - y, z$] and O(2)–Co(1)–O(2') [$1.5 - x, 1.5 - y, z$].

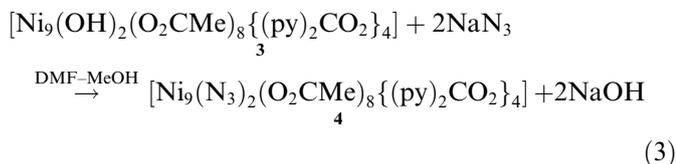
The weak minimum in the $\chi_M T$ vs. T plot at 116 K for **2** (Fig. 4) is the ferrimagnetic signature of the antiferromagnetic coupling between the central Co^{II} ion and the two ferromagnetically-coupled squares in the bases of the cage (Fig. 5). The ferromagnetic coupling in the square bases of the double square pyramid is mediated by the end-on $\mu_4\text{-N}_3^-$ ligands [7].

A similar reaction performed by using NaOCN instead of NaN_3 yielded the cyanate analogue of **2** containing novel μ_4 end-on (through the single N atom) OCN^- ligands (Fig. 3).¹

Using procedures similar to those described in Eqs. (1) and (2), the nickel(II) analogues of **1** and **2**, i.e. complexes $[\text{Ni}_9(\text{OH})_2(\text{O}_2\text{CMe})_8\{(\text{py})_2\text{CO}_2\}_4]$ (**3**) and $[\text{Ni}_9(\text{N}_3)_2$

¹ Details will be given in another paper.

(O₂CMe)₈{(py)₂CO₂}₄] (**4**), respectively, were prepared in very good yields and structurally characterized. Their molecular structures (Figs. 6 and 7) are very similar to those of the analogous Co₉^{II}/OH⁻ and Co₉^{II}/N₃⁻ clusters. Complex **4** can also be prepared by the reaction of the pre-formed hydroxo cluster **3** with a slight excess of N₃⁻ ions in DMF–MeOH (2:1 v/v) in ~80% yield.



Variable temperature (300–2.0 K) dc magnetic susceptibility data for **3** (Fig. 8) indicate a dominant antiferromagnetic superexchange pattern. Full analysis of the data [8] shows that the antiferromagnetic behaviour is due to the OH⁻ bridges and that the ground-state total spin is 1.

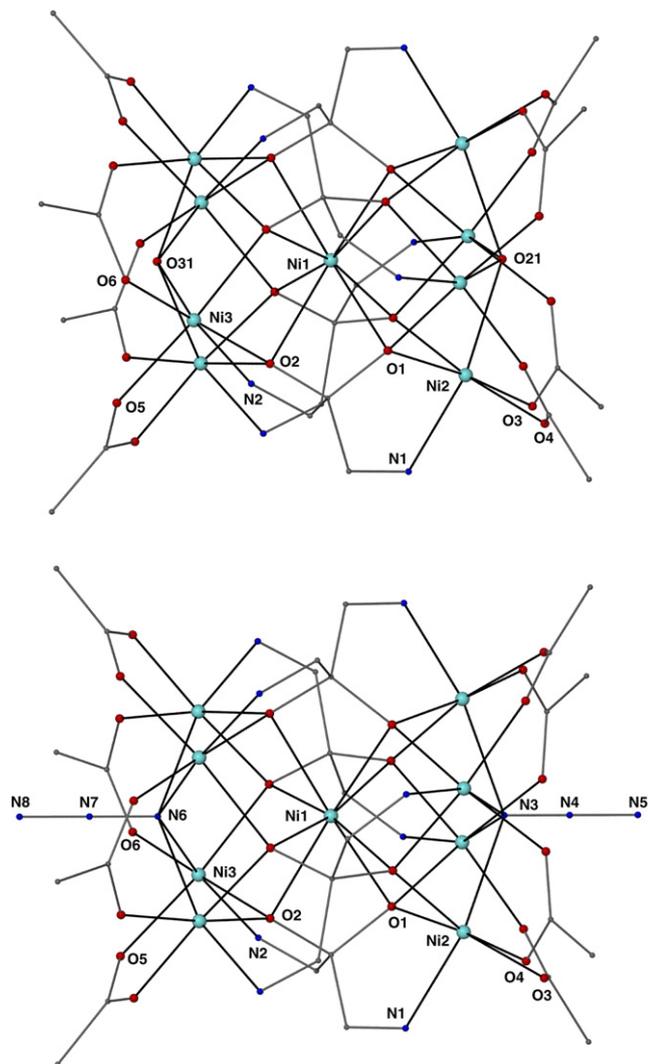


Fig. 6. Partially labeled plots of [Ni₉(OH)₂(O₂CMe)₈{(py)₂CO₂}₄] (**3**, top) and [Ni₉(N₃)₂(O₂CMe)₈{(py)₂CO₂}₄] (**4**, bottom). Both complexes have a fourfold axis. All H atoms and most C atoms of the (py)₂CO₂²⁻ ligands have been omitted for clarity.

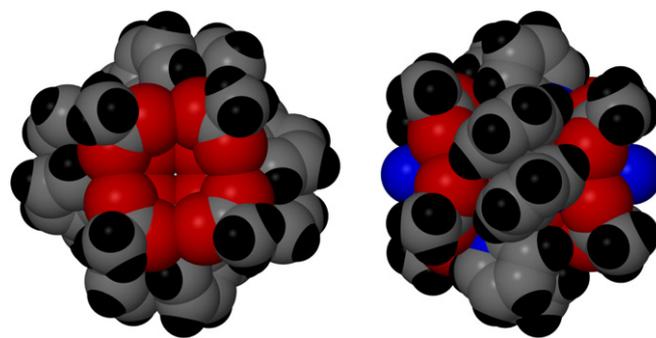


Fig. 7. Space filling models of [Ni₉(N₃)₂(O₂CMe)₈{(py)₂CO₂}₄] (**4**); a view perpendicular to the base of the double square pyramid showing the N₃⁻-trapping cavity (left) and a view showing the azides within the cavities (right).

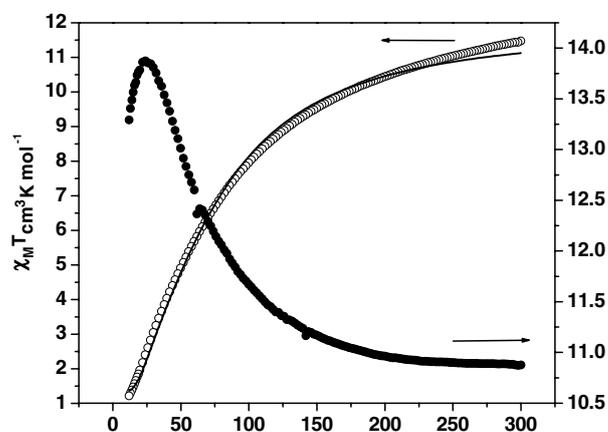


Fig. 8. Plots of the $\chi_M T$ vs. T products for **3** (left y axis, open circles) and **4** (right y axis, solid circles). The solid line is fit of the data to the appropriate 3-J model [8].

The dc $\chi_M T$ product of **4** increases from the 300 K value of 10.87 cm³ mol⁻¹ K to a maximum of 13.88 cm³ mol⁻¹ K at 24 K, and then decreases continuously down to 2.0 K (Fig. 8). This behaviour is compatible with moderate ferromagnetic coupling. Full analysis of the data shows that the ferromagnetic behaviour is due to the end-on azido bridges and that the ground-state total spin of the cluster is probably 9 (Fig. 9).

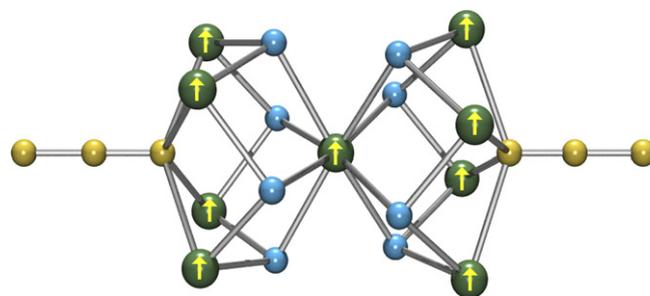


Fig. 9. The ferromagnetic “structure” of complex **4**.

The pivalate analogues of **1–4** have also been prepared.¹ These clusters have very similar molecular structures and magnetic properties with their corresponding acetate clusters. Similar chemistry occurs also with iron(II). Reactions of the initially isolated OH⁻-bridged cluster [Fe₉(OH)₂(O₂CMe)₈{(py)₂CO₂}₄] with N₃⁻ and OCN⁻ ions in refluxing MeCN under an inert atmosphere yielded complexes [Fe₉(N₃)₂(O₂CMe)₈{(py)₂CO₂}₄] and [Fe₉(NCO)₂(O₂CMe)₈{(py)₂CO₂}₄], respectively, that contain quadruply bridging pseudohalogeno ligands. Not only the N₃⁻ and OCN⁻-bridged clusters are ferromagnetic in nature, but these also display SMM behaviour [9].

4. Conclusions and perspectives

In summary, the end-on azido (and probably N-cyanato ligands) are good substitutes for hydroxo bridges in 3d-metal clusters to increase the *S* value of the ground state. The described N₃⁻ or OCN⁻ for OH⁻ substitution has the potential for wide application in the area of high-spin molecules. Often this approach involves “true” reactivity chemistry on pre-isolated clusters. Results at the time of writing reveal that application of the described strategy in at least 10 different hydroxo and alkoxo clusters leads to the retainment of the core and the introduction of specific ferromagnetic components in the superexchange scheme.

Acknowledgements

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Appendix A. Supplementary material

CCDCs 102038, 147542, 169287 and 169286 contain the supplementary crystallographic data for (**1** · 14.6H₂O), (**2** · 4DMF · 2.5H₂O), (**3** · 19H₂O) and (**4** · 4DMF ·

4.5H₂O). 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.2006.10.009.

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