DALTON
FULL PAPER

Novel polynuclear Cu^{II}/Co^{II} complexes constructed from one and two Cu_2Co triangles with antiferromagnetic exchange coupling

Valeriya G. Makhankova,[a] Olga Yu. Vassilyeva,*[a] Volodymyr N. Kokozay,[a] Brian W. Skelton,[b] Lorenzo Sorace[c] and Dante Gatteschi[c]

[a] *Department of Inorganic Chemistry, National Taras Shevchenko University, Volodimirska str. 64, Kyiv 01033, Ukraine. E-mail: vassilyeva@chem.univ.kiev.ua*
[b] *Department of Chemistry, University of Western Australia, Crawley, Western Australia 6009, Australia*
[c] *Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*

Received 5th June 2002, Accepted 10th September 2002
First published as an Advance Article on the web 21st October 2002

The reaction of acetonitrile solutions of $CoX_2{\cdot}2H_2O$ (X = NCS, I, Br) and 2-dimethylaminoethanol (HL) with copper powder in air leads to the formation of new tri- and hexa-nuclear complexes $[Cu_2Co(NCS)_3L_3]{\cdot}\frac{1}{2}CH_3CN$ (**1**), $[Cu_2Co(\mu_3\text{-}OH)I_2L_3]_2{\cdot}4CH_3CN$ (**2**) and $[Cu_2Co(\mu_3\text{-}OH)Br_2L_3]_2{\cdot}2CH_3CN$ (**3**). X-Ray crystallographic analysis of **1** reveals a symmetrical triangular core with one Co and two Cu atoms. The amino alkoxo- and S_{NCS}-bridges between metal centres result in copper–copper and copper–cobalt separations of 3.413(2) and 3.103(2) Å, respectively. Additional intermolecular association occurs through the NCS groups bridging Co and Cu centres of adjacent complex molecules to give chains. In the solid-state structures of **2** and **3** two symmetry-related Cu_2Co units are linked by amino alkoxo bridges to form a hexanuclear molecule with intermetallic distances ranging from 3.102(2)–3.260(2) (Cu ··· Co) to 3.287(3)–3.931(2) Å (Cu ··· Cu). The triangular planes formed by two copper and one cobalt atoms bridged by oxygen atoms from L groups are capped by a μ_3-hydroxide not found in the core of **1**. The hexanuclear units show no significant intermolecular contacts in the solid state. Variable-temperature magnetic susceptibility studies performed on **1** and **2** in the temperature range 5–280 K gave satisfactory fits to the observed susceptibility data by assuming isotropic magnetic exchange interactions and using the appropriate spin Hamiltonians considering **1** as a trinuclear entity and **2** as a combination of two trinuclear entities. An antiferromagnetic spin exchange operates in the Cu_2Co units of both complexes [J_{CuCu} = 40.1(4) (**1**), 48.7(9) (**2**); J_{CuCo} = 141(2) (**1**), 86.2(1.3) cm^{-1} (**2**)] while a weak ferromagnetic coupling is active between Cu and Co ions from different trinuclear entities in **2** ($J_{CuCo'} = -8.0(4)$ cm^{-1}).

Introduction

Polynuclear mixed-metal complexes are of considerable interest in current inorganic chemistry because they provide tractable examples of real-life electron transfer reactions in nature and also because they supply insights into the magnetic states of new and exciting materials which show promise for information storage and transfer.[1–4] Model compounds establish systematic magnetostructural correlations which permit an understanding of the controlling factors for the spin states of polynuclear transition metal complexes. However, despite the impressive progress in the preparation of polynuclear complexes of the d-block elements, the number of high nuclearity Cu/Co coordination compounds is limited to only a few examples.[5] The distinct philosophies of "designed synthesis" and "self assembly" offer two different approaches to achieving the objective of creating new polynuclear materials with which to extend the range of present working theories. Intellectually the former approach is appealing because of the control exercised over the course of the synthesis and the products. It is disappointing, however, that this approach has not proved to be very effective in the field of high nuclearity mixed-metal complexes, probably because of synthetic difficulties in obtaining elaborate ligands and molecular synthons that can be used as ligands. Also, the ability of such a design approach to create a species as novel as the $\{Ni_{24}\}$ cage,[6] for example, is very far from extant at this time. To reveal new modalities of assembly the multi-dimensional explorations accomplished in a typical reaction vessel will continue to provide the novelties and excitement of synthetic chemistry.[7]

As we showed earlier, metal powders (Cu^0, Ni^0, Zn^0) dissolved to form metal complexes in the presence of ammonium salt (a proton-donating agent) and dioxygen from the air *via* the following reaction

$$M^0 + 2NH_4^+ + \tfrac{1}{2}O_2 \longrightarrow M^{2+} + H_2O + 2NH_3 \qquad (1)$$

in which dioxygen is reduced to give H_2O and copper oxidation occurs in the two-step process $Cu \longrightarrow Cu^+ \longrightarrow Cu^{2+}$.[8] The concept of the necessity of a proton-donating agent in syntheses of coordination compounds from elemental metals in air was further developed into a strategy for the preparation of mixed-metal complexes that consisted of reacting zerovalent copper with a salt of another metal in a non-aqueous solution of amino alcohol.[9] We believed that coordinatively unsaturated copper amino alkoxide generated *in situ* could easily interact with other metal ions present in solution to afford formation of a mixed-metal compound due to the established ability of amino alcohols to form polynuclear metal complexes.[10] A further advance in the "one pot" synthesis of mixed-metal complexes was employing two elemental metals in reactions with proton-donating agents, in air, to give mixed-metal complexes directly. A novel heterotrinuclear complex with the asymmetric Cu_2ZnO_3I core was prepared using zerovalent copper and zinc as starting materials.[11] The synthetic approach

DOI: 10.1039/b205389f

developed can lead to different reactivity than is found for the conventional synthesis and produce complexes that are inaccessible by traditional synthetic routes (using Cu(II) instead of metallic copper).[12]

The principal aims of these studies have been the preparation of a broad range of species containing a variety of mixed-metal stoichiometries and the investigation of the dependence of the individual structures and mixed-metal stoichiometries on the reaction system employed. Recently, we have reported the synthesis of Cu^{II}/Co^{III} mixed-metal complexes featuring heterotetranuclear cations of a puckered cyclic structure with diethanolamine and diethanolamine(2−) as bridging ligands[13] and a unique pentanuclear mixed-valence complex $Cu^{II}/Co^{II}/Co^{III}$ obtained by the reaction of copper powder with cobalt(II) acetate and triethanolamine.[12] A marked decrease of the χT value below 40 K for the latter compound was attributed to antiferromagnetic exchange coupling between the Cu(II) and Co(II) magnetic centres interacting through the diamagnetic Co(III) ions.

As the reaction systems employed have been so productive in generating new Cu/Co structures, we have now commenced systematic investigations into reactions of zerovalent copper and a cobalt(II) salt in the presence of another amino alcohol, 2-dimethylaminoethanol $[N(CH_3)_2C_2H_4OH]$, HL, and wish to report here on the synthesis, crystal structures and magnetochemistry of the compounds $[Cu_2Co(NCS)_3L_3]\cdot\frac{1}{2}CH_3CN$ (**1**), $[Cu_2Co(\mu_3\text{-}OH)I_2L_3]_2\cdot4CH_3CN$ (**2**) and $[Cu_2Co(\mu_3\text{-}OH)Br_2L_3]_2\cdot2CH_3CN$ (**3**).

Experimental

Materials and synthesis

Commercial reagents were used without further purification; all experiments were carried out in air. Elemental analyses were performed by atomic absorption spectroscopy and standard titrimetric methods for metals and anions, respectively, and by the Department of Chemistry, Cambridge University microanalytical service (for C, H and N). Compounds **1**–**3** were prepared by mixing copper powder (0.64 g, 10 mmol), $CoX_2\cdot2H_2O$ (5 mmol, X = NCS, I, Br) in 20 cm^3 CH_3CN solution of HL (2 cm^3), in air, while warming the stirred solution until total dissolution of copper was observed (30–60 min). A dark crystalline powder of **1** was obtained from the brown–violet reaction mixture in the presence of Pr^iOH after 5 days. Dark-green microcrystals of **2** and **3** precipitated from the resulting green solutions after cooling. Recrystallisation from CH_3CN gave single crystals suitable for X-ray diffraction studies. The compounds are soluble in CH_3CN, CH_3OH, dmso and dmf under warming. All the complexes are indefinitely stable in air.

$[Cu_2Co(NCS)_3L_3]\cdot\frac{1}{2}CH_3CN$ (1). Mass collected: 0.83 g, yield 26%. Anal. calc. for $C_{16}H_{31.5}CoCu_2N_{6.5}O_3S_3$: Cu, 19.70; Co, 9.13; NCS, 27.01; C, 29.79; H, 4.92; N, 14.11. Found: Cu, 19.2; Co, 9.0; NCS, 26.7; C, 28.1; H, 5.1; N, 14.9%. IR (KBr, cm^{-1}): 3450br, 3000m, 2980m, 2965sh, 2910m, 2870m, 2800w, 2364m, 2340m, 2090vs (CN), 1650w, 1480sh, 1465m, 1410w, 1380w, 1350w, 1280w, 1250w, 1240w, 1180w, 1100sh, 1085s, 1070s, 1015m, 950m, 910m, 895m, 830w (CS), 785m, 645m, 605w, 530m, 490sh, 470m, 430w.

$[Cu_2Co(\mu_3\text{-}OH)I_2L_3]_2\cdot4CH_3CN$ (2). Mass collected: 2.96 g, yield 74%. Anal. calc. for $C_{32}H_{74}Co_2Cu_4I_4N_{10}O_8$: Cu, 15.82; Co, 7.34; I, 31.59; C, 23.92; H, 4.64; N, 8.72. Found: Cu, 15.8; Co, 8.4; I, 33.0; C, 24.6; H, 4.8; N, 8.9%. IR (KBr, cm^{-1}): 3520m, 3000m, 2970m, 2900s, 2965s, 2950sh, 2940sh, 2895w, 2740w, 2690w, 2365m, 2340m, 1650w, 1480sh, 1470s, 1425sh, 1405w, 1475w, 1460w, 1280w, 1250w, 1180w, 1090s, 1075s, 1020m, 955m, 910m, 795m, 645m, 520m, 495m, 465m, 430w.

$[Cu_2Co(\mu_3\text{-}OH)Br_2L_3]_2\cdot2CH_3CN$ (3). Mass collected: 2.69 g, yield 80%. Anal. calc. for $C_{28}H_{68}Br_4Co_2Cu_4N_8O_8$: Cu, 19.02; Co, 8.82; Br, 23.91; C, 25.16; H, 5.13; N, 8.38. Found: Cu, 19.0; Co, 8.9; Br, 23.1; C, 25.3; H, 5.2; N, 8.2%. IR (KBr, cm^{-1}): 3500br, 3000m, 2970m, 2900sh, 2965s, 2950s, 2895m, 2740w, 2690w, 2360m, 2340m, 1640w, 1480sh, 1470s, 1425w, 1405w, 1375w, 1350w, 1275w, 1250w, 1180w, 1095s, 1075s, 1020m, 955m, 910m, 795m, 705w, 645m, 520m, 495m, 465m, 430w.

Physical measurements

The IR spectra (4000–400 cm^{-1}) were recorded on KBr pellets with a UR-10 spectrophotometer. UV/VIS spectra were recorded on Perkin-Elmer 330 (diffuse-reflectance technique) and Perkin-Elmer Lambda 12 (CH_3CN and dmf solutions) spectrometers. X-Band EPR spectra in solution (CH_3OH, dmf) and in the solid state were measured at 293 and 77 K using Bruker ER 200 D and JEOL RE2x spectrometers. Variable-temperature magnetic measurements on complexes **1** and **2** in the region 5–280 K were made with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.[14]

Crystallography

Details of the data collection and processing, structure analysis and refinement are summarized in Table 1. Diffraction experiments were performed on freshly recrystallised samples on a Bruker SMART CCD (ω rotation scans with narrow frames) diffractometer (**1**, **2**) and an Enraf-Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (**3**) equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz-polarization effects and for the effects of absorption [multi-scan (**1**,**2**), Gaussian (**3**)]. The structures were solved by direct methods using the XTAL3.7[15] (**1**,**2**) and SHELXS 86[16] (**3**) programs, and refined by full-matrix least-squares methods on F (**1**,**2**) and F^2 (**3**) using XTAL3.7 and SHELXL 93.[17]

The non-hydrogen atoms were refined anisotropically, hydrogen atoms included but not refined. Ligand 2 in **1** is partially disordered about the crystallographic mirror plane, with atoms C(23), C(241) and C(241′) being assigned occupancies of 0.5. The position of the OH proton in **2** was located in the difference Fourier map but not refined. The OH proton in **3** was not located.

CCDC reference numbers 187030–187032.

See http://www.rsc.org/suppdata/dt/b2/b205389f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses and spectroscopic characterization

The reaction of copper powder with cobalt(II) salts (bromide, iodide and thiocyanate) and 2-dimethylaminoethanol in CH_3CN, in open air, gave microcrystals of the trinuclear **1** (in low yield) and hexanuclear complexes **2** and **3** in high yield. The title compounds could also be isolated as corresponding solvates from CH_3OH, dmf and dmso solutions. Their formation can be understood if one considers the following reaction schemes:

$$2Cu^0 + 2Co(NCS)_2 + 4HL + O_2 \longrightarrow Cu_2Co(NCS)_3L_3 + Co(NCS)L + 2H_2O \quad (2)$$

$$4Cu^0 + 2CoX_2 + 6HL + 2O_2 \longrightarrow [Cu_2Co(\mu_3\text{-}OH)X_2L_3]_2 + 2H_2O, X = I, Br \quad (3)$$

Table 1 Crystal data and structure refinement for **1**–**3**

	1	**2**	**3**
Chemical formula	$C_{16}H_{31.5}CoCu_2N_{6.5}O_3S_3$	$C_{32}H_{74}Co_2Cu_4I_4N_{10}O_8$	$C_{28}H_{68}Br_4Co_2Cu_4N_8O_8$
Formula weight	645.19	1606.68	1336.56
Crystal size/mm	0.20 × 0.07 × 0.05	0.45 × 0.18 × 0.15	0.48 × 0.43 × 0.40
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Cmc2_1$	$P2_1/n$	$P2_1/n$
a/Å	14.036(2)	15.372(2)	10.408(2)
b/Å	20.009(3)	10.781(2)	10.631(2)
c/Å	10.097(2)	16.487(3)	22.474(4)
β/°	90	95.647(2)	91.54(3)
V/Å^3	2835.7(8)	2719.1(8)	2485.8(8)
Z	4	2	2
μ/mm^{-1}	2.313	4.452	5.593
F(000)	1320	1564	1332
T/K	150	150	293
Reflections collected	17013	25794	4630
Reflections unique	2046	6782	4371
Reflections observed	1531 [$F > 4.00\sigma(F)$]	5367 [$F > 4.00\sigma(F)$]	2220 [$I > 2\sigma(I)$]
R	0.043	0.073	0.0796
wR	0.048	0.083	0.1445
No. of variables	169	271	248

We do not consider synthetic reactions using zerovalent metals as an alternative to well established methods of preparation of complexes but rather as another synthetic strategy that appeared convenient and fruitful in the case studied. However, attempts to prepare mixed-metal Cu/Co complexes with HL in the conventional synthesis (when $CuCl_2$ and $CuBr_2$ were used instead of metallic copper) failed—the resulting reaction solutions after the successive addition of Pr^iOH yielded purely Cu(II) complexes with 2-dimethylaminoethanol according to elemental analyses and IR spectroscopy.

The IR spectra of complexes **1**–**3** in the range 4000–400 cm^{-1} are quite similar and show all the characteristic ligand peaks. Crystals of **1**–**3** formed in CH_3CN appeared to lose solvent if left to stand exposed to a solvent-free atmosphere which may account for the absence of apparent CN stretching vibrations corresponding to acetonitrile in the spectra. The spectra of **2** and **3** indicate the presence of OH groups (3600–3500 cm^{-1}) with a distinctive band at 3520 cm^{-1} resolved in the spectrum of **2**.[18] Compound **1** shows a sharp intense ν(CN) absorption at 2090 cm^{-1} and a weak band for ν(CS) at 830 cm^{-1} of a thiocyanate group. The δ(NCS) mode is obscured by other vibrations. The frequencies of the observed bands imply a terminal N-bonded thiocyanate.

The diffuse reflectance spectrum of **1** exhibits broad non-symmetrical bands with maxima at *ca.* 380, 525 and 700 nm. The spectra of **2** and **3** are slightly different showing ligand field bands at 390, 604 (shoulder) and 810 nm. The bands at high energy are clearly assigned to charge transfer ligand-to-metal transitions. The d–d transitions are associated with both the cobalt(II) and copper(II) centres and are not distinguishable. The charge-transfer region of the solution (CH_3CN, dmf) spectra of 300–400 nm is characterized by the occurrence of intense bands for all three complexes with clear shoulders at 383 (dmf) and 389 nm (CH_3CN) for **3**. A broad visible band of low intensity around 614–642 (CH_3CN) and 634–659 nm (dmf) is attributed to a superposition of Cu(II) and Co(II) d–d transitions.

Crystal structures of complexes 1–3

$[Cu_2Co(NCS)_3L_3]\cdot½CH_3CN$ (1). X-Ray crystallographic analysis of **1** reveals a symmetrical three-metal atom core (containing a crystallographic mirror plane) with one Co and two Cu atoms in a triangular array (Fig. 1). The alkoxy O atoms of L groups bridge the Cu and Co centres, whereby two μ [O(11), O(11a)] and one μ_3 bridge [O(21)] exist. The copper atom adopts a square pyramidal coordination sphere, with a chromophore $\{CuN_2O_2S\}$ in which the axial sulfur atom belongs to a thiocyanate group of the neighboring molecule. The four copper-ligand bonds in the equatorial plane vary between 1.899(6) and 2.024(8) Å, the axial bond is elongated [2.751(3) Å]. The two copper square pyramids are tilted toward each other as a result of the bridging function of the axial sulfur atom, S(02) $\{-x, -y, ½ + z\}$. The cobalt atom has four quite short bonds with the nitrogen and oxygen atoms, O(11), O(11) $\{-x, y, z\}$, N(02) and N(24), and a longer bonding distance to the oxygen atom O(21) at 2.262(8) Å, making a distorted trigonal bipyramidal geometry (Table 2). Five-coordinate Co(II) is not very common and many of its complexes have tripod-type or bulky macrocyclic ligands.[19] The amino alkoxo- and S_{NCS}-bridges between metal centres result in copper–copper and copper–cobalt separations of 3.413(2) and 3.103(2) Å, respectively.

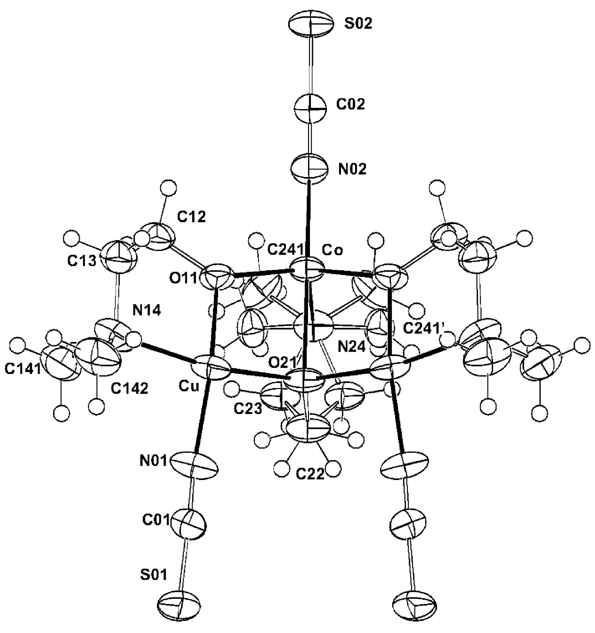

Fig. 1 ORTEP[23] plot of **1** with the atom numbering scheme and the non-hydrogen atoms shown as 50% thermal ellipsoids.

Additional intermolecular association in the structure of **1** occurs through the Cu–S interactions between the S(02) atom of the NCS group coordinated to Co and two copper atoms of the adjacent complex molecule. As a consequence, a polymeric

Table 2 Selected bond distances (Å) and angles (°) for **1**

Cu–O(11)	1.899(6)	Co–O(21)	2.262(8)
Cu–O(21)	1.982(5)	Co–N(02)	2.02(1)
Cu–N(14)	2.024(8)	Co–O(11)	1.928(6)
Cu–N(01)	1.917(7)	Co–N(24)	2.09(1)
Cu–S(02^{i})	2.751(3)	Co–Cu	3.103(2)
Cu ··· Cu^{ii}	3.413(2)		
O(11)–Co–(21)	75.1(2)	O(11)–Co–N(24)	113.5(2)
O(11)–Co–N(02)	103.9(2)	O(11)–Co–O(11^{ii})	117.5(3)
O(21)–Co–N(24)	79.9(4)	O(21)–Co–N(02)	177.8(4)
O(21)–Co–O(11^{ii})	75.1(2)	N(24)–Co–N(02)	102.3(4)
N(24)–Co–O(11^{ii})	113.5(2)	N(02)–Co–O(11^{ii})	103.9(2)
O(11)–Cu–N(14)	84.9(3)	O(11)–Cu–O(21)	82.8(3)
O(11)–Cu–N(01)	163.6(3)	O(11)–Cu–S(02^{i})	102.1(2)
N(14)–Cu–O(21)	167.5(3)	N(14)–Cu–N(01)	95.3(3)
N(14)–Cu–S(02^{i})	102.6(3)	O(21)–Cu–N(01)	96.0(3)
O(21)–Cu–S(02^{i})	82.1(2)	N(01)–Cu–S(02^{i})	93.9(3)

Symmetry transformations used to generate equivalent atoms (indicated by superscript): ^{i} $-x, -y, \frac{1}{2} + z$; ^{ii} $-x, y, z$.

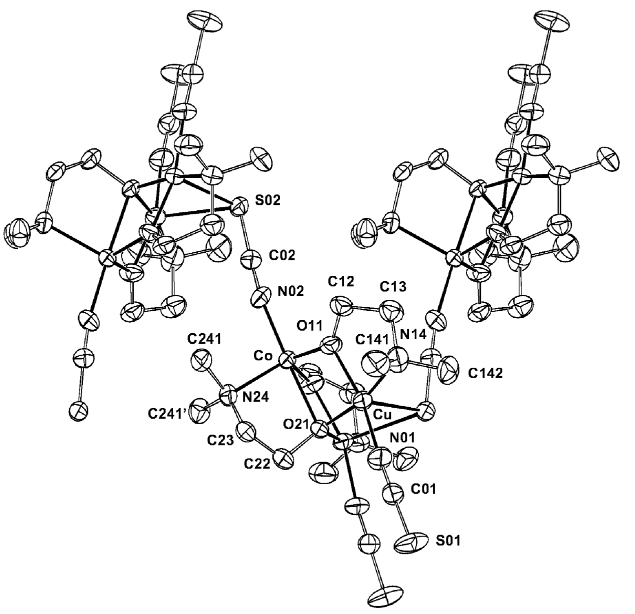

Fig. 2 Fragment of the polymeric chain present in the crystal structure of **1**, showing the intermolecular Cu–S_{NCS} interactions (H atoms omitted for clarity; only one of the two sets of disordered C(23), C(241) and C(241′) atoms is shown).

chain assembly is evident along the *c*-axis of the crystal (see Fig. 2). The chains are held together through intermolecular interactions. The acetonitrile solvent molecules of crystallization occupy cavities in the crystal lattice.

$[Cu_2Co(\mu_3\text{-}OH)I_2L_3]_2\cdot 4CH_3CN$ (2) and $[Cu_2Co(\mu_3\text{-}OH)Br_2L_3]_2\cdot 2CH_3CN$ (3). The overall structural configurations of **2** and **3** are similar. The important differences show up as relatively small changes in bond lengths and angles (Table 3). The molecular diagram and numbering scheme of **2** is shown in Fig. 3, which illustrates the general geometry of the two compounds. Two centrosymmetrically-related Cu_2Co units with a similar triangular topology to the central core in **1** are now linked by amino alkoxo bridges to form a hexanuclear molecule. Whereas in **1** all the bridging oxygen atoms are derived from L groups, in **2** and **3** one of the bridging groups is a μ_3-hydroxide leading to a less symmetrical array of metal sites. The positions of metal atoms were assigned to the differing metals based on structure refinement and on elemental analysis by atomic absorption spectroscopy. The elemental analysis indicates the Cu_2Co stoichiometry and X-ray crystallographic refinement for both **2** and **3** leads to consistent displacement parameters for the metal sites only if they are assigned as shown in Fig. 3.

Table 3 Selected bond distances (Å) and angles (°) for **2** and **3**

	2 (X = I)	**3** (X = Br)
Cu(1)–X(1)	3.019(1)	2.742(2)
Cu(2)–X(1)	3.060(1)	2.780(2)
Cu(1)–X(2)	2.644(1)	2.453(2)
Cu(1)–O(1)	1.961(7)	1.936(9)
Cu(1)–O(4)	1.958(6)	1.951(8)
Cu(1)–N(1)	2.036(9)	2.03(1)
Cu(2)–O(3)	1.940(7)	1.925(9)
Cu(2)–O(4)	1.976(7)	1.963(9)
Cu(2)–N(3)	2.035(8)	2.03(1)
Cu(2)–O(2^{i})	1.917(6)	1.918(9)
Co(3)–O(1)	1.930(7)	1.936(8)
Co(3)–O(2)	1.963(6)	1.957(8)
Co(3)–O(3)	1.947(7)	1.943(9)
Co(3)–O(4)	2.309(6)	2.28(1)
Cu(1) ··· Cu(2)	3.405(2)	3.287(3)
Cu(1) ··· Co(3)	3.145(2)	3.128(3)
Cu(2) ··· Co(3)	3.102(2)	3.093(3)
Cu(2) ··· Cu(2^{i})	3.931(2)	3.902(3)
Cu(2) ··· Co(3^{i})	3.260(2)	3.257(3)
Co(3)–N(2)	2.149(8)	2.13(1)
X(1)–Cu(1)–X(2)	103.05(4)	105.17(8)
X(1)–Cu(1)–O(1)	106.1(2)	102.8(3)
X(1)–Cu(1)–O(4)	86.5(2)	86.9(3)
X(1)–Cu(1)–N(1)	97.5(2)	98.3(3)
X(2)–Cu(1)–O(1)	150.5(2)	151.6(3)
X(2)–Cu(1)–O(4)	95.22(18)	94.1(3)
X(2)–Cu(1)–N(1)	97.0(2)	97.8(4)
O(1)–Cu(1)–O(4)	82.6(3)	82.4(4)
O(1)–Cu(1)–N(1)	83.4(3)	83.0(4)
O(4)–Cu(1)–N(1)	166.0(3)	165.3(5)
X(1)–Cu(2)–O(3)	99.8(2)	99.6(3)
X(1)–Cu(2)–O(4)	85.03(18)	85.7(2)
X(1)–Cu(2)–N(3)	97.7(2)	97.3(4)
X(1)–Cu(2)–O(2^{i})	107.35(19)	109.2(3)
O(3)–Cu(2)–O(4)	85.1(3)	84.4(4)
O(3)–Cu(2)–N(3)	84.5(3)	84.6(5)
O(3)–Cu(2)–O(2^{i})	152.6(3)	150.9(4)
O(4)–Cu(2)–N(3)	169.5(3)	169.0(5)
O(4)–Cu(2)–O(2^{i})	93.1(3)	93.6(4)
N(3)–Cu(2)–O(2)	95.8(3)	95.4(5)
O(1)–Co(3)–O(2)	126.2(3)	128.1(4)
O(1)–Co(3)–O(3)	115.0(3)	113.2(4)
O(1)–Co(3)–O(4)	74.6(3)	74.4(3)
O(1)–Co(3)–N(2)	106.1(3)	108.1(4)
O(2)–Co(3)–O(3)	112.8(3)	111.3(4)
O(2)–Co(3)–O(4)	94.3(2)	92.2(3)
O(2)–Co(3)–N(2)	82.5(3)	82.6(4)
O(3)–Co(3)–O(4)	76.4(2)	76.0(4)
O(3)–Co(3)–N(2)	106.1(3)	106.7(5)
O(4)–Co(3)–N(2)	176.5(3)	174.7(4)

Symmetry transformation used to generate equivalent atoms (indicated by superscript): For **2**: $-x, 1 - y, -z$; For **3**: $1 - x, 2 - y, 2 - z$.

Each L group adopts a chelating-bridging mode linking two metal atoms. The triangular planes formed by two copper and one cobalt atoms are capped by a μ_3-OH group that adopts an asymmetric bonding mode with two shorter distances (mean 1.962(9) Å) to the copper atoms and a longer one to the cobalt centre (mean 2.293(10) Å).

The two unique copper centres have distinct chemical environments but both adopt a distorted square-pyramidal coordination, $Cu(1)NO_2X_2$ and $Cu(2)NO_3X$, X = I (**2**), Br (**3**), with average Cu–O and Cu–N equatorial distances of 1.945(9) and 2.032(11) Å, respectively. The Cu–X bond lengths vary in the range 2.453(2)–2.780(2) and 2.643(1)–3.060(1) Å for **3** and **2**, respectively; the axial Cu–X(1) bonds are somewhat weaker compared with the corresponding in-plane Cu(1)–X(2) distances (Table 3) consistent with the Jahn–Teller effect in the d^9 electronic configuration. The two copper square pyramids are tilted toward each other as a result of the bridging function of the axial halide atom. Positions of the iodide atoms in the

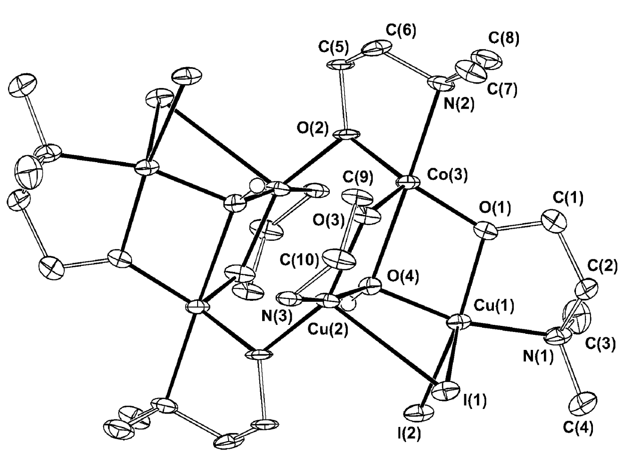

Fig. 3 ORTEP plot of **2** with the atom numbering scheme and the non-hydrogen atoms shown as 50% thermal ellipsoids (H atoms, N(3) and N(3a) methyl groups omitted for clarity).

coordination sphere of copper atoms and Cu–I bond distances in **2** (Table 3) correspond very well to those for the compound $[Cu_2Zn(NH_3)I_3L_3]$ with the closely related structure: Cu(1)–I(1) 2.982(2), Cu(2)–I(1) 3.072(1), Cu(2)–I(2) 2.631(1) Å.[11]

Five-coordination of the cobalt atom in **2** and **3** is completed by three O atoms (average 1.946(9) Å) and a nitrogen atom, N(2), of three L groups and the μ_3-hydroxide in an elongated trigonal bipyramidal geometry. The O(4)–Co(3)–N(2) angles of *ca.* 175° show that the three atoms are nearly linear.

The intermetallic distances in **2** and **3** range from 3.102(2)–3.260(2) (Cu ··· Co) to 3.287(3)–3.931(2) Å (Cu ··· Cu). The hexanuclear units show no significant intermolecular contacts in the solid state, solvent molecules occupy cavities in the crystal lattice.

Magnetic properties

The X-band EPR spectra of **1**–**3** in the solid state are very weak both at room temperature and at 77 K. Frozen solutions (77 K) of all the compounds in dmf and methanol exhibit axial spectra typical for monomeric Cu(II) species thus suggesting dissociation of **1**–**3** in solution. The temperature dependences of the molar magnetic susceptibility of **1** and **2** measured as solids in the range 5–280 K are shown in Figs. 4 and 5 in the form of $\chi_M T$ *vs.* T. $\chi_M T$ for **1** is equal to 2.58 cm^3 K mol^{-1} at room temperature (μ_{eff} = 4.55 μ_B), a value which is lower than that expected for non-interacting pentacoordinated Co(II) and two Cu(II) centres (3.2 cm^3 K mol^{-1} for an average g = 2.20).[20] As the temperature is lowered $\chi_M T$ decreases to a plateau characterized by $\chi_M T$ = 1.94 cm^3 K mol^{-1}, then decreases again below 30 K and reaches a value of 1.66 cm^3 K mol^{-1} at 5 K. These features are consistent with antiferromagnetic coupling between metal centres.

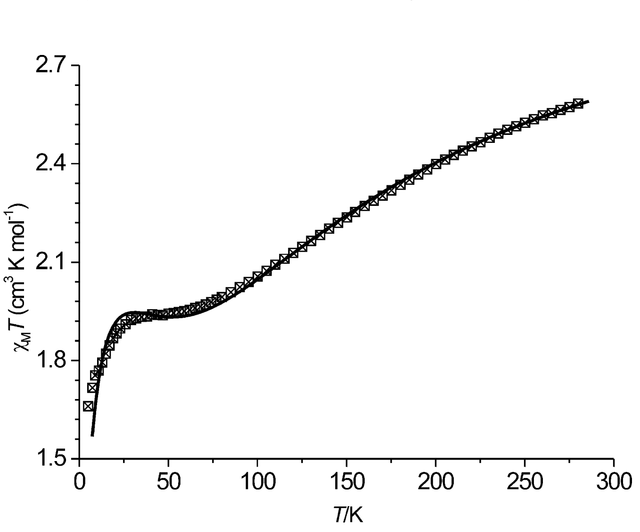

Fig. 4 $\chi_M T$ *vs.* T curve for **1**. The continuous line is the fit obtained using parameters reported in the text.

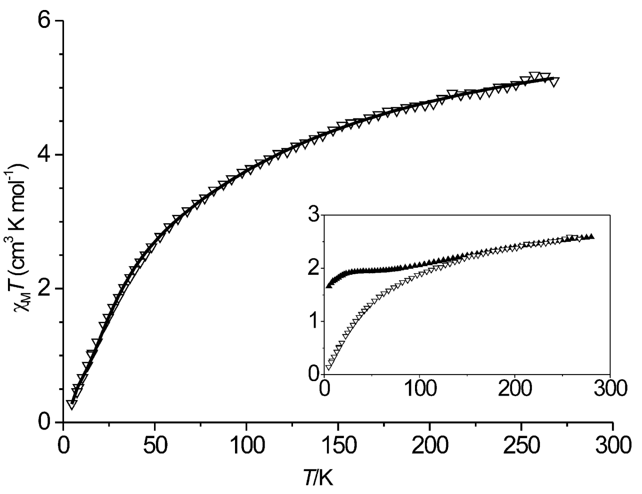

Fig. 5 $\chi_M T$ *vs.* T curve for **2**. The continuous line is the fit obtained using parameters reported in the text. The inset shows a comparison of the temperature dependence of χT for **1** (▲) and **2** (▽) by plotting them per mole of Cu_2Co.

The magnetic susceptibility data can be quantitatively analysed in the 280–5 K temperature range on the assumption of isotropic coupling between the magnetic centres as the ground electronic state of the trigonal bipyramidal Co(II) centre is orbitally non-degenerate.[20] We employed the spin Hamiltonian for a symmetrical three-spin system:

$$H = J_1(S_{Cu1}\cdot S_{Co} + S_{Co}\cdot S_{Cu2}) + J_2 S_{Cu1}\cdot S_{Cu2} \qquad (4)$$

which yields energy levels

$$E(S,S') = J_1 S(S+1)/2 + [(J_2 - J_1)/2]S'(S'+1) \qquad (5)$$

S' being the intermediate spin resulting from the coupling between the two Cu(II) ions. The theoretical expression of the molar susceptibility deduced from eqn. (4) is the following:[1]

$$\chi T = \frac{N\mu_B^{\,2} g^2}{kT}\cdot \frac{\left(10 + 35\exp\left(-\frac{J_2+1.5J_1}{kT}\right) + 35\exp\left(-\frac{J_2-J_1}{kT}\right) + \exp\left(-\frac{J_2-2.5J_1}{kT}\right)\right)}{\left(8 + 12\exp\left(-\frac{J_2+1.5J_1}{kT}\right) + 8\exp\left(-\frac{J_2-J_1}{kT}\right) + 4\exp\left(-\frac{J_2-2.5J_1}{kT}\right)\right)} \qquad (6)$$

where N, μ_B and k have their usual meanings, and we did not take into account differences between g values for different metals to avoid overparametrization of the system. The decrease of $\chi_M T$ observed in the low temperature region was fitted by including a term of intermolecular interaction, $\chi_{corr} = \chi'/(1 - \theta\chi')$, with $\theta = 2zJ_{inter}/Ng^2\mu_B^{\,2}$.[14] This term can easily be related to the presence of thiocyanate bridging ligand, which may provide an effective pathway to transmit the exchange interaction between neighbouring molecules. The best fit parameters are J_1 = 40.1(4), J_2 = 141(2) cm^{-1}, θ = −1.45(4) K and g_{ave} = 2.20 (agreement factor R^2 = 0.995). The existence of competing antiferromagnetic interactions results in the ground state $|S,S'\rangle = |3/2,0\rangle$, with the first excited state, $|½,1\rangle$, lying *ca.* 60 K above in energy.

A comparison of the $\chi_M T$ data of **1** and **2** (plotted in the inset of Fig. 5) clearly shows that at high temperature the magnetic behaviour of the two complexes is essentially the same, while below 100 K a marked decrease in $\chi_M T$ values is observed for **2**, strongly suggesting a singlet ground state ($\chi_M T = 0.2$ cm^3 K mol^{-1} at 5 K) for this complex. The differences in the magnetic behaviour of the two complexes can be traced back to the presence of additional exchange interactions between Cu2 and Co′, and Cu2′ and Co. Furthermore, while the main structural features determining the Cu1–Co exchange coupling are only slightly altered with respect to **1**, and its magnitude in the two systems is then expected to be similar, Cu–Cu coupling can be influenced by the presence in **2** of a μ_3-hydroxo bridge in place of the μ-oxo bridge of **1**.

A quantitative analysis of the magnetic behaviour of **2** was performed according to the following Hamiltonian:

$$H = J_1(\boldsymbol{S}_{\mathrm{Cu1}}\cdot\boldsymbol{S}_{\mathrm{Co}} + \boldsymbol{S}_{\mathrm{Co}}\cdot\boldsymbol{S}_{\mathrm{Cu2}} + \boldsymbol{S}_{\mathrm{Cu1'}}\cdot\boldsymbol{S}_{\mathrm{Co'}} + \boldsymbol{S}_{\mathrm{Co'}}\cdot\boldsymbol{S}_{\mathrm{Cu2'}}) + J_2(\boldsymbol{S}_{\mathrm{Cu1}}\cdot\boldsymbol{S}_{\mathrm{Cu2}} + \boldsymbol{S}_{\mathrm{Cu1'}}\cdot\boldsymbol{S}_{\mathrm{Cu2'}}) + J_3(\boldsymbol{S}_{\mathrm{Cu2'}}\cdot\boldsymbol{S}_{\mathrm{Co}} + \boldsymbol{S}_{\mathrm{Co'}}\cdot\boldsymbol{S}_{\mathrm{Cu2}}) \quad (7)$$

where J_1 and J_2 correspond to the Cu–Co and Cu–Cu coupling, respectively, within the trinuclear units and J_3 to the coupling between the trinuclear units (Fig. 6). For the sake of simplicity we assumed the Cu–Co interactions within the trinuclear units to be the same. The fit performed by the full-matrix diagonalization method[21] gave the following results: $J_1 = 48.7(9)$, $J_2 = 86.2(1.3)$, $J_3 = -8.0(4)$ cm^{-1}, $g_{\mathrm{ave}} = 2.20$ and $R^2 = 0.998$ with a singlet ground state as expected (the first excited state $S = 1$ lying only 8 cm^{-1} above in energy). The intensity of Cu–Cu interactions is then reduced in **2** with respect to **1**, while the strength of antiferromagnetic Cu–Co between metal centres within the trinuclear units in **2** is similar to that observed in **1**; finally Cu–Co′ coupling between the trinuclear units is much weaker than the former interactions and ferromagnetic. Even if it may sound surprising that the onset of ferromagnetic interaction results in a singlet ground state, the peculiar spin topology of the system easily accounts for this result. The relative magnitude of the competing antiferromagnetic interactions J_2 and J_1 is such that even if $J_2 > J_1$, each trinuclear unit would experience—according to eqn. (5)—a doublet ground state, with a parallel alignment of copper spins in each triangular unit. The additional ferromagnetic coupling between cobalt and copper of different units finally leads to a singlet ground state, as sketched in Fig. 6.

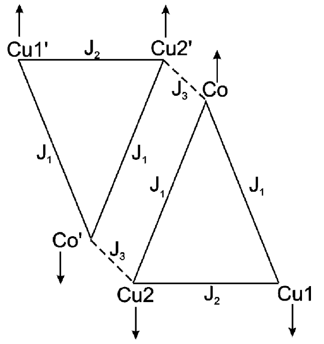

Fig. 6 Exchange coupling pattern for complex **2** with the scheme of the spin topology assuming ferromagnetic coupling between the trinuclear units leading to the singlet ground state.

To the best of our knowledge, this is the first time that the structural and magnetic properties of a Cu_2Co triangular assembly and—what is more important—those of a hexanuclear Cu_4Co_2 array have been reported. Magnetostructural correlation cannot then easily be worked out by comparison with literature data but, as long as the Cu–Cu (J_2) interactions are concerned, the quite strong antiferromagnetic values obtained for both complexes fall in the range previously observed for related systems.[22] On the other hand various factors can be invoked to justify the different sign of the Cu–Co interactions within (J_1) and between (J_3) the trinuclear units: the presence of two exchange pathways for J_1, through μ- and μ_3-oxo bridges, whereas μ-O(2) only is available to transmit J_3; the substantially larger angle of the μ-oxo bridge [Cu(2)–O(2′)–Co′] transmitting the ferromagnetic interaction with respect to those involved in the antiferromagnetic one. It has also to be considered that the magnetic orbital of Cu, which on the basis of its coordination environment is supposed to be essentially $x^2 - y^2$, is mainly interacting with z^2 and $x^2 - y^2$ of Co and only with $x^2 - y^2$ for Co′. This may result in the enhanced overlap between magnetic orbitals of the two centres in the former case and then in antiferromagnetic coupling for J_1.

Finally, it has to be stressed that minor structural changes observed in the Cu_2Co units of the two complexes, resulting in some differences in the coordination environment of metal centres may lead to somewhat different energetic patterns for magnetic orbitals of Cu(II) and Co(II) in both cases. A deeper theoretical analysis based on DFT calculations, which could substantiate the observed findings on a quantitative basis, is beyond the scope of this article and we have left it for the future, whenever more data on similar complexes will be reported.

Conclusions

The formation process of the tri- and hexa-nuclear structures is another example of new spin systems formed in reactions with zerovalent metal. Obviously for new heterometallic compounds generated in the reaction systems involving zerovalent copper, cobalt salts and amino alcohol in air, described in the present paper and before,[12,13] the nature of the amino alcohol is of crucial importance in determining the nuclearity and structure of the Cu/Co complexes formed. Generalizing the structure of the Cu_2Co core to the hexanuclear compound leads to an explanation of the magnetic properties and, particularly, the singlet ground state for the latter complex.

Acknowledgements

The work was supported in part by the Science and Technology Center in Ukraine (Project Gr-32j). We thank Professor J. Reedijk for helpful discussions and Mr G. A. van Albada for recording the magnetic and EPR measurements. Further thanks to the European Science Foundation under the Program “Molecular Magnets”.

References

1 (*a*) O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993; (*b*) O. Kahn, *Struct. Bonding (Berlin)*, 1987, **68**, 89; (*c*) O. Kahn, *Adv. Inorg. Chem.*, 1996, **4**, 179.
2 J. S. Miller and A. J. Epstein, *Chem. Eng. News*, 1995, 30.
3 *Molecular Magnetic Materials*, eds. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, NATO ASI Series, Kluwer, Dordrecht, The Netherlands, 1991.
4 (*a*) B. J. Wallar and J. D. Lipscomb, *Chem. Rev.*, 1996, **96**, 2625; (*b*) E. I. Solomon, T. C. Brunold, M. Z. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, A. J. Skulan, Y. S. Yang and J. Zhou, *Chem. Rev.*, 2000, **100**, 235.
5 (*a*) M. G. F. Vaz, L. M. M. Pinherio, H. O. Stumpf, A. F. C. Alcantara, S. Golhen, L. Ouahab, O. Cador, C. Mathoniere and O. Kahn, *Chem. Eur. J.*, 1999, **5**, 1486; (*b*) E. K. Brechin, S. G. Harris, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 3403; (*c*) I. N. Polyakova, V. S. Sergienko, A. L. Poznyak and O. G. Ellert, *Zh. Neorg. Khim.*, 1997, **42**, 1653; (*d*) M. A. Banners, L. Dauphin, X.-J. Lei, W. Cen, M. Shang, E. E. Wolf and T. P. Fehlner, *Chem. Mater.*, 1995, **7**, 553.
6 A. L. Dearden, S. Parsons and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2001, **40**, 151.
7 R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2002, 1.
8 (*a*) V. A. Pavlenko, V. V. Skopenko and V. N. Kokozay, *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol. Khim. Biol. Nauki*, 1983, 47; (*b*) V. A. Pavlenko, V. N. Kokozay and V. V. Skopenko, *Dopov. Akad.*

Nauk Ukr. RSR, Ser. B: Geol. Khim. Biol. Nauki, 1985, 42; (*c*) O. Yu. Vassilyeva, N. D. Nevesenko, V. V. Skopenko, Yu. S. Gerasimenko and V. N. Kokozay, *Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol. Khim. Biol. Nauki*, 1988, 36; (*d*) O. Yu. Vassilyeva and V. N. Kokozay, *Ukr. Khim. Zh. (Russ. Ed.)*, 1993, **59**, 176.

9 (*a*) L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, J. Reedijk, B. W. Skelton and A. G. Oliver, *J. Chem. Soc., Dalton Trans.*, 1998, 2735; (*b*) L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, B. W. Skelton and A. G. Oliver, *New J. Chem.*, 1998, **22**, 931 and refs therein.

10 (*a*) K. Smolander, *Ann. Acad. Sci. Fenn., Ser. A*, 1983, **2**, 1; (*b*) J. A. Bertrand and P. G. Eller, *Prog. Inorg. Chem.*, 1976, **21**, 29; (*c*) S. Wang, Z. Pang, K. D. L. Smith and M. J. Wagner, *J. Chem. Soc., Dalton Trans.*, 1994, 955; (*d*) A. Lehtonen and R. Sillanpaa, *J. Chem. Soc., Dalton Trans.*, 1995, 2701.

11 E. A. Vinogradova, O. Yu. Vassilyeva and V. N. Kokozay, *Inorg. Chem. Commun.*, 2002, **5**, 19.

12 V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, B. W. Skelton, J. Reedijk, G. A. van Albada, L. Sorace and D. Gatteschi, *New J. Chem.*, 2001, **25**, 685.

13 V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, J. Reedijk, G. A. van Albada, J. Jezierska and B. W. Skelton, *Eur. J. Inorg. Chem.*, 2002, 2163.

14 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 103.

15 S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, eds., XTAL3.7 System, University of Western Australia, 2000.

16 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

17 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1993.

18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

19 (*a*) M. B. Davies, *Coord. Chem. Rev.*, 1994, **134**, A195; (*b*) H. Plenio, C. Aberle, Y. Al Shihadeh, J. M. Lloris, R. Martinez-Manez, T. Pardo and J. Soto, *Chem. Eur. J.*, 2001, **7**, 2848; (*c*) C.-M. Che, S.-T. Mak and T. C. W. Mak, *Inorg. Chem.*, 1986, **25**, 4705; (*d*) A. L. Nivorozhkin, H. Toftlund and M. Nielsen, *J. Chem. Soc., Dalton Trans.*, 1994, 361; (*e*) P. Zanello, R. Cini, A. Cinquantini and P. L. Orioli, *J. Chem. Soc., Dalton Trans.*, 1983, 2159; (*f*) C. Benelli, I. Bertini, M. Di Vaira and F. Mani, *Inorg. Chem.*, 1984, **23**, 1422; (*g*) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastoianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stromberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728.

20 E. A. Boudreax and L. N. Mulay, *Theory and Application of Molecular Paramagnetism*, Wiley Interscience, New York, 1976.

21 The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator formalism (ITO): D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.*, 1993, **123**, 231.

22 E. A. Vinogradova, O. Yu. Vassilyeva, V. N. Kokozay, P. J. Squattrito, J. Reedijk, G. A. Van Albada, W. Linert, S. K. Tiwary and P. R. Raithby, *New J. Chem.*, 2001, **25**, 949.

23 G. Davenport, S. R. Hall and W. Dreissig, ORTEP, XTAL3.7 System, eds. S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, University of Western Australia, 2000.