

New Metal Oxamates as Precursors of Low-Dimensional Heterobimetallics

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The goal of this work was to synthesize new molecular bricks which could be used as precursors of heterobimetallic low-dimensional compounds. Along this line, four compounds have been synthesized and structurally characterized, namely (NBu₄)₂[Ni(Cl₂opba)] (**1**), (NBu₄)₂[Cu(Cl₂opba)] (**2**), (NBu₄)₅[Mn(Cl₂opba)(DMSO)₂]₄ (**3**), and Cu(en)₂[Mn(Cl₂opba)(H₂O)₂]₂·2DMSO (**4**), with Cl₂opba = (4,5-dichloro-*o*-phenylene)bis(oxamato), NBu₄ = tetra-*n*-butylammonium, en = ethylenediamine, and DMSO = dimethyl sulfoxide. Compounds **1** and **2** are isostructural; they crystallize in the monoclinic system, space group *C*2/*c*, *Z* = 4, with *a* = 18.708(2) Å, *b* = 17.525(2) Å, *c* = 14.763(9) Å, and β = 92.03(4)° for **1** and *a* = 18.928(2) Å, *b* = 17.634(2) Å, *c* = 14.704(9) Å, and β = 92.38(3)° for **2**. **3** crystallizes in the tetragonal system, space group *P*4₂/*c*, *Z* = 2, with *a* = 26.295(10) Å and *c* = 12.342(7) Å. The structure shows a random occupation of the metal site by Mn(III) and Mn(II) ions in 3/4 and 1/4 ratios, respectively. **4** crystallizes in the triclinic system, space group *P*1̄, *Z* = 1, with *a* = 7.066(7) Å, *b* = 11.844(1) Å, *c* = 14.292(5) Å, α = 105.64(2)°, β = 97.67(5)°, and γ = 102.13(3)°. The structure consists of Mn^{III}Cu^{II}Mn^{III} trinuclear species, with Cu–O–Mn bridges involving oxygen atoms of the oxamato groups already linked to the metal atom. The magnetic properties of compounds **1–4** have been investigated and quantitatively interpreted. For **3**, this magnetic investigation has been performed on a single crystal, which allows us to determine unambiguously the sign of the axial zero-field splitting parameter for the Mn(III) ion. The potentialities of these new molecular bricks have been discussed.

Introduction

The first molecular-based magnets have been reported a decade ago,^{1–4} and in the last period a significant number of new compounds of this type have been described.^{5–10} Quite a few of them contain two different transition metal ions.⁶ The usual synthetic route to obtain such bimetallic species consists of reacting an anionic metal-containing precursor with a metal cation. The most extensively used metal precursors are the Cu(II) oxamates^{2,4,11} and oxamides,^{12,13} the Cr(III) and Fe(III)

tris(oxalates)^{14–18} and tris(dithiooxalates),¹⁹ the Cu(II) oximates,²⁰ and the hexacyanometalates.^{21–23} The chemistry and physics of the heterobimetallics obtained from these precursors were recently reviewed.²⁴

Our own contribution to this area of research has essentially concerned the ferrimagnetic one- and two-dimensional compounds prepared from Cu(II) oxamates and oxamides.^{7,24} It turns out that, in all our bimetallic compounds, one of the spin carriers was the Cu(II) ion. In one case, a third spin carrier was involved, a radical cation, which has led to a unique structure consisting of two honeycomb networks fully interlocked.^{25,26} An obvious extension of our work was to seek new precursors, in particular containing a metal ion different from

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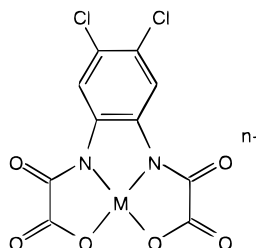
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Cu(II). This paper will deal with our first results along this line. More precisely, we explored the coordination chemistry of the (4,5-dichloro-*o*-phenylene)bis(oxamato), hereafter abbreviated as Cl₂opba, and characterized three compounds **1–3** with the following core:



M is Ni(II) in **1** and Cu(II) in **2**; the charge is then 2−. The situation encountered in **3** is by far the most interesting. The formula of the compound is (NBu₄)₅[Mn(Cl₂opba)(DMSO)₂]₄ with NBu₄ = tetra-*n*-butylammonium and DMSO = dimethyl sulfoxide. It follows that three of the Mn atoms are Mn(III) ions and one is a Mn(II) ion. In addition, we will report on the trinuclear species Cu(en)₂[Mn(Cl₂opba)(H₂O)₂]₂·2DMSO (**4**), with en = ethylenediamine. This paper will describe the syntheses, crystal structures, and magnetic properties of compounds **1–4**.

Experimental Section

Syntheses. The diethyl ester Et₂H₂(Cl₂opba) of the (4,5-dichloro-*o*-phenylene)bis(oxamic acid) was prepared in a similar way as the unsubstituted analogue.¹¹ In this case the evaporation of THF affords a brick-red powder which was washed with water and ethanol and dried under vacuum (yield 91%). Anal. Calc for C₁₄H₁₄N₂O₆Cl₂: C, 44.56; H, 3.71; N, 7.43; Cl, 18.83. Found: C, 44.39; H, 3.71; N, 7.70; Cl, 19.54. The Cu(II) complex Na₂[Cu(Cl₂opba)]·3H₂O was prepared as the unsubstituted analogue (yield 85%).¹¹ This compound has a very poor solubility, and all attempts of crystallization have been unsuccessful. Anal. Calc for C₁₀H₈N₂O₉Cl₂CuNa₂: C, 24.97; H, 1.66; N, 5.83; Cl, 14.77; Cu, 13.22; Na, 9.57. Found: C, 26.23; H, 1.67; N, 6.19; Cl, 14.39; Cu, 12.99; Na, 9.10.

(NBu₄)₂[Ni(Cl₂opba)] (**1**) was prepared as follows: A 6.5 mL volume of a 1.25 M NaOH solution is added to a suspension of 0.7 g (1.86 mmol) of Et₂H₂(Cl₂opba) in 30 mL of a water/ethanol (9/1) mixture. The resulting suspension was stirred at 60 °C for 30 min. A solution of 1.82 g (5.65 mmol) of (NBu₄)Br in 20 mL of water was added. After homogenization, 15 mL of an aqueous solution of 0.523 g (1.86 mmol) of Ni(SO₄)·7H₂O was added dropwise. The yellow-orange precipitate was collected by filtration, washed with water and ethanol, and air dried. Recrystallization from DMSO gave 1.39 g of well-shaped orange needles (yield 87%). Anal. Calc for C₁₂H₇N₄O₄Cl₂Ni: C, 58.56; H, 8.60; N, 6.51; Cl, 8.25; Ni, 6.82. Found: C, 57.60; H, 8.59; N, 6.61; Cl, 8.18; Ni, 6.37.

(NBu₄)₂[Cu(Cl₂opba)] (**2**). When the previous synthetic route is used to prepare the Cu(II) complex, the sodium salt precipitates as a purple powder. The synthesis was then performed by following a metal-exchange based method, in the same way as compound **3**, using copper(II) acetate instead of manganese(II) acetate. Well-shaped cubic purple single crystals were obtained in low yield. They were characterized by an X-ray crystal structure analysis.

(NBu₄)₅[Mn(Cl₂opba)(DMSO)₂]₄ (**3**) was synthesized by following a metal-exchange based method: A solution of 1 g (1.20 mmol) of (NBu₄)₂[Ni(Cl₂opba)] in 35 mL of DMSO was treated with 0.32 mL (4.78 mmol) of ethylenediamine and stirred at 70 °C for 15 min. A 294 mg (1.20 mmol) amount of Mn(CH₃COO)₂·4H₂O was then added. A dominant brown color was then obtained, and the solution was stirred for 1 h and filtered. Well-shaped brown crystals were obtained after 2 weeks. Yield: 0.75 g (75%). Anal. Calc for C₁₃₆H₂₃₆N₁₃O₃₂Cl₈S₈·

Mn₄ (**3**): C, 49.13; H, 7.10; N, 5.55; Cl, 8.55; Mn, 6.62. Found: C, 48.30; H, 7.02; N, 5.54; Cl, 8.50; Mn, 6.26.

Finally, the trinuclear species Cu(en)₂[Mn(Cl₂opba)(H₂O)₂]₂·2DMSO (**4**) was synthesized as follows: A 2 g (4.16 mmol) amount of Na₂[Cu(Cl₂opba)]·3H₂O was dissolved in 45 mL of DMSO at 80 °C. A 1.11 mL (16.6 mmol) volume of ethylenediamine was then added, and the solution was stirred for 10 min. The addition of 1.05 g (4.28 mmol) of Mn(CH₃COO)₂·4H₂O allows the product to precipitate as a brown mass which was collected by filtration, washed with a H₂O/DMSO (3/1) mixture and ethanol, and dried under vacuum. Yield: 1.68 g (70%). Recrystallization from DMSO gave thin brown needles. Anal. Calc for C₂₈H₄₀N₈O₁₈Cl₄S₂CuMn₂ (**4**): C, 29.01; H, 3.46; N, 5.52; Cl, 12.28; S, 5.54; Cu, 5.49; Mn, 9.50. Found: C, 29.15; H, 3.49; N, 9.69; Cl, 12.44; S, 5.74; Cu, 5.38; Mn, 9.35.

Crystallographic Data Collection and Structure Determination.

The X-ray data collections were performed on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centered reflections. Data were collected with the θ–2θ scan method. Three standard reflections were measured every 1 h and revealed no fluctuations in intensities. Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods and successive Fourier difference syntheses. An empirical absorption correction was applied using the ψ scan method or the DIFABS procedure.²⁷ The refinements (on *F*) were performed by the full-matrix least squares method (H atoms, both found by Fourier synthesis and placed at computed positions, were not refined). The scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a MicroVAX 3100 using the Molén programs.²⁸

The crystal data for all compounds are presented in Table 1. Atomic coordinates are given in Tables 2–5. Selected bond lengths and bond angles are given in Table 6.

Magnetic Measurements. These were carried out with a Quantum Design MPMS-5S SQUID magnetometer working down to 2 K. The principal susceptibilities for **3** were measured on a single crystal weighing 0.46 mg.

Results

Crystal Structures. (NBu₄)₂[M(Cl₂opba)], M = Ni(II) and Cu(II). Compounds **1** and **2** are isostructural, and owing to the C₂ symmetry they have a planar structure, as depicted in Figure 1. The metal ion is surrounded by two nitrogen and two oxygen atoms of the Cl₂opba ligand. Within the lattice, zigzag molecular chains are observed with a shortest intermolecular metal–metal separation of 8.036(1) Å for the Ni compound **1** and 7.918(1) Å for the Cu compound **2**.

(NBu₄)₅[Mn(Cl₂opba)(DMSO)₂]₄. The metal site in the [Mn(Cl₂opba)(DMSO)₂]₄ unit was found to be randomly occupied by Mn(III) and Mn(II) ions in 3/4 and 1/4 ratios, respectively. It follows that the observed structure is an average between the Jahn–Teller-distorted [Mn(Cl₂opba)(DMSO)₂][−] unit involving the Mn(III) ion and the undistorted [Mn(Cl₂opba)(DMSO)₂]^{2−} unit involving the Mn(II) ion. This average structure is shown in Figure 2, and the structure of the mixed-valence unit cell is shown in Figure 3. As expected, the Mn atom has an elongated octahedral environment. Two nitrogen and two oxygen atoms of the oxamate group occupy the equatorial positions (the mean Mn–N and Mn–O bond lengths are equal to 1.95 and 1.98 Å, respectively), and two oxygen atoms of DMSO molecules occupy the axial positions (the mean Mn–O bond length is then equal to 2.24 Å). The anionic [Mn(Cl₂opba)(DMSO)₂]^{4/5−} units are well separated from each other; the shortest Mn···Mn intermolecular separation is equal to 8.77 Å.

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Table 1. Crystal and Refinement Data for Compounds **1–4**

	(Bu ₄ N) ₂ Ni(Cl ₂ opba)	(Bu ₄ N) ₂ Cu(Cl ₂ opba)	(Bu ₄ N) ₅ [Mn(Cl ₂ opba)(DMSO) ₂] ₄	Cu(en) ₂ [Mn(Cl ₂ opba)(H ₂ O) ₂] ₂ ·2DMSO
formula	NiCl ₂ O ₆ N ₄ C ₄₂ H ₇₄	CuCl ₂ O ₆ N ₄ C ₄₂ H ₇₄	Mn ₄ Cl ₈ S ₈ O ₃₂ N ₁₃ C ₁₂₁ H ₁₃₆	CuMn ₂ Cl ₄ S ₂ O ₁₈ N ₈ C ₂₈ H ₄₀
fw	860.70	865.53	3145.19	1156.03
cryst syst	monoclinic	monoclinic	tetragonal	triclinic
space gp	C2/c	C2/c	P4 ₂ /c	P1
a, Å	18.708(2)	18.928(2)	26.295(10)	7.066(7)
b, Å	17.525(2)	17.634(2)	26.295(10)	11.844(1)
c, Å	14.763(9)	14.704(9)	12.342(7)	14.292(5)
α, deg	90	90	90	105.64(2)
β, deg	92.03(4)	92.38(3)	90	97.67(5)
γ, deg	90	90	90	102.13(3)
V, Å ³	4837.0(5)	4903.6(5)	8533.6(5)	1103.0(5)
Z	4	4	2	1
T, K	293	293	293	293
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ _c , g·cm ⁻³	1.182	1.172	1.804	1.740
μ(Mo Kα), cm ⁻¹	5.562	5.977	5.592	14.320
R ^a	0.049	0.044	0.074	0.064
R _w ^a	0.066	0.066	0.093	0.088

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|; R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}.$$

Table 2. Fractional Atomic Coordinates and B_{eq} Values (Å²) for **1**

	x	y	z	B_{eq}^a
Ni	0.5	0.09068(7)	0.25	4.13(3)
Cl	0.4347(1)	0.4608(1)	0.1784(2)	8.28(6)
O1	0.4340(2)	0.0228(3)	0.1957(3)	5.2(1)
O2	0.3335(3)	0.0254(3)	0.1095(3)	6.8(1)
O3	0.3421(2)	0.1869(3)	0.1128(3)	5.7(1)
N1	0.4459(3)	0.1665(3)	0.2020(3)	4.1(1)
N2	0.1663(3)	0.3513(3)	0.1606(3)	4.3(1)
C1	0.3821(4)	0.0586(4)	0.1507(4)	5.1(2)
C2	0.3864(3)	0.1451(4)	0.1519(4)	4.4(2)
C3	0.4694(3)	0.2397(4)	0.2204(4)	3.9(1)
C4	0.4411(3)	0.3080(4)	0.1886(4)	4.7(2)
C5	0.4707(3)	0.3758(4)	0.2184(5)	5.1(2)
C6	0.1840(3)	0.2774(4)	0.1119(4)	4.5(2)
C7	0.1409(4)	0.2082(4)	0.1366(5)	5.6(2)
C8	0.1621(4)	0.1409(4)	0.0794(6)	7.3(2)
C9	0.1200(6)	0.0678(5)	0.0975(8)	12.3(3)
C10	0.1882(4)	0.3474(4)	0.2630(4)	4.7(2)
C11	0.2669(4)	0.3387(4)	0.2831(4)	4.7(2)
C12	0.2799(4)	0.3455(5)	0.3871(4)	6.3(2)
C13	0.3577(4)	0.3399(5)	0.4152(5)	8.1(3)
C14	0.2077(3)	0.4142(4)	0.1141(4)	4.6(2)
C15	0.2016(4)	0.4905(4)	0.1561(4)	5.0(2)
C16	0.2477(4)	0.5483(4)	0.1082(5)	6.4(2)
C17	0.2420(6)	0.6263(5)	0.1464(6)	9.3(3)
C18	0.0866(3)	0.3673(4)	0.1571(4)	4.9(2)
C19	0.0518(4)	0.3747(5)	0.0648(5)	6.2(2)
C20	-0.0294(4)	0.3616(6)	0.0730(5)	8.5(2)
C21	-0.0672(5)	0.3726(7)	-0.0070(7)	13.5(4)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Cu(en)₂[Mn(Cl₂opba)(H₂O)₂]₂·2DMSO. The structure of compound **4** is depicted in Figure 4. This structure consists of centrosymmetrical Mn^{III}Cu^IMn^{III} trinuclear units and noncoordinated DMSO molecules. The Mn(III) ion is in a strongly distorted octahedral environment. Two nitrogen and two oxygen atoms of the oxamato group occupy the equatorial positions (the mean Mn–N and Mn–O bond lengths are equal to 1.918 and 1.966 Å, respectively), and two water molecules occupy the apical positions (the mean Mn–O bond length is equal to 2.250 Å). The bond angles around the manganese ion significantly deviate from 90 and 180°. The copper atom is also located in a distorted octahedral environment. Four nitrogen atoms of the ethylenediamine molecules occupy the equatorial positions (the mean Cu–N bond lengths are equal to 2.016 Å), and two oxygen atoms arising from oxamato groups, already

Table 3. Fractional Atomic Coordinates and B_{eq} Values (Å²) for **2**

	x	y	z	B_{eq}^a
Cu	0.5	0.08340(4)	0.25	4.12(1)
Cl	0.43437(8)	0.45508(8)	0.1783(1)	7.94(4)
O1	0.4278(2)	0.0182(2)	0.1951(2)	5.13(7)
O2	0.3280(2)	0.0268(2)	0.1096(2)	6.35(8)
O3	0.3399(2)	0.1847(2)	0.1144(2)	5.40(7)
N1	0.4437(2)	0.1634(2)	0.2008(2)	4.32(7)
N2	0.1676(2)	0.3450(2)	0.1619(2)	4.02(7)
C1	0.3778(2)	0.0555(3)	0.1508(3)	4.68(9)
C2	0.3842(2)	0.1434(2)	0.1533(3)	4.34(9)
C3	0.4688(2)	0.2359(2)	0.2205(3)	3.88(8)
C4	0.4406(2)	0.3036(2)	0.1900(3)	4.59(9)
C5	0.4716(2)	0.3716(2)	0.2189(3)	5.0(1)
C6	0.1831(2)	0.2713(2)	0.1128(3)	4.39(9)
C7	0.1398(3)	0.2034(3)	0.1376(3)	5.4(1)
C8	0.1596(3)	0.1353(3)	0.0785(3)	6.4(1)
C9	0.1190(4)	0.0668(4)	0.0977(5)	10.8(2)
C10	0.1905(2)	0.3405(2)	0.2643(3)	4.46(9)
C11	0.2680(2)	0.3318(3)	0.2873(3)	4.80(9)
C12	0.2811(3)	0.3353(3)	0.3909(3)	6.0(1)
C13	0.3586(3)	0.3308(4)	0.4187(4)	8.1(2)
C14	0.2087(2)	0.4064(2)	0.1143(3)	4.32(9)
C15	0.2041(2)	0.4838(2)	0.1558(3)	5.0(1)
C16	0.2502(2)	0.0392(2)	0.3937(3)	5.5(1)
C17	0.2517(3)	0.1175(3)	0.3506(4)	8.4(2)
C18	0.0892(2)	0.3627(3)	0.1592(3)	4.53(9)
C19	0.0541(2)	0.3696(3)	0.0648(3)	5.0(1)
C20	0.0257(2)	0.3664(4)	0.4278(4)	6.8(1)
C21	0.4344(3)	0.1179(4)	0.4852(4)	8.6(2)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

linked to the manganese atom, occupy the apical positions (the Cu–O bond length is equal to 2.454 Å). The ethylene groups of the five-membered Cu(en) rings around the copper atom adopt such a conformation that the dihedral angle between the two rings is equal to 51.1(1)°, and owing to symmetry requirements the total conformation for these two rings is staggered. The intramolecular Mn---Cu and Mn---Mn separations are equal to 3.836(1) and 7.671(2) Å, respectively. The shortest intermolecular metal---metal separation is Mn---Mn = 6.998(2) Å.

Magnetic Properties. As expected, (NBu₄)₂[Ni(Cl₂opba)] (**1**) containing a Ni(II) ion in a square planar N₂O₂ core is diamagnetic, and (NBu₄)₂[Cu(Cl₂opba)] (**2**) presents the magnetic properties of an isolated Cu(II) ion. In the following of this magnetic section, we will focus on compounds (NBu₄)₅-

Table 4. Fractional Atomic Coordinates and B_{eq} Values (\AA^2) for **3**

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Mn	0.69116(7)	0.02364(7)	0.2047(2)	4.64(4)
Cl1	0.9395(2)	0.0260(2)	0.3604(4)	7.5(1)
Cl2	0.9200(1)	−0.0891(2)	0.2994(4)	7.6(1)
S1	0.6422(2)	−0.0335(2)	0.4267(4)	8.6(1)
S2	0.6711(4)	0.0824(3)	−0.0453(8)	7.6(2)
S2P	0.0493(4)	0.3556(4)	0.0385(8)	9.5(3)
O1	0.7390(4)	−0.1205(3)	0.1725(8)	6.4(3)
O1s	0.6635(5)	0.0120(4)	0.3734(8)	8.2(3)
O2	0.6374(4)	−0.1084(4)	0.1134(9)	8.1(3)
O2s	0.6913(4)	0.0420(4)	0.0265(8)	6.7(3)
O3	0.6408(3)	−0.0291(4)	0.1639(8)	6.3(2)
O4	0.6631(3)	0.0932(3)	0.2222(8)	5.4(2)
O5	0.6866(4)	0.1715(4)	0.259(1)	7.4(3)
O6	0.7872(4)	0.1386(3)	0.2675(8)	5.7(2)
N1	0.7541(4)	0.0585(4)	0.2431(8)	4.2(2)
N2	0.7371(4)	−0.0347(4)	0.1981(9)	4.6(2)
N3	0.5	0.5	0.5	8.6(5)
N4	0.7451(4)	0.2785(4)	0.0377(8)	5.7(3)
C1	0.7169(5)	−0.0791(5)	0.1757(9)	4.2(3)
Cl1s	0.645(1)	−0.0253(8)	0.563(2)	10.9(6)
C2	0.6586(6)	−0.0744(5)	0.149(1)	5.6(3)
C2s	0.575(1)	−0.030(1)	0.401(2)	20(1)
C3	0.6964(5)	0.1277(5)	0.244(1)	5.2(3)
C3s	0.654(2)	0.060(1)	−0.166(2)	19(1)
C4	0.7513(5)	0.1101(5)	0.254(1)	5.0(3)
C4s	0.092(2)	0.383(1)	0.022(2)	22(2)
C5	0.7973(5)	0.0276(4)	0.254(1)	4.2(3)
C6	0.8434(5)	0.0420(4)	0.294(1)	4.5(3)
C7	0.8824(5)	0.0071(6)	0.306(1)	5.6(3)
C8	0.8741(5)	−0.0449(5)	0.280(1)	4.7(3)
C9	0.8274(5)	−0.0586(5)	0.243(1)	5.0(3)
C10	0.7883(5)	−0.0239(4)	0.2291(8)	4.0(3)
C11	0.4855(6)	0.4550(6)	0.426(1)	6.9(4)
C12	0.4745(7)	0.4049(7)	0.482(2)	7.6(4)
C13	0.4595(8)	0.3692(8)	0.394(2)	10.5(6)
C14	0.448(1)	0.318(1)	0.431(2)	13.1(8)
C15	0.7816(6)	0.2846(6)	0.130(1)	6.1(4)
C16	0.8313(8)	0.2971(7)	0.095(1)	8.8(5)
C17	0.8697(7)	0.2947(7)	0.195(1)	8.1(5)
C18	0.9160(9)	0.319(1)	0.170(2)	12.0(7)
C19	0.7382(7)	0.3279(6)	−0.027(1)	7.0(4)
C20	0.7229(8)	0.3726(6)	0.039(2)	9.2(5)
C21	0.7180(9)	0.4217(8)	−0.032(2)	9.9(6)
C22	0.671(1)	0.422(1)	−0.086(2)	16(1)
C23	0.6956(7)	0.2631(8)	0.095(1)	7.9(5)
C24	0.6537(8)	0.261(1)	0.022(2)	11.7(6)
C25	0.608(1)	0.247(2)	0.090(3)	30(1)
C26	0.572(1)	0.266(1)	0.086(4)	17(1)
C27	0.7613(5)	0.2404(6)	−0.041(1)	5.3(3)
C28	0.7722(6)	0.1866(6)	0.005(1)	6.2(4)
C29	0.7951(6)	0.1545(6)	−0.081(1)	6.8(4)
C30	0.8097(7)	0.1073(9)	−0.045(2)	10.9(6)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

$[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]_4$ (**3**) and $\text{Cu}(\text{en})_2[\text{Mn}(\text{Cl}_2\text{opba})(\text{H}_2\text{O})_2]_2 \cdot 2\text{DMSO}$ (**4**).

Single-Crystal Magnetic Susceptibilities of $(\text{NBu}_4)_5[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]_4$ (3**).** We have seen that this compound crystallizes in the tetragonal $P4_21c$ space group, and we measured the temperature dependences of the molar magnetic susceptibilities both along the c unique axis and perpendicular to this axis. The results are represented in Figure 5 in the form of the $\chi_{\text{M},t}T$ ($t = z$ for the parallel and $t = x$ for the perpendicular susceptibilities) versus T plots, where $\chi_{\text{M},t}$ is the principal molar susceptibility and T the temperature. At room temperature, both $\chi_{\text{M},z}T$ and $\chi_{\text{M},x}T$ are equal to $15.0 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds to what is expected for three Mn(III) and one Mn(II) ions. As T is lowered down to ca. 100 K, $\chi_{\text{M},z}T$ increases and

Table 5. Fractional Atomic Coordinates and B_{eq} Values (\AA^2) for **4**

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
Cu	0	0	0	2.77(3)
Mn	0.1255(1)	0.2387(1)	−0.13329(9)	2.57(2)
Cl1	−0.2921(4)	0.5364(2)	−0.4144(2)	5.14(6)
Cl2	0.1675(4)	0.6610(2)	−0.3763(2)	5.36(6)
O1W	0.0799(7)	0.3581(5)	0.0102(4)	3.3(1)
O1	0.3852(7)	0.2553(5)	−0.0547(4)	3.4(1)
O2	−0.0825(7)	0.1107(4)	−0.1156(4)	2.8(1)
O2W	0.1988(7)	0.0850(5)	−0.2396(4)	3.3(1)
O3	−0.4028(7)	0.0178(5)	−0.1680(4)	3.7(1)
O4	−0.4314(7)	0.1758(5)	−0.2808(4)	3.2(1)
O5	0.6955(7)	0.3675(6)	−0.0176(5)	4.8(2)
O6	0.5791(7)	0.4996(5)	−0.1393(4)	4.0(1)
N1	−0.0953(8)	0.2579(5)	−0.2168(4)	2.4(1)
N2	0.2665(8)	0.3681(6)	−0.1733(5)	2.9(1)
N3	0.157(1)	0.1559(6)	0.1044(5)	3.8(2)
N4	−0.2332(9)	0.0338(6)	0.0588(5)	3.9(2)
C1	0.525(1)	0.3412(7)	−0.0617(6)	3.2(2)
C2	0.461(1)	0.4140(7)	−0.1300(6)	3.1(2)
C3	−0.2726(9)	0.1815(6)	−0.2298(5)	2.5(2)
C4	−0.258(1)	0.0957(6)	−0.1676(6)	2.6(2)
C5	−0.052(1)	0.3539(6)	−0.2578(5)	2.5(2)
C6	−0.184(1)	0.3917(7)	−0.3143(5)	2.8(2)
C7	−0.117(1)	0.4858(7)	−0.3493(6)	3.3(2)
C8	0.084(1)	0.5441(7)	−0.3289(6)	3.7(2)
C9	0.219(1)	0.5093(7)	−0.2704(6)	3.2(2)
C10	0.153(1)	0.4146(7)	−0.2344(5)	2.6(2)
C11	0.035(2)	0.1903(9)	0.1766(7)	4.7(2)
C12	−0.180(1)	0.1587(9)	0.1215(7)	4.9(2)
S	−0.2455(5)	−0.0790(3)	−0.4693(3)	7.9(1)
C1S	−0.472(2)	−0.146(1)	−0.4470(9)	7.8(4)
C2S	−0.197(2)	−0.208(1)	−0.5451(9)	6.4(3)
O1S	0.107(1)	0.039(1)	0.3794(7)	12.9(4)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 6. Selected Geometrical Data for the Metal Environment in Compounds **1** to **4**

	compd				
	1	2	3	4	
metal(s)	Ni	Cu	Mn	Mn	Cu
geometry ^a	ML ₄ , planar	ML ₄ , planar	ML ₆ , dO	ML ₆ , dO ^b	ML ₆ , dO
M–O (\AA)	1.874(4)	1.936(3)	1.98(1)	1.961(5)	2.454(6)
			1.984(9)	1.973(5)	
			2.23(1)	2.261(5)	
			2.25(1)	2.238(5)	
M–N (\AA)	1.801(5)	1.894(3)	1.95(1)	1.925(6)	2.012(7)
			1.95(1)	1.911(7)	2.020(6)
O–M–O (deg)	93.0(2)	95.3(1)	115.1(4)	112.2(2)	
			160.6(4)	160.0(2)	180
N–M–N (deg)			81.6(4)	82.2(3)	85.3(3)

^a M = metal, L = ligand. ^b Severe distortion from the octahedral symmetry.

reaches $23.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. On the other hand, $\chi_{\text{M},x}T$ decreases to a value of $3.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. These deviations with respect to the Curie law arise from the zero-field splitting of the Mn(III) $S = 2$ ground state. The zero-field spin Hamiltonian may be written as

$$H = D(\mathbf{S}_{1,z}^2 + \mathbf{S}_{2,z}^2 + \mathbf{S}_{3,z}^2) + \beta[g_1(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3) + g_4\mathbf{S}_4] \cdot \mathbf{H}$$

where the indices 1–3 refer to the Mn(III) ions and the index 4 refers to the Mn(II) ion. D is the axial zero-field splitting parameter for the Mn(III) ion, and g_1 and g_4 are the Zeeman factors supposed to be isotropic for the Mn(III) and Mn(II) ions, respectively. If the crystal is axial, each Mn(III) unit has a

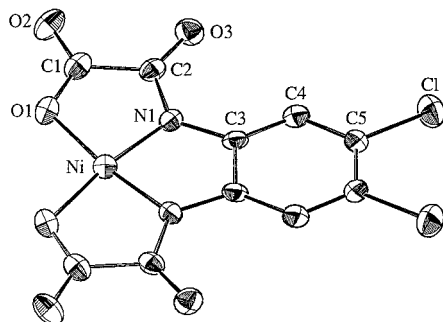


Figure 1. Structure of the anion $[\text{Ni}(\text{Cl}_2\text{opba})]^{2-}$ in compound 1. Ellipsoids are presented with 20% probability.

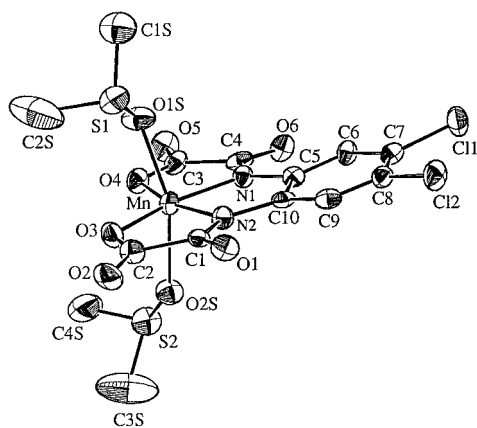


Figure 2. Structure of the anion $[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]^{5/4-}$ in compound 3. Ellipsoids are presented with 20% probability.

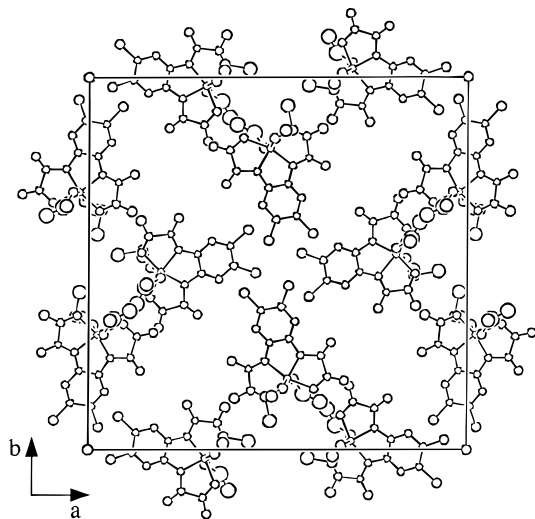


Figure 3. Projection down the c axis of the anionic sublattice for $(\text{NBu}_4)_5[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]_4 \cdot 2\text{H}_2\text{O}$ (3).

rhombic symmetry. Therefore, the perpendicular susceptibility for the crystal, $\chi_{M,x}$, contains the average of the susceptibilities along the x and y directions of each $[\text{Mn}^{\text{III}}(\text{Cl}_2\text{opba})(\text{DMSO})_2]^-$ unit along with the susceptibility of $[\text{Mn}^{\text{II}}(\text{Cl}_2\text{opba})(\text{DMSO})_2]^{2-}$. We checked that the introduction of the molecular rhombicity of the Mn(III)-containing unit has a very weak effect on $\chi_{M,z}T$, which is almost within the experimental uncertainties, and we ignored it. The theoretical expressions for $\chi_{M,z}T$ and $\chi_{M,x}T$ are then as follows:

$$\chi_{M,z}T = \frac{35}{32}g_4^2 + \frac{9}{48}g_1^2 \frac{\exp(-x) + 4\exp(-4x)}{1 + 2\exp(-x) + 2\exp(-4x)}$$

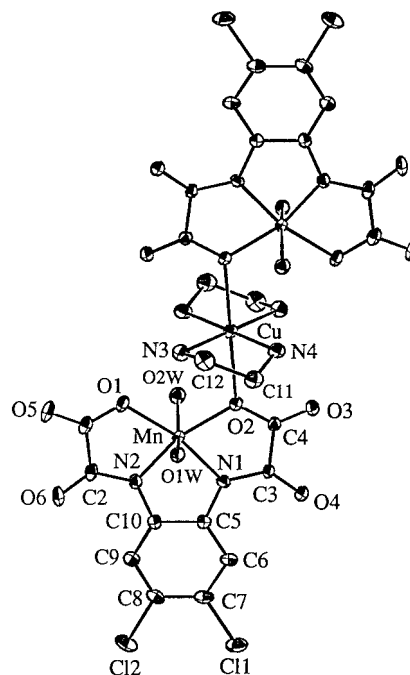


Figure 4. Structure of the trinuclear unit $\text{Cu}(\text{en})_2[\text{Mn}(\text{Cl}_2\text{opba})(\text{H}_2\text{O})_2]$ in compound 4. Ellipsoids are presented with 20% probability.

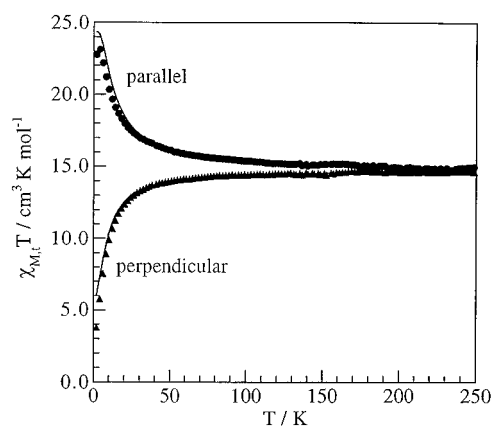


Figure 5. Experimental (\cdots , \blacktriangle) and calculated ($—$) $\chi_{M,z}T$ and $\chi_{M,x}T$ versus T curves for $(\text{NBu}_4)_5[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]_4 \cdot 2\text{H}_2\text{O}$ (3).

$$\chi_{M,x}T = \frac{35}{32}g_4^2 + \frac{3}{48}g_1^2 \frac{(x^{-1})(9 - 7\exp(-x) - 2\exp(-4x))}{1 + 2\exp(-x) + 2\exp(-4x)}$$

with

$$x = -D/kT$$

A least-squares fitting of the experimental data led to $g_1 = 2.0$, $g_4 = 2.0$, and $D = -4.0 \pm 0.2 \text{ cm}^{-1}$. The sign of D indicates that the ground state is the $M_S = \pm 2$ component of the spin quintet state. It is interesting to note here that an EPR investigation of Mn(III) in rutile TiO_2 was interpreted with $g_z = 1.99$, $g_x = 2.00$, and $D = -3.4 \text{ cm}^{-1}$,²⁹ which justifies our assumption concerning the isotropy of the g_1 Zeeman factor.

$\text{Cu}(\text{en})_2[\text{Mn}(\text{Cl}_2\text{opba})(\text{H}_2\text{O})_2]_2 \cdot 2\text{DMSO}$ (4). The $\chi_{M,T}$ versus T plot for this compound, measured on a powder sample, is shown in Figure 6. At room temperature, $\chi_{M,T}$ is equal to $6.40 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds to what is expected for two Mn(III) and one Cu(II) ions without interaction. As T is lowered, $\chi_{M,T}$ is first constant, then slightly decreases, and

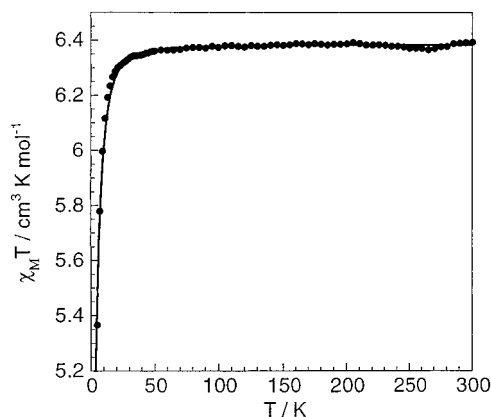


Figure 6. Experimental (···) and calculated (—) $\chi_M T$ versus T curves for $\text{Cu(en)}_2[\text{Mn}(\text{Cl}_2\text{opba})(\text{H}_2\text{O})_2]_2 \cdot 2\text{DMSO}$ (**4**).

reaches $5.36 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The decrease of $\chi_M T$ below ca. 60 K cannot be attributed to Mn–Cu antiferromagnetic interactions. Indeed, the spin density delocalized from the Cu(II) ion to the oxamate oxygen atoms occupying the apical positions in the Cu(II) coordination sphere is anticipated to be negligibly small. Moreover, Mn–Cu antiferromagnetic interactions in a linear $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ trinuclear species would give rise to a minimum in the $\chi_M T$ versus T curve. It follows that the deviation with respect to the Curie law observed in the magnetic behavior of compound **4** may be attributed to the zero-field splitting within the $S = 2$ local ground states of the Mn(III) ions. The theoretical expression of $\chi_M T$ is then

$$\chi_M T = \frac{{}^3/_{32}g_{\text{Cu}}^2 + {}^1/_{2}g_{\text{Mn}}^2 \times 6x^{-1} + (1 - {}^{14}/_{3}x^{-1}) \exp(-x) + (4 - {}^4/_{3}x^{-1}) \exp(-4x)}{1 + 2 \exp(-x) + 2 \exp(-4x)}$$

with

$$x = -D/kT$$

g_{Mn} and g_{Cu} are the local Zeeman factors, and D again is the axial zero-field splitting parameter for Mn(III). Least-squares fitting led to $g_{\text{Mn}} = 2.0$, $g_{\text{Cu}} = 2.10$, and $D = -4.0 \text{ cm}^{-1}$. The sign of D cannot be determined unambiguously from powder susceptibility data. The minus sign was chosen by analogy with compound **2**.

Discussion and Concluding Remarks

We discuss first the synthesis of the precursors described in this paper and then their potentialities to design novel low-dimensional compounds.

Up to now, only the Cu(II) oxamate precursors were known. All the attempts to prepare oxamate precursors with another metal ion to the best of our knowledge failed. This work shows that Ni(II), Mn(III), and Mn(II) precursors can be synthesized with the $\text{Cl}_2\text{opba}^{4-}$ ligand. The Mn(III) and Mn(II) compounds are synthesized using a method which consists of extracting the Ni(II) or Cu(II) ion from the N_2O_2 cavity in the presence of a ligand with a strong affinity for this ion and replacing it by Mn(III) or Mn(II).

Compound **2** is another copper(II) precursor which should lead to one- and two-dimensional molecular materials similar to those already described.²⁴ We checked that the reaction of **2** with the Mn(II) ion in the 1/1 ratio affords the expected $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$ ferrimagnetic chain compound, but we do not intend to explore further this direction. **1** is a diamagnetic precursor which could be utilized to design MNi compounds in which the M magnetic ions would be too far from each other to interact. Such compounds could be useful to characterize the single-ion properties of M. This information is often necessary to understand in a thorough manner the magnetic properties of magnetic networks involving M and another magnetic ion. The manganese containing precursors **3** and **4** are the most interesting. **3** is in itself an unexpected mixed-valence compound. Of course, there is no electron delocalization between the $[\text{Mn}(\text{Cl}_2\text{opba})(\text{DMSO})_2]$ units; the crystallographic equivalence of the four manganese sites arises from a disorder effect, similar to that observed for $[(\text{phen})_2\text{MnO}_2\text{Mn}(\text{phen})_2]^{3+}$.³⁰ The reaction with a M ion should afford MMn^{III} and/or MMn^{II} low-dimensional materials. It is worth emphasizing here that the Mn(III)–Cu(II) interaction is expected to be ferromagnetic, owing to the orthogonality of the magnetic orbitals.^{6,20} Compound **4** might also react with M ions, which would link the trinuclear units to each other, affording trimetallic lattices.

In the near future, we intend to explore the chemistry of the new precursors described in this paper.

Supporting Information Available: Tables of crystal data, hydrogen positional and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (18 pages). Ordering information is given on any current masthead page.

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(30) Stebler, M.; Ludi, A.; Bürgi, H. B. *Inorg. Chem.* **1986**, 25, 4743.