Synthesis, structure and magnetic properties of oligometallic systems derived from di- and trinuclear copper(II) amido-oximate complexes†

Sergey V. Kolotilov,[a] Dieter Schollmeyer,[b] Laurence K. Thompson,[c] Vladimir Golub,[d] Anthony W. Addison[e] and Vitaly V. Pavlishchuk*[a]

Received 19th February 2008, Accepted 12th March 2008
First published as an Advance Article on the web 18th April 2008
DOI: 10.1039/b802822b

Three heterometallic complexes $[M(H_2O)_n][Cu_3L_2(H_2O)]$ ($M = Mn^{2+}$, Co^{2+} or Ba^{2+}) and one dinuclear compound $(CuDien)(CuL\{H_2O\})$ were prepared by interaction of anionic compounds $Cu_3L_2^{2-}$ or CuL^{2-} with the corresponding cations (H_4L = 1,9-dicyano-1,9-bis(hydroximino)-3,7-diazanonane-2,8-dione; Dien = 1,5-diamino-3-azapentane). The complexes $[M(H_2O)_n][Cu_3L_2(H_2O)]$ have a polymeric structure, formed *via* oligomerization of $Cu_3L_2^{2-}$ units and additionally, in the case of the Ba-salt, by binding of $Cu_3L_2^{2-}$ units through Ba^{2+}. Antiferromagnetic interactions occur in all the complexes, while for $[Co(H_2O)_6][Cu_3L_2(H_2O)]$ there is evidence of some ferromagnetic ordering at low temperatures. The values of J are lower in magnitude than for similar, previously reported systems, which is attributed to the electron-withdrawing effect of the ligand cyano groups.

Introduction

Polynuclear complexes of 3d metals, which have been extensively studied for several decades because of their non-trivial magnetic properties, may be used as building blocks for more complex 2D and 3D systems.[1] Directed assembly of such units allows the construction of new compounds and materials, the properties of which are determined by the nature of the starting blocks and the mode of their organization. Recent examples of such systems include porous[1a–d] ferromagnetic,[1e,f] conducting[1h] or ferroelectric[1i] materials, made *via* specific organization of polynuclear multispin particles. Such assembling of polymeric systems from polynuclear "blocks" may open the way for creation of materials with new properties, such as various types of magnetic ordering, as well as for introduction of other characteristics.

In this paper we describe the synthesis, structure and magnetic properties of new polynuclear heterometallic systems, built by self-organization of trinuclear Cu(II) anions with 3d or 6s metal cations as counterions, along with a dinuclear Cu(II) complex, representative of this family of oximate-bridged coordination compounds. The aim of the work was to create the conditions for self-organization of Cu(II) oximate blocks and to study the influence of the "external" metal counter cation on the magnetic properties of the system. Amido-oximate ligands were chosen due to their ability to form anionic coordination compounds,[2] which should favor formation of polynuclear species arising through μ_3-(N,O) metal to metal bridge formation (which may allow further oligomerization).[3] Copper(II) was chosen because this ion forms stable square-based units, which may reversibly coordinate axial ligands; such behavior is well-suited for studies of oligomerization through O-atoms of oximate groups.

Experimental

Reagents and solvents were commercially available (Aldrich and UkrReaChim) and were used without further purification. X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer, using the ω–2θ scan technique. Structures were solved with the help of SIR-92[4] and refined by SHELXL-97[5] by full-matrix least-squares on F^2. H-Atoms were treated by a riding model. Details of structure refinement are presented in Table 1. Not all hydrogen atoms of water molecules, both coordinated and solvated, could be localized. IR spectra were measured in KBr disks using a Specord M75 spectrometer; electronic spectra were measured on a Specord M40 spectrometer in the range 11000–30000 cm^{-1}, and ESR spectra were obtained on a Varian-E-12 X-band spectrometer, calibrated near $g = 2$ with diphenylpicrylhydrazyl. Variable-temperature magnetic data (3–300 K) were obtained using a Quantum Design MPMS5S SQUID magnetometer with field strengths in the range of 0.1–1.0 T. Samples were prepared in gelatin capsules, mounted inside straws, and then fixed to the end of the sample transport rod. Background corrections for the sample holder assembly were applied. Susceptibility data were corrected for diamagnetism using Pascal's constants[6] and $Co[Hg(SCN)_4]$ was used as a calibration standard.

---

[a] *L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine. E-mail: shchuk@svitonline.com; Fax: (38 044) 525 62 16; Tel: (38 044) 525 42 28*
[b] *University of Mainz, Institute of Organic Chemistry, Duesbergweg 10-14, 55099, Mainz, Germany*
[c] *Department of Chemistry, Memorial University, St. John's, NL, Canada A1B 3X7*
[d] *Institute of Magnetism NAS and MES of Ukraine, 36-B Vernadsky str., Kiev, 03142, Ukraine*
[e] *Department of Chemistry, Drexel University, Philadelphia, PA, 19104-2875, USA*

† CCDC reference numbers 662399–662402 for **2**, **5**, **3** and **4**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b802822b

Table 1 Crystallographic data for complexes **2–5**

	2	**3**	**4**	**5**
Empirical formula	$C_{13}H_{14}Cu_2N_9O_{10.25}$	$C_{18}H_{24}Cu_3MnN_{12}O_{19}$	$C_{18}H_{30}Cu_3CoN_{12}O_{19}$	$C_{18}H_{26}BaCu_3N_{12}O_{16}$
M_r	611.86	960.06	968.10	994.47
Crystal size/mm	0.2 × 0.1 × 0.1	0.5 × 0.18 × 0.18	0.27 × 0.08 × 0.08	0.19 × 0.15 × 0.09
Space group	$R\bar{3}$	$C2/c$	$C2/c$	$C2/c$
T/°C	298(2)	298(2)	298(2)	193(2)
λ/Å	0.71069	0.71069	0.71069	0.71069
a/Å	26.551(5)	20.315(11)	20.262(4)	18.2664(10)
b/Å	26.551(5)	16.8866(14)	16.8033(9)	19.1141(11)
c/Å	19.976(5)	11.475(8)	11.446(2)	11.0179(6)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	113.88(2)	114.3650(10)	119.647(3)
γ/°	120.00	90.00	90.00	90.00
V/Å^3	12196(4)	3599(3)	3549.9(10)	3343.3(3)
Z	18	8	8	4
μ/m^{-1}	1.635	2.182	2.324	3.131
Reflections measured	6759	5239	5181	4163
$wR2$	0.2023	0.1540	0.1272	0.2043
$R1$ [$I > 2\sigma(I)$]	0.0777	0.0672	0.0678	0.0876

1,9-Dicyano-1,9-bis(oximino)-3,7-diazanonane-2,8-dione (LH_4)

Propane-1,3-diamine (0.74 g, 10 mmol) and ethyl cyanoacetate (2.26 g, 20 mmol) were mixed without solvent. Within several minutes the reaction mixture became hot and finally solidified. The 1,9-dicyano-3,7-diazanonane-2,8-dione, which formed in essentially quantitative yield, was washed with EtOH and dried over P_2O_5. This compound (2.08 g, 10 mmol) was partially dissolved/suspended in solution of EtONa (20 mmol, prepared from 0.46 g (20 mmol) of Na) in 60 mL of absolute EtOH, and treated with gaseous EtONO (20.5 mmol) prepared separately by reaction of $NaNO_2$ (1.41 g, 20.5 mmol) with an excess of H_2SO_4 in EtOH–water solution. After 5 h, 2 eq. of aqueous HCl were added to the mixture, which was then filtered and concentrated by (rotary) evaporation until yellow–orange crystals appeared. The resulting 1,9-dicyano-1,9-bis(hydroximino)-3,7-diazanonane-2,8-dione was filtered off and dried over P_2O_5. Yield 0.93 g, 35%. Anal. (found/calc. for $C_9H_{10}N_6O_4$): C 40.6/40.6; H 3.85/3.76; N 31.6/31.6%. ^{1}H NMR (in DMSO-d$_6$): 1.74 (2H, central CH_2), 3.37 (4H, terminal CH_2), 7.90 (2 H, NH). IR, cm^{-1}: 3370, 3120 (ν(NH) and ν(OH)), 2960 (ν(C–H)), 2110 (ν(C≡N)), 1680, 1560 (ν(C=O) and ν(C=N)), 1420.

$Na_2CuL\cdot H_2O$ (1)

0.10 g of LH_4 (0.38 mmol) were dissolved in solution of 0.14 g of $Cu(ClO_4)_2\cdot 6H_2O$ (0.38 mmol) in 5 mL of water, followed by the addition of 0.15 g of Et_3N (1.52 mmol). The addition of one half of the Et_3N caused formation of a bulky brown precipitate, which rapidly dissolved on addition of the remaining Et_3N. 0.25 g of $NaClO_4$ was then dissolved in the solution, followed by 10 mL of ethanol, which caused precipitation of the complex. The product was filtered off and air-dried. Yield 0.12 g (80%). Anal. (found/calc. for $C_9H_8N_6O_5CuNa_2$): C 28.0/27.9; H 2.70/2.59; N 21.6/21.7; Cu 16.5/16.4%. IR, cm^{-1}: 3400 (ν(OH)), 2920, 2840 (ν(C–H)), 1595 (ν(C=O) and ν(C=N)), 1400, 1174. Electronic spectrum (DMF solution), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 455 (sh) (1.7 × 10^3).

[{CuL(H_2O)}{CuDien}]·$5H_2O$ (2)

0.080 g of **1** (0.21 mmol) were dissolved in 5 mL of water, followed by the addition of a solution prepared by reaction of 0.078 g (0.21 mmol) $Cu(ClO_4)_2\cdot 6H_2O$ with 0.022 g (0.21 mmol) of Dien in 5 mL of water. The dark-blue (almost black) precipitate was filtered off, recrystallized from a 1 : 1 DMF–CH_3CN mixture and air-dried. Yield 0.088 g (70%). Anal. (found/calc. for $C_{13}H_{31}N_9O_{10}Cu_2$): C 26.2/26.0; H 5.10/5.12; N 21.3/21.0; Cu 21.0/21.2. IR, cm^{-1}: 3250 (ν(OH)), 2920 (ν(C–H)), 2105 (ν(C≡N)), 1590, 1410. Electronic spectrum (DMF solution), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 514 (9.4 × 10^2), 370 (sh) (2.4 × 10^4).

[$Cu_3L_2(H_2O)$][$M(H_2O)_n$]·mH_2O (3: M= Mn, n = 6, m = 3; 4, M = Co, n = 6, m = 3; 5, M = Ba, n = 5, m = 1)

0.080 g of **1** (0.21 mmol) were dissolved in 5 mL of water, and 0.037 g of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1 mmol) were added with vigorous stirring. The brown solution was filtered and 0.1 g of solid $M(ClO_4)_2\cdot 6H_2O$ (M = Mn or Co; about 0.3 mmol, three-fold excess) were dissolved in the solution. After several days, the brown crystalline precipitate which had formed was filtered off, washed with acetonitrile and air-dried. The yield varied greatly, from 5 to 70% (see discussion below). For **3**: Anal. (found/calc. for $Cu_3MnC_{18}H_{32}N_{12}O_{18}$): C 22.4/22.7; H 3.34/3.37; N 17.3/17.7; Cu 19.8/20.0; Mn 6.2/5.8%; IR, cm^{-1}: 3400 (ν(OH)), 2920, 2846 (ν(C–H)), 1575 (ν(C=O) and ν(C=N)), 1373, 1175; electronic spectrum (DMF solution), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 503 (3.0·10^3). For **4**: Anal. (found/calc. for $Cu_3CoC_{18}H_{32}N_{12}O_{18}$): C 22.3/22.6; H 3.62/3.35; N 17.3/17.6; Cu 19.2/20.0; Co 6.1/6.2%. IR, cm^{-1}: 3330 (ν(OH)), 2920, 2840 (ν(C–H)), 1575 (ν(C=O) and ν(C=N)), 1385, 1175; electronic spectrum (DMF solution), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 508 (3.0 × 10^3). For **5**: Anal. (found/calc. for $Cu_3BaC_{18}H_{26}N_{12}O_{15}$): C 22.1/22.1; H 2.73/2.65; N 17.1/17.2; Cu 19.5/19.4%. IR, cm^{-1}: 3380 (ν(OH)), 2929, 2846 (ν(C–H)), 1590 (ν(C=O) and ν(C=N)), 1390, 1160; electronic spectrum (DMF solution), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 508 (3.0 × 10^3).

Results and discussion

Synthesis

1,9-Dicyano-3,7-diazanonane-2,8-dione was prepared by the direct reaction of 1,3-diaminopropane with 2 equivalents of ethyl cyanoacetate, and nitrosation of this compound by ethyl nitrite lead to the desired dioxime (H_4L, Fig. 1). We note, that the nitrosation reaction was effective only in the presence of ethoxide, evidencing that activation of the methylene groups even by both cyano- and amido- groups is not sufficient for direct nitrosation.[7] Interaction of L with copper(II) perchlorate in 96% ethanol gave a green solution; addition of 2 eq. of base (triethylamine, Et_3N) resulted in the precipitation of a brown gel, which rapidly dissolved after addition of another 2 eq. of Et_3N. Addition of an excess of $NaClO_4$ gave a brown precipitate of $Na_2CuL{\cdot}H_2O$.

The trinuclear complexes were prepared by interaction of Na_2CuL (2 eq.) with $Cu(ClO_4)_2$ (1 eq.) in water, through addition of $M(ClO_4)_2$ ($M = Mn^{2+}$, Co^{2+} or Ba^{2+}). As shown by the X-ray structure determination (see below), the Cu^{2+} ion acts as a coordination center, uniting two CuL^{2-} blocks, to produce a trinuclear species $(CuL–Cu–LCu)^{2-}$. However, this reaction could be performed successfully only in dilute solutions ([Na_2CuL] *ca.* 2–5 mM), whereas attempts to perform the first step of the reaction (generation of $Cu_3L_2^{2-}$) in more concentrated solutions resulted in precipitation of insoluble compounds of probably polymeric structure. These compounds can form because of the possibility of reactants combining in unintended ratios during mixing of reactants, or through hydrolysis of Cu^{2+} ions (the complex anion CuL^{2-} acting as a base in the latter case).

When three coordination positions of the otherwise central Cu^{2+} ion were occupied by an additional tridentate ligand, its capacity to link two CuL units was blocked: reaction of Na_2CuL with $Cu(Dien)(ClO_4)_2$ produced dinuclear (CuL)(Cu[Dien]).

X-Ray molecular and crystal structures

Compounds **3** and **4** were found to be isomorphous, and bond lengths and distances in these two compounds are very similar (Tables 1 and 2). The trinuclear cuprate anions are built by linking two mononuclear complexes *via* a central Cu(2) atom, bound to oximato oxygen atoms (Fig. 2); Cu(2) is situated on a local C_2 axis. The terminal Cu(1) possess tetragonal N_4 donor sets, the Cu atoms lying in the plane of four oximate nitrogen atoms. In addition, each terminal Cu(II) has an axially semicoordinated oxygen atom from the oximate of a neighboring trimer's CuL anion (the axial O–Cu bond length is 2.818(6) Å in **3** and 2.831(6) Å in **4**). Thus, one of the oximate groups in each CuL fragment interacts with three copper(II) atoms. The central Cu(2), also pentacoordinate, is bonded to four oximate and one water oxygen atoms. The average Cu(1)–N and Cu(2)–O bond lengths in **3** (excluding the axial Cu(1)–O bond) are 1.96(1) and 1.99(1) Å, respectively, and are typical of such bonds in Cu(II) complexes with N- and O-donor ligands. The τ parameter[8] for the central $Cu(2)O_5$ chromophore is 0.67 (in both **3** and **4**), evidencing that the coordination polyhedron is close to trigonal-bipyramidal geometry, the oximate-O's along O(1)–Cu(2)–O(1′) defining the pseudo-trigonal axis. As exemplified by the Cu(1)–N–O–Cu(2) torsion angles (42.9(1) and 31.1(1)° in **3**), the $Cu_2N_2O_2$ metallocycles are not planar. Bond lengths in the $M(H_2O)_6^{2+}$ ($M = Mn^{2+}$ or Co^{2+}) cations are typical for aqua-complexes of these metals and show no tetragonal distortion. Other relevant distances and separations are shown in Fig. 2(c) (almost identical for **3** and **4**).

In the crystal, neighboring trinuclear anions interact through rather long Cu–O bonds (2.818(6)–2.831(6) Å in **3** and **4**, respectively, see above) and are packed in such way, that they form infinite stacks (Fig. 2(b)). These stacks are aligned along the *c* axis; the space between them is filled by $M(H_2O)_6^{2+}$ cations and solvate H_2O molecules (Fig. 2(b)). A system of hydrogen bonds links cations and anions.

The molecular structure of the trinuclear Cu_3L_2 unit in **5** is generally similar to those in **3** and **4** (Fig. 3(a)), the only distinctive feature is that the torsions Cu(1)–N–O–Cu(2) in **5** (48.3(1) and 33.0(1)°) are slightly greater than in **3** and **4**. The separations between copper(II) atoms in the trinuclear units of **5** are close to that of **3** and **4** (Cu(1)–Cu(2) 3.719(1) Å, Cu(1)–Cu(1) 5.008(1) Å (*cf*. Fig. 2(c) and Table 2). However, there are considerable differences between the crystal structure of the Ba-containing complex **5** and the Mn- or Co-analogues **3** and **4** (Fig. 3b). The Cu_2L_2 units in **5** are packed more closely; the length of Cu–O bond between Cu(1) and the oximate oxygen atom of the neighboring Cu_2L_2 unit is 2.620(5) Å (*vs.* 2.818(6)–2.831(6) Å in **3–4**), the Cu(1)–Cu(1)′ distance is 4.396(4) Å (compared to 4.45 Å in **3** and **4**; exact separations are presented in Table 2) and the

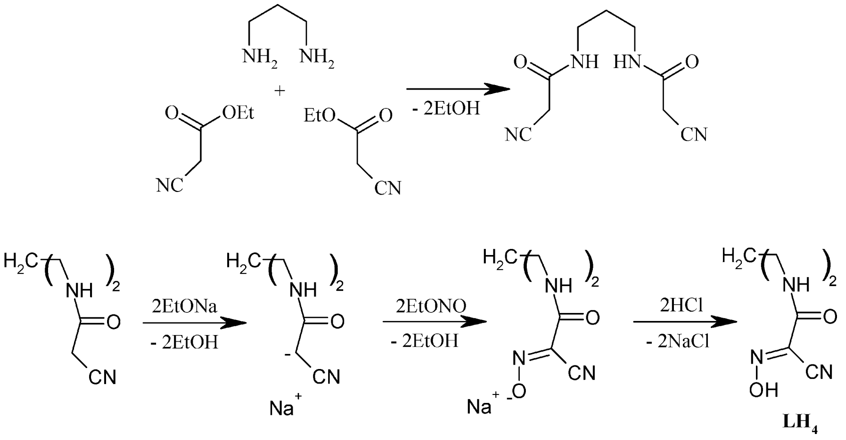

Fig. 1 Synthesis of the ligand; the nitrosation processes in the two "arms" are most likely sequential.

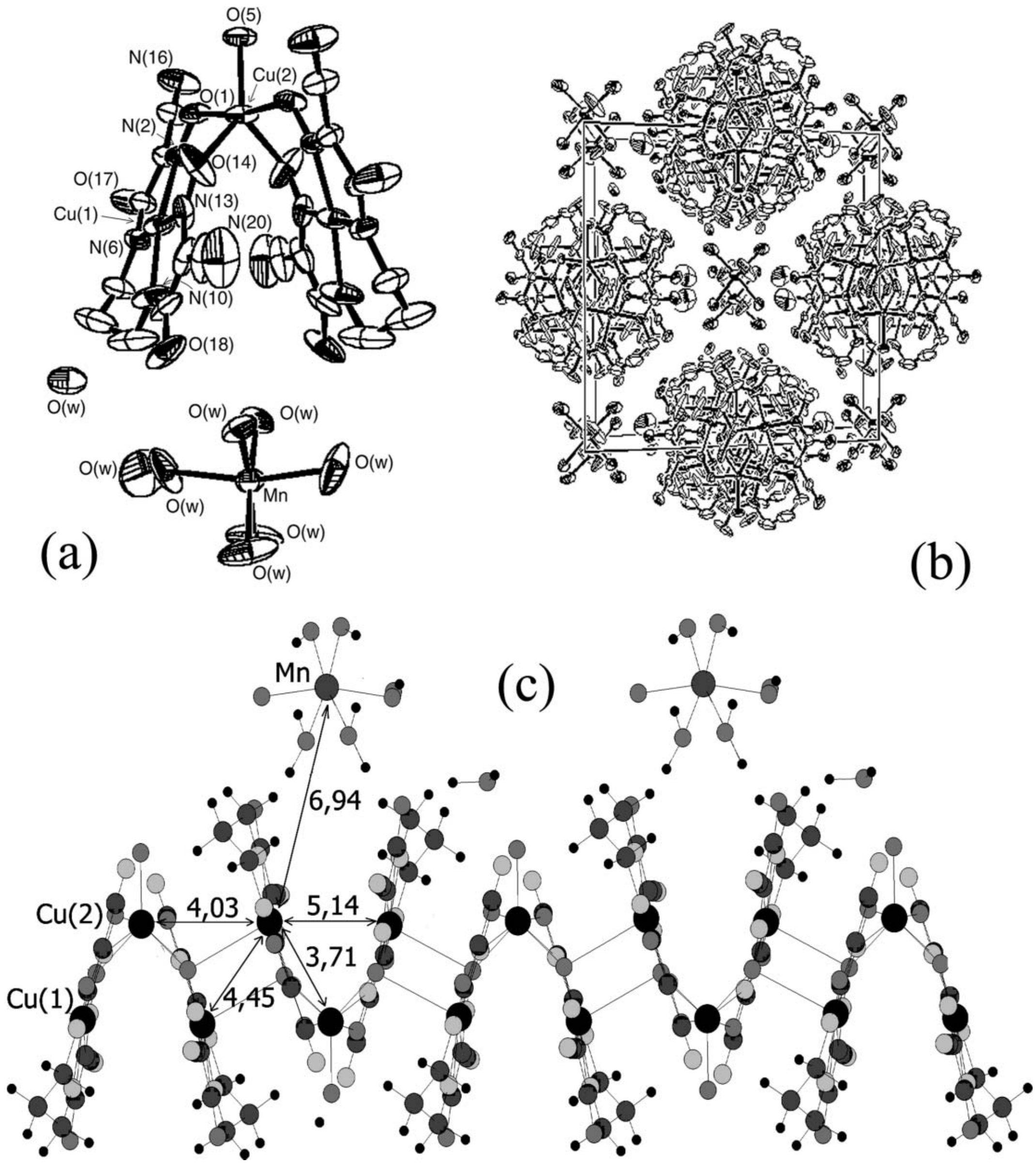

Fig. 2 Molecular and crystal structure of **3** (hydrogen atoms are omitted for clarity) (a), packing of molecular units in crystal cell normal to axis *c* (b) and along axis *c* (c). Symmetry equivalent positions are the following: x, x, z; $-x, y, -z + 1/2$; $x + 1/2, y + 1/2, z$; $-x + 1/2, y + 1/2, -z + 1/2$; $-x, -y, -z$; $x, -y, z - 1/2$; $-x + 1/2, -y + 1/2, -z$; $x + 1/2, -y + 1/2, z - 1/2$. Selected bonds (Å): Cu(1)–N(6) 1.926(5), Cu(1)–N(10) 1.934(5), Cu(1)–N(13) 1.988(6), Cu(1)–N(2) 2.002(4), Cu(2)–O(1) 1.933(4), Cu(2)–O(5) 1.953(6), Cu(2)–O(14) 2.056(4), Mn(1)–O(2I) 2.165(6), Mn(1)–O(3I) 2.174(6), Mn(1)–O(1I) 2.184(6); selected angles (°): N(6)–Cu(1)–N(10) 95.9(3), N(13)–Cu(1)–N(6) 178.1(2), N(13)–Cu(1)–N(10) 82.6(3), N(2)–Cu(1)–N(6) 82.7(2), N(2)–Cu(1)–N(10) 170.3(2), N(2)–Cu(1)–N(13) 98.6(2), O(1)–Cu(2)–O(5) 84.7(1), O(1)–Cu(2)–O(14) 97.8(2), O(14)–Cu(2)–O(5) 129.2(2), O(1)–Cu(2)–O(1)′ 169.3(2), O(14)–Cu(2)–O(14)′ 101.5(2)

Cu(1)–Cu(2)′ separation is 3.940(4) Å (compared to 4.03 Å in **3** and **4**). In contrast to the Mn- and Co-analogues, the Ba atom in **5** links two Cu_2L_2 anions through oxygen atoms of amide groups (Fig. 3). These differences in coordination behavior between Ba^{2+} and the 3d metals are likely related to the ability of the larger-radius Ba^{2+} ion to be heptacoordinate, each Ba additionally coordinating five water molecules.

Several Cu(II) complexes with similar oximate ligands have been reported,[2b,3b,c] in which oximate O-atoms form coordinative bridges to neighbouring molecules, resulting in polymerization of mononuclear Cu(II) complexes with oximes[3c] to form tetranuclear

Table 2 Selected distances (Å) between metal ions in complexes **3**–**5**

	3 (Cu_3Mn)	**4** (Cu_3Co)	**5** (Cu_3Ba)
Cu(1)–Cu(2)	3.711(1)	3.708(1)	3.719(1)
Cu(1)–Cu(1)′	4.448(1)	4.465(1)	4.396(1)
Cu(1)–Cu(2)′	4.032(1)	4.030(1)	3.940(1)
Cu(1)–Cu(1)	5.138(1)	5.136(1)	5.008(1)
Cu(2)–Cu(2)′	6.347(1)	6.328(1)	6.276(1)
Cu(1)–M[a]	6.936(1)	6.898(1)	6.452(1)
Cu(2)–M[a]	7.765(1)	7.726(1)	8.226(1)

[a] M = Mn, Co or Ba for **3**, **4** and **5**, respectively.

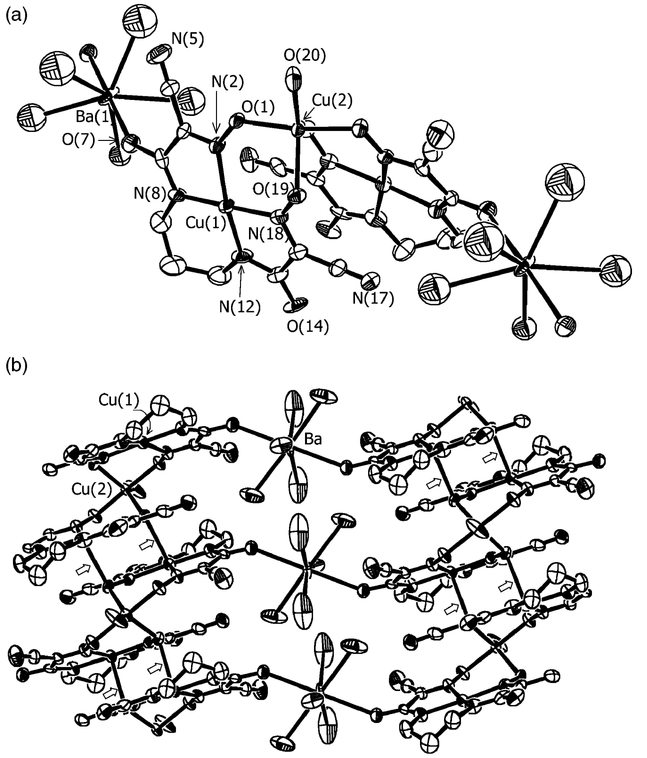

Fig. 3 Crystal structure of **5** (hydrogen atoms are omitted for clarity). (a) Fragment of polymeric structure containing Cu_3 unit and two adjacent $Ba(H_2O)_5^{2+}$ units. Not labeled atoms bonded to Ba(1) are oxygens, atom in *trans*-position to O(7) is the O(7)″ atom of neighboring Cu_3 unit, whereas other oxygen atoms are the ones of water. (b) Crystal packing of **5**. Arrows indicate Cu(1)–O(19)″ bonds, which join Cu_3 units. Symmetry equivalent positions are the following: x, y, z; $-x, y, -z + 1/2$; $x + 1/2, y + 1/2, z$; $-x + 1/2, y + 1/2, -z + 1/2$; $-x, -y, -z$; $x, -y, z - 1/2$; $-x + 1/2, -y + 1/2, -z$; $x + 1/2, -y + 1/2, z - 1/2$. Selected bonds (Å): Cu(1)–N(12) 1.917(9), Cu(1)–N(8) 1.954(9), Cu(1)–N(18) 1.969(9), Cu(1)–N(2) 2.031(9), Cu(2)–O(1) 1.932(6), Cu(2)–O(20) 1.956(11), Cu(2)–O(19) 2.112(7), Ba(1)–O(7) 2.697(7), Ba(1)–O(1W) 2.747(9), Ba(1)–(2W) 2.643(12), Ba(1)–O(3W) 2.772(11); selected angles (°): N(12)–Cu(1)–N(8) 96.0(4), N(12)–Cu(1)–N(18) 83.2(4), N(8)–Cu(1)–N(18) 177.8(4), N(12)–Cu(1)–N(2) 167.0(4), N(8)–Cu(1)–N(2) 82.8(3), N(18)–Cu(1)–N(2) 97.6(4), O(1)–Cu(2)–O(1)′ 169.3(4), O(1)–Cu(2)–O(20) 84.6(2), O(1)–Cu(2)–O(19) 97.6(3), O(1)–Cu(2)–O(19)′ 89.3(3), O(20)–Cu(2)–O(19) 129.8(2), O(19)–Cu(2)–O(19)′ 100.5(4).

Cu_2Mn_2 and Cu_2Ni_2 complexes from CuMn and CuNi dimers, respectively,[3d] as well as polymerization of Cu_3 units.[9]

In the dinuclear complex **2** (Fig. 4) the Cu(2) of the $[Cu(Dien)]^{2+}$ moiety is bound by the two oximate O-atoms from the CuL^{2-} unit, forming a six-membered $Cu_2N_2O_2$ ring. The Dien-chelated Cu(2) has a distorted square pyramidal donor set, with $\tau = 0.32$; the axial position is occupied by O(1), and the longest Cu–ligand bond is to O(1) (2.274(5) Å). The Cu-oximate unit's Cu(1) is essentially square-pyramidal (τ = 0.03) with basal Cu–N bonds averaging 2.00(5) Å and a water on the axial position (at 2.327(5) Å). The $Cu_2N_2O_2$ ring in **2** is fairly planar, the Cu(1)–N-O–Cu(2) torsion angles, at 14.5(1) and 4.8(1)°, being about half those in **3**–**5**. The Cu–Cu separation is 3.743(5) Å, while the remaining structural features are unremarkable.

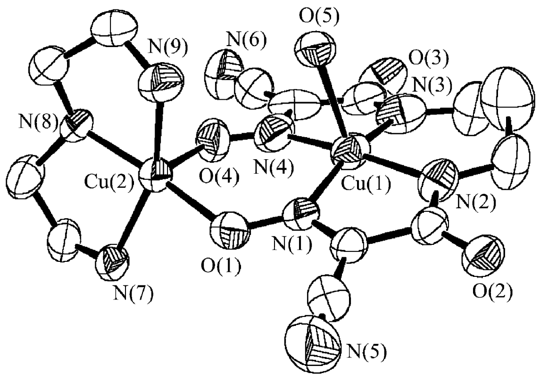

Fig. 4 ORTEP view of **2** (hydrogen atoms are omitted for clarity). Selected bonds (Å): Cu(1)–N(1) 1.991(6), Cu(1)–N(2) 1.990(7), Cu(1)–N(3) 1.946(5), Cu(1)–N(4) 2.076(6), Cu(1)–O(5) 2.327(4), Cu(2)–O(4) 1.956(4), Cu(2)–N(7) 2.006(5), Cu(2)–N(8) 2.012(5), Cu(2)–N(9) 2.016(5), Cu(2)–O(1) 2.274(6); selected angles (°): N(3)–Cu(1)–N(2) 93.5(3), N(1)–Cu(1)–N(2) 79.8(3), N(3)–Cu(1)–N(4) 81.2(2), N(1)–Cu(1)–O(5) 89.0(2), N(4)–Cu(1)–O(5) 87.1(2), O(4)–Cu(2)–N(7) 90.9(2), N(7)–Cu(2)–N(8) 85.5(2), O(4)–Cu(2)–N(9) 96.5(2), N(8)–Cu(2)–N(9) 85.4(2), O(4)–Cu(2)–O(1) 102.9(2), N(7)–Cu(2)–O(1) 99.1(2), N(8)–Cu(2)–O(1) 81.3(2), N(9)–Cu(2)–O(1) 101.5(2)

Electronic spectra

Absorption bands in the region 455–514 nm with high ε (10^3) were observed in the solution electronic spectra of all the complexes (see Experimental section). Their high intensities recommend a charge-transfer origin for these bands. Although these have previously been attributed to MLCT transitions,[10] the strong donor ability of the ligands, the reductive nature of oximes, the general tendency of copper(II) to act as oxidant rather than reductant and its attendantly high optical electronegativity leads us to favour an LMCT assignment (such as $\sigma_{oxime} \rightarrow d_{Cu}$). Any Cu(II), Mn(II) or Co(II) d–d transitions are obscured by these more intense bands. The shoulder at 455 nm, which is observed in the spectrum of the mononuclear complex **1** is shifted in the spectra of di- and trinuclear **2**–**4** to 503–514 nm.

Magnetic properties

The magnetic behaviours of polycrystalline samples of the polynuclear complexes were measured in the temperature range 2–300 K. For dinuclear **2**, $\chi_m T$ decreased from 0.743 cm^3 K mol^{-1} at 300 K to 0.006 cm^3 K mol^{-1} at 2 K. For the Mn-salt **3**, $\chi_m T$ decreased from 5.01 at 300 K to 4.43 cm^3 K mol^{-1} at 4 K and then grew to 4.51 at 2 K. For the Co-salt **4** and the Ba-salt **5** $\chi_m T$ again decreased over the whole T-range studied: from 4.48 at 300 K to 3.29 cm^3 K mol^{-1} at 2 K in the case of **4** and from 0.899 at 300 K to 0.242 cm^3 K mol^{-1} at 2 K in the case of **5** (Fig. 5). Keeping in mind that the spin-only value for a $g = 2.0$ Cu_2 system is 0.75 cm^3 K mol^{-1}, and for Cu_3, Cu_3Co and Cu_3Mn, 1.125, 3.0 and 5.5 cm^3 K mol^{-1} respectively, it is clear that the dominant interactions in **2**, **3** and **5** are antiferromagnetic. The situation is not so obvious for the Cu_3Co compound (**4**), *vide infra.*

For the dinuclear compound **2**, the magnetic behaviour was fitted by a modified Bleaney–Bowers expression, defining *J via* $\mathscr{H} = -2JS_1S_2$,[11] including temperature-independent paramagnetism, paramagnetic impurity with $S = 0.5$ (ρ, which quantity was estimated from $\chi_m T$ at 2 K as 1.8%) and a fixed $g = 2$, which gave

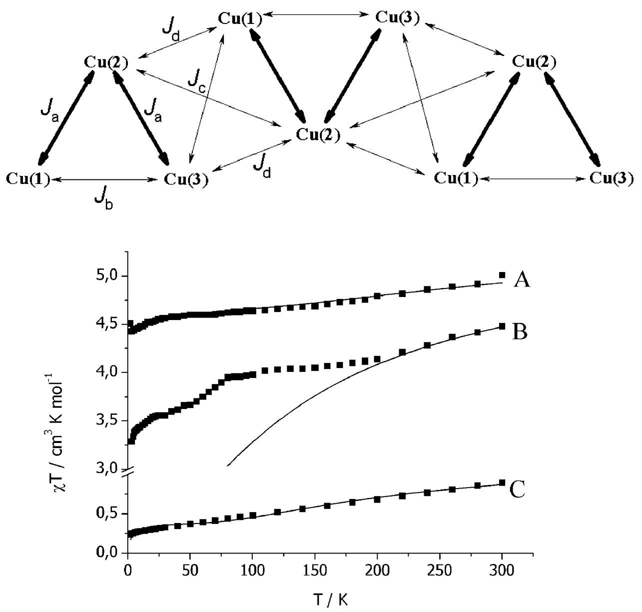

Fig. 5 (a) Definition of exchange parameters for fitting of magnetic properties of **3–5**; (b), experimental data and calculated curves for **3–5** (A, B and C, respectively, see text for the parameters).

$J = -30.4(3)$ cm^{-1}, tip = 0.00018(2), $R^2 = 1.1 \times 10^{-3}$ (Fig. 6). The angle between the mean planes N_2O_2 and CuO_2 may be taken as a measure of the bending of the $Cu_2N_2O_2$ metallocycle, and this will affect the coupling between the coppers. For **2**, the angle between the mean planes Cu(1)N(1)N(4)O(1)O(2) and Cu(2)O(1)O(4) is 154.3°. In CuDopnCu(phen)$(CH_3OH)_2^{2+}$ the angle between corresponding planes was found to be 153.3°, and $J = -433$ cm^{-1},[12] and the related metrics for Cu(Dopn)Cu(bipy)$(H_2O)_2^{2+}$ are 162.5° and -674 cm^{-1}, respectively[13] (H_2Dopn = 2 : 1 Schiff base of butanedione monoxime and 1,3-diaminopropane). For dinuclear copper(II) oximato-bridged complexes with Schiff bases prepared from butanedione monoxime and 2-aminoalkylpyridines, the dihedral angles between CuD_4 planes (D is donor atom) vary from *ca.* 180 to 128°, and the J values lie in the range -410 to -255 cm^{-1}.[14] For dinuclear **2**, J is significantly lower (in magnitude) compared with these similar complexes. However, the presence of electron-withdrawing substituents breaks the correlation between J and geometry, as noted for some other oligonuclear oximate complexes.[10,15]

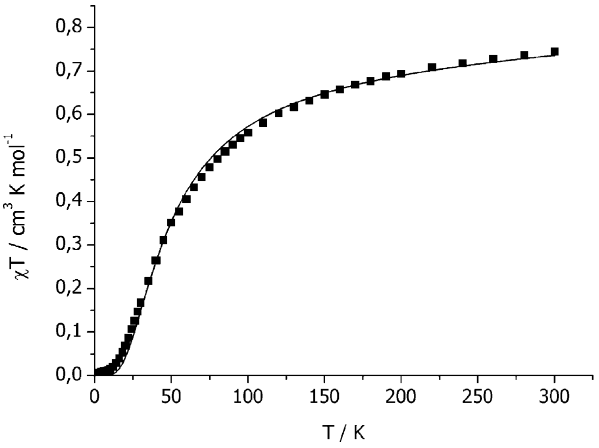

Fig. 6 Experimental data and calculated curve for **2**.

The decrease in $\chi_m T$ was not monotonic for either of **3** or **4**. Two inflections were found for **3**, at 95 K and 43 K (Fig. 4); the behavior of **4** was more complicated. However, some similarity may be seen in the $\chi_m T$ *vs.* T curves for compounds **3** and **4**.

From the structural viewpoint, at least four types of Cu–Cu couplings should be expected for **3–5** (Fig. 5). Two of them (J_a and J_b) occur within trinuclear Cu_3L_2 building blocks, whereas two others (J_c and J_d) represent coupling to neighboring blocks; an alternative would be to treat the compounds as alternating infinite chains. Additional interactions may be expected between the Cu-trimers and the 3d metals (Mn or Co). In any case, it appears unlikely that a reliably unique set of so-derived J-values could be obtained from susceptibility data alone, because of over-parametrization.

The trinuclear salts **3–5** were approximated as (i) the superposition of independent anionic (Cu^{2+}_3) and cationic (M^{2+}) sublattices, and (ii) the coupling between trinuclear units (J_c and J_d) was treated *via* a molecular field (effective parameter zJ').[6,16] The intratrimer coupling was described by an exchange Hamiltonian for an isosceles triangle of three spins $S_1 = S_2 = S_3 = 1/2$:[11]

$$\mathscr{H} = -2J_a[(S_1S_2) + (S_2S_3)] - 2J_b(S_3S_1)$$

the exchange integrals J_a and J_b being as defined as in Fig. 5, though it was anticipated that J_b would be small compared to J_a.

For the Cu_3Ba complex **5**, where there is no spin contribution from the cation, the best agreement was achieved with $J_1 = -85(7)$ cm^{-1}, $g = 2.00(1)$, *tip* = 0.0003(1) and $2zJ' = -1.7(2)$ cm^{-1} (Fig. 5, $R^2 = 2.5 \times 10^{-3}$). The observation that χT falls below the $S = 1/2$ value of 0.375 as T approaches 0 K indicates the need to take into account a nonzero value of zJ'. The fit was insensitive to J_b: variation of J_b from 0 to +1,000 cm^{-1} had little influence on R^2, however, negative values of J_b were clearly unworkable. It has been pointed out, that for Cu_3 systems, the value for a weak J_b cannot be reliably obtained from measurements of $\chi_m T$ *vs.* T.[10,17] On the other hand, for these trinuclear units, the dominant antiferromagnetic interactions Cu(1)-Cu(2) force the spins of the two Cu(1) atoms to be parallel, corresponding to their ferromagnetic ordering. A similar situation was recently described, where it was impossible to determine exact values of the ferromagnetic exchange parameter in rhombic tetranuclear nickel(II) complexes with dominantly antiferromagnetic couplings because of such "spin forcing".[18]

For the Mn^{2+}-salt **3**, $\chi_m T$ was represented as the sum of $\chi_{Cu_3} T$ and a superimposed $\chi_{Mn} T$, the latter being taken to be temperature-independent, corresponding to $S = 5/2$ ($\chi_{Mn} T = 4.375 + tip$). This model gave $J_a = -130(5)$ cm^{-1}, $2zJ' = -23(1)$ cm^{-1} at fixed $g = 2$, with $R^2 = 3.4 \times 10^{-5}$ (Fig. 5). The value of g was fixed to the lowest reasonable value, because it otherwise tended to decrease to unrealistically low values during the fitting routine. ESR measurements of **3** in DMF solution yielded broad spectra, with no resolution of any Cu(II) g-anisotropy or hyperfine structure (though the resonances of the isolated Mn^{2+} were apparent). The Cu-associated apparent g-values were 2.040 (293 K) and 2.046 (77 K), which correspond reasonably well to these magnetochemical results.

The result, that zJ' for the Cu_3Mn salt, **3**, appears to be of larger magnitude than for the Ba^{2+} salt **5** ($-23(1)$ cm^{-1} *vs.* $-1.7(2)$ cm^{-1}), is a little surprising, because it could be expected that interactions between trinuclear units would be less efficient than in **5**, because of the looser packing of the trinuclear units (see X-ray structure description). Reasonable explanations may be that in the case of **5**, (i) the contributions of all types of couplings, presented in Fig. 5, are comparable, and the couplings Cu(1)–Cu(2) are not dominant, or (ii) the value for zJ' in the Cu_3Ba compound is less than in the Cu_3Mn one. This suggests that in the Mn^{2+} compound (where the Cu_3–Cu_3 distances are longer) the larger zJ' is acting as the proxy for some Mn^{2+}–Cu_3 interaction. The increase of $\chi_m T$ at 2 K may be caused by ferromagnetic ordering, which may occur in Cu–Mn systems[1f] (also compare with the magnetic properties of **4**, *vide infra*). Thus, the proposed model provides a satisfactory phenomenological fit of the Cu_3–Mn system in **3**, there being no detectable interaction between the Mn^{2+} cation and the Cu_3 anion, at least above 4 K.

The structural features that govern the exchange parameter J_a in such oximate-bridged trinuclear Cu(II) complexes (containing $Cu(N–O)_2Cu(N–O)_2Cu$ cores) appear indexible by the Cu(1)–Cu(2)–Cu(3) angle (denoted as γ). Strong antiferromagnetic coupling amounting to complete spin pairing was found in "planar" ($\gamma = 0$) complexes such as $Cu_3L_2L'_2{}^{2+}$ (H_2L = dimethylglyoxime, hereinafter H_2Dmg, or diphenylglyoxime, L' = 2,2′-bipyridyl or 1,10-phenanthroline),[19] $Cu(Dmg)_2\{Cu(bipy)(CH_3OH)\}_2{}^{2+}$.[20] This is entirely reasonable, if unpaired spin in Cu $d_{x^2-y^2}$ orbitals is to be exchange coupled by the bridges. Buckling of the $Cu_2N_2O_2$ metallocycle then renders the transmission of antiferromagnetic exchange interactions less favourable. It may be noted that the absolute value of J_a grows with γ in the order $L_2Cu_2Cu(Dmg)_2Br^+$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, $J_a = -448\ cm^{-1}$, $\gamma = 152°$ [10]) < $Cu(CuDopn)_2{}^{2+}$ (H_2Dopn = 2 : 1 Schiff base of butanedione monoxime and 1,3-diaminopropane, $J_a = -290\ cm^{-1}$, $\gamma = 119°$ [9]) < **3** ($J_a = -130\ cm^{-1}$, $\gamma = 87.6°$). However, as pointed out by Chaudhuri *at al.*,[10] electron-withdrawing effects of ligand substitutents are also important, as appears to be validated by the comparison of the J value for dinuclear compound **2** with other dinuclear oximato-bridged copper(II) complexes, *vide infra.*

In the case of the Co-containing analogue **4**, the situation is complicated by the temperature-dependence of the susceptibility due to spin–orbit coupling within the $^4T_{1g}$ ground state of the octahedral cobalt(II).[6,21] in the cobalt sublattice. When the previous "superimposed lattice" approach was used for this system, reasonable values of spin–orbit coupling constant λ yielded fits of only the high-temperature part of the data (Fig. 4). The curve shown on Fig. 4, corresponds to $J_a = -110\ cm^{-1}$, $J_b = 0$, $g_{Cu} = 2$, $2zJ' = -20\ cm^{-1}$, $tip = 0.002$, $A = 1.4$ and $\lambda = -140\ cm^{-1}$, where A is a crystal field strength parameter which lies in the range from 1.5 (weak field) to 1.0 (strong field)[21a]

The most probable origin for the high χT of **4** at low T is a ferromagnetic interaction involving Co^{2+} and Cu_3 ions in the Cu_3Co system **4**.[22] However, we are unable to discriminate definitively amongst the possible interactions (Cu_3–Cu_3, Co–Co or Cu_3–Co) which could give rise to this low-T ferromagnetic ordering (Fig. 7). The possibility of ferromagnetic interactions between the trinuclear Cu(II) units and Co^{2+} through a system of hydrogen bonds cannot be excluded. Though the distance from Co(II) to the other metal ions in **4** is rather large (5.88 Å to neighboring Co(II) and 6.94 Å to Cu(II)), the $Co(H_2O)_6{}^{2+}$ ions take part in formation of a system of H-bonds. The distance between O atoms coordinated to neighboring Co(II) ions is only 2.72 Å, while the smallest distance from an O atom of $Co(H_2O)_6{}^{2+}$ to the O-atom of an amide group is 2.62 Å. Such H-bonds have been shown to transmit weak exchange interactions, for example, in solution dimers of nitroxide radical, 1-[*N*-*tert*-butyl-*N*-(oxyl)amino]-4-benzoic acid (though the overall interactions in the solid state were antiferromagnetic).[23] Similarly, there is quite efficient coupling in Cu(II) complexes through H-bonds.[24a] or $H_3O_2{}^-$ bridges[24b] Also, the magnetic properties of layered Co(II) hydroxides $Co_2(OH)_{4-x}X_x{\cdot}zH_2O$ ($X = C_nH_{2n+1}SO_4{}^-$ or $C_nH_{2n+1}CO_2{}^-$) are strongly dependent on interlayer separation r, at r even above 1 nm, without any covalent bonds between the layers[25] (χT increases from 55 to 220 $cm^3{\cdot}K\ mol^{-1}$ when r is increased from 12.7 to 27.4 Å).

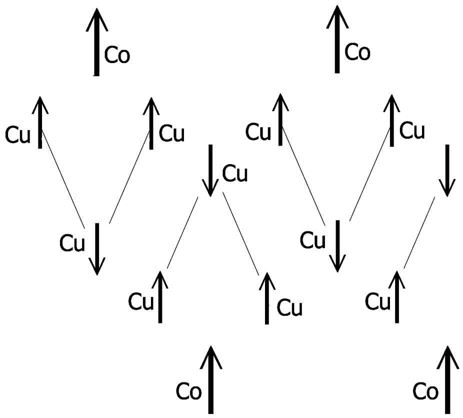

Fig. 7 Possible alignment of spins in **4** (zero-temperature approximation).

Concluding remarks

Trinuclear anions, based on a diamido-dioximate, are suitable building blocks for the generation of polymeric heterometallic systems. Two isostructural complexes, containing infinite stacks of trinuclear Cu_3 anions and $Mn(H_2O)^{2+}$ or $Co(H_2O)^{2+}$ counterions, and a similar compound with a diamagnetic $Ba(H_2O)_5{}^{2+}$ bridge, were prepared and characterized crystallographically and magnetochemically. Antiferromagnetic interactions dominate within the Cu_3 blocks, as well as between them in the stacks, and magnetic data for Cu_3Mn could be accounted for by this model, involving no significant interactions between the anionic and cationic sub-lattices. The magnetic behavior of the Cu_3Co analogue, namely, significant growth of $\chi_m T$ (*vs.* the expected values) is consistent with additional ferromagnetic ordering in the lattice. Exchange interactions within the trinuclear block in **3** and in the dinuclear complex **2** are weaker than in similar previously reported compounds, which is presumably associated with differences in the bridging angles between the Cu(II) ions, as well as with an electron-withdrawing effect of cyano substituents in the ligand.

Acknowledgements

A. W. A. thanks Drexel University for support. V. V. P. and S. V. K. thank the L. V. Pisarzhevskii Institute for support.

References

1 (*a*) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190; (*b*) L. G. Beauvais and J. R. Long, *J. Am. Chem. Soc.*, 2002, **124**, 12096; (*c*) M. V. Bennett, M. P. Shores, L. G. Beauvais and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 6664; (*d*) M. Oh, G. B. Carpenter and D. A. Sweigart, *Angew. Chem., Int. Ed.*, 2003, **42**, 2026; (*e*) O. Kahn, *Acc. Chem. Res.*, 2000, **33**, 647; (*f*) N. Fukita, M. Ohba, T. Shiga, H. Ōkawa and Y. Ajiro, *J. Chem. Soc., Dalton Trans.*, 2001, 64; (*g*) E.-Q. Gao, Q.-H. Zhao, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang and S.-P. Yan, *J. Chem. Soc., Dalton Trans.*, 2001, 1537; (*h*) L. Ouahab and T. Enoki, *Eur. J. Inorg. Chem.*, 2004, 933; (*i*) Z.-G. Gu, X.-H. Zhou, Y.-B. Jin, R.-G. Xiong, J.-L. Zuo and X.-Z. You, *Inorg. Chem.*, 2007, **46**, 5462.

2 (*a*) R. Ruiz, J. Faus, F. Lloret, M. Julvé and Y. Journaux, *Coord. Chem. Rev.*, 1999, **193–195**, 1069; (*b*) A. M. Duda, A. Karaczyn, H. Kozlowski, I. O. Fritsky, T. Glowiak, E. V. Prisyazhnaya, T. Yu. Sliva and J. Swiatek-Kozlowska, *J. Chem. Soc., Dalton Trans.*, 1997, **3853**; (*c*) E. T. Nomkoko, G. E. Jackson and B. S. Nakani, *Inorg. Chem. Commun.*, 2003, **6**, 335.

3 (*a*) V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, M. J. Prushan, R. J. Butcher and L. K. Thompson, *Inorg. Chem.*, 1999, **38**, 1759; (*b*) A. Vaciago and L. Zambonelli, *J. Chem. Soc. A*, 1970, 218; (*c*) J. A. Bertrand, J. H. Smith and D. G. VanDerveer, *Inorg. Chem.*, 1977, **16**, 1484; (*d*) B. Cervera, R. Ruiz, F. Lloret, M. Julvé, J. Faus, M. C. Muñoz and Y. Journaux, *Inorg. Chim. Acta*, 1999, **288**, 57.

4 A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

5 G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, 1997.

6 V. T. Kalinnikov, and Yu. V. Rakitin, *Introduction to Magnetochemistry*, Nauka, Moscow, 1980, p. 273.

7 (*a*) Weygand-Hilgetag, *Methods of Experiment in Organic Chemistry*, Khimiya, Moscow, 1968, p. 393; (*b*) E. Iglesias, *J. Chem. Res. (S)*, 1995, 98.

8 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

9 D. Luneau, H. Oshio, H. Okawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1990, 2283.

10 P. Chaudhuri, M. Winter, B. P. C. Della Védova, E. Bill, A. Trautwein, S. Gehring, P. Fleischhauer, B. Nuber and J. Weiss, *Inorg. Chem.*, 1991, **30**, 2148.

11 E. Sinn, *Coord. Chem. Rev.*, 1970, **5**, 313; *tip* is the temperature-independent paramagnetism; the goodness-of-fit measure is $R^2(\chi T) = \sum(\chi T_{obs} - \chi T_{calc})^2/\sum(\chi T_{obs})^2$.

12 D. Luneau, H. Oshio, H. Okawa, M. Koikawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2212.

13 R. Ruiz, F. Lloret, M. Julve, M. C. Munoz and C. Bois, *Inorg. Chim. Acta*, 1994, **219**, 179.

14 M. Maekawa, S. Kitagawa, Y. Nakao, S. Sakamoto, A. Yatani, W. Mori, S. Kashino and M. Munakata, *Inorg. Chim. Acta*, 1999, **293**, 20.

15 V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, M. J. Prushan, D. Schollmeyer, L. K. Thompson, T. Weyhermüller and E. A. Goreshnik, *Dalton Trans.*, 2003, 1588.

16 (*a*) E.-Q. Gao, Q.-H. Zhao, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang and S.-P. Yan, *J. Chem. Soc., Dalton Trans.*, 2001, 1537; (*b*) A. P. Ginsberg and M. E. Lines, *Inorg. Chem.*, 1972, **11**, 2289.

17 L. Banci, A. Bencini and D. Gatteschi, *Inorg. Chem.*, 1983, **22**, 2681.

18 V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, M. J. Prushan, D. Schollmeyer, L. K. Thompson and E. A. Goreshnik, *Angew. Chem., Int. Ed.*, 2001, **40**, 4734.

19 H. Okawa, M. Koikawa, S. Kida, D. Luneau and H. Oshio, *J. Chem. Soc., Dalton Trans.*, 1990, 469.

20 D. Luneau, H. Oshio, H. Ōkawa and S. Kida, *Chem. Lett.*, 1989, 443.

21 (*a*) A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York, 1968; p. 62; B. N. Figgis, *Introduction to Ligand Fields*, Interscience Publishers, Sydney, 1966, p. 271, p. 339; B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 37; (*b*) N. Fukita, M. Ohba, T. Shiga, H. Okawa and Y. Ajiro, *J. Chem. Soc., Dalton Trans.*, 2001, 64; (*c*) H. Sakiyama, R. Ito, H. Kumagai, K. Inoue, M. Sakamoto, Y. Nishida and M. Yamasaki, *Eur. J. Inorg. Chem.*, 2001, 2027; (*d*) H. Sakiyama, *Inorg. Chim. Acta*, 2006, **359**, 2097; (*e*) L. Vaiana, C. Platas-Iglesias, D. Esteban-Gómez, F. Avecilla, J. M. Clemente-Juan, J. A. Real, A. de Blas and T. Rodríguez-Blas, *Dalton Trans.*, 2005, 2031.

22 C. L. M. Pereira, E. F. Pedroso, M. A. Novak, A. L. Brandl, M. Knobel and H. O. Stumpf, *Polyhedron*, 2003, **22**, 2387.

23 D. Maspoch, L. Catala, P. Gerbier, D. Ruiz-Molina, J. Vidal-Gancedo, K. Wurst, C. Rovira and J. Veciana, *Chem.–Eur. J.*, 2002, **8**, 3635.

24 (*a*) J. A. Bertrand, E. Fujita and D. G. VanDerveer, *Inorg. Chem.*, 1980, **19**, 2022; (*b*) G. De Munno, D. Viterbo, A. Canechi, F. Lloret and M. Julve, *Inorg. Chem.*, 1994, **33**, 1585.

25 V. Laget, C. Hornick, P. Rabu, M. Drillon and R. Ziessel, *Coord. Chem. Rev.*, 1998, **178–180**, 1533.