$[Cr(bipy)(C_2O_4)_2]^-$: A Versatile Building Block for the Design of Heteropolymetallic Systems. Crystal Structures of $[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n \cdot nH_2O$, $[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$, and $[CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2] \cdot H_2O$

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The self-assembly of the building blocks $[Cr(bipy)(C_2O_4)_2]^-$ with bivalent metal ions (Ba(II), Mn(II), and Co(II)) led to three completely different structures: $[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n \cdot nH_2O$ (**1**), $[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (**2**), and $CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2 \cdot H_2O$ (**3**). The molecular and crystal structures of the three compounds were determined. Crystal **1** is monoclinic, $P2_1/n$, with $a = 15.949(11)$ Å, $b = 13.206(9)$ Å, $c = 16.957(12)$ Å, $\beta = 113.39(4)°$, and $Z = 4$. The compound is a scaffolding-like material with a unique three-dimensional structure. Crystal **2** is monoclinic, $P2_1/c$, with $a = 8.674(4)$ Å, $b = 13.416(8)$ Å, $c = 27.82(2)$ Å, $\beta = 107.30(4)°$, and $Z = 4$. Its structure reveals a novel heterobimetallic chain with octacoordinated manganese(II) atoms. The geometry of the manganese atoms is described as a flattened square antiprism. The Co compound (**3**) is monoclinic, $C2/c$, with $a = 20.505(5)$ Å, $b = 11.093(3)$ Å, $c = 17.346(4)$ Å, $\beta = 125.02(2)°$, and $Z = 4$. Its structure consists of discrete linear {CrCoCr} trinuclear species with the cobalt atom lying on an inversion center. The $[Cr(bipy)(C_2O_4)_2]^-$ units retain their original environment and accomplish different coordination functions, acting as terminal and/or bridging ligands. The synthetic approach, namely the reaction of an aqueous suspension of the barium derivative, **1**, with a transition metal sulfate, seems to have a wide applicability in designing new heterobimetallic systems.

Introduction

The search for molecular building blocks in the design of new extended supramolecular architectures, with tailored electronic or catalytic properties, is a current interest in inorganic chemistry. The synthetic effort is mainly directed toward the preparation of molecular-based magnets[1] and of inorganic materials with inner cavities and channels, mimicking zeolites.[2]

A successful strategy leading to heteropolynuclear one-, two-, and three-dimensional systems is the use of metal cations to link relatively stable coordination compounds containing potential bridging units. The overall topography of the extended structure is strongly influenced by the coordination algorithm[3] of the linking metal ion. As a general rule, the building blocks are complex anions acting as "ligands" toward another metal ion. Following this rational synthetic approach, various heterometallic systems, ranging from discrete entities to 3D extended structures, can be obtained.

Versatile building blocks containing transition metal ions are quite scarce in the literature except for copper precursors, which have generated a rich coordination chemistry of heteropolynuclear systems. Cu(II)−M(II) chains and oligomeric species (M = Mn, Co, Ni) have been synthesized using copper(II) precursors such as: $[Cu(pba)]^{2-}$ (pba = 1,3-propylenebis(oxamato)),[4] $[Cu(pbaOH)]^{2-}$,[5] and $[Cu(obp)]^{2-}$ (obp = oxamidobis(*N*,*N*′-propionato)).[6] By alteration of the stoichiometry and/or oxidation state of the second metal ion, compounds with higher dimensionality have been reported. For example, two- and three-dimensional molecular based magnets of formula $(cat)_2Mn_2\{Cu(opba)\}_3 \cdot S$ have been recently synthesized (cat = organic cation, opba = *o*-phenylenebis(oxamato), and S = solvent).[1b,7] Using similar copper(II)-containing building blocks and three-valent lanthanides, ladder-type and tubelike one-dimensional chains were obtained.[8] Other copper(II) complexes which can act as bridges are those containing oximato ligands, such as the dianion of dimethylglyoxime, and the dianion of 1,2-cyclohexanedione oxime.[9] The infinite M(III)−Cu(II) oximato-bridged chains (M = Mn, Fe) are further linked by carboxylato bridges, leading to two-dimensional materials.

The oxalato ion is an efficient bridging ligand for the stepwise synthesis of homo- and heteropolynuclear complexes. Numerous oxalato-bridged homometallic assemblies have been reported over the past few years and their magnetic properties have been

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(1) See for example: (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866 and references therein. (c) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (d) Mallah, T.; Thiébaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554. (e) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397.

(2) For example: (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) K. Park, M.; Kuroda, R.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 884. (c) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. (d) Batten, S. R.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 820.

(3) (a) Baxter, P. N. W.; Lehn, J. M.; Fischer, J.; Youinou, M. T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2284. (b) Hanan, G. S.; Arana, C. R.; Lehn, J. M.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1122.

(4) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1988**, *27*, 399.

(5) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7428.

(6) (a) Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P.; Georges, R.; Gianduzzo, J. C.; Curely, J.; Xu, Q. *Inorg. Chem.* **1988**, *27*, 2741. (b) Gulbrandsen, A.; Sletten, J.; Nakatani, K.; Pei, Y.; Kahn, O. *Inorg. Chim. Acta* **1993**, *212*, 271.

(7) (a) Stumpf, H. O.; Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738. (b) Stumpf, H. O.; Pei, Y.; Michaut, C.; Kahn, O.; Renard, J. P.; Ouahab, L. *Chem. Mater.* **1994**, *6*, 257.

(8) (a) Guillou, O.; Oushoorn, R.; Kahn, O.; Boubeker, K.; Batail, P. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 626. (b) Guillou, O.; Kahn, O.; Oushoorn, R.; Boubeker, K.; Batail, P. *Inorg. Chim. Acta* **1992**, *198−200*, 119.

(9) (a) Lloret, F.; Ruiz, R.; Julve, M.; Faus, J.; Journaux, Y.; Castro, I.; Verdaguer, M. *Chem. Mater.* **1992**, *4*, 1150. (b) Lloret, F.; Ruiz, R.; Cervera, B.; Castro, I.; Julve, M.; Faus, J.; Real, J. A.; Sapina, F.; Journaux, Y.; Colin, J. C.; Verdaguer, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2615.

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extensively investigated,[10] but the number of structurally characterized oxalato-bridged heterometallic systems is much more limited. The chemistry of the heteropolynuclear complexes containing chromium(III) and another transition metal ion has received a strong impulse from the growing interest in the design of molecular based magnets. It is well-known that chromium(III) complexes are quite inert toward ligand substitution, allowing a good control over the reaction products. Two molecular bricks containing chromium(III) and oxalato ions have been proposed so far to design of M(II)−Cr(III) systems: $[Cr(salen)(C_2O_4)]^-$ and $[Cr(C_2O_4)_3]^{3-}$. The former generates heterobinuclear complexes,[11] while the latter, with three potentially bridging ligands, is appropriate for the synthesis of two- or three-dimensional networks.[12] Building blocks containing bis(oxalato) units, such as $[Cr(AA)(C_2O_4)_2]^-$ (AA = neutral chelating ligands) have not been studied so far.

The presence of one or both $[Cr(C_2O_4)_3]^{3-}$ enantiomers plays a very important role on the dimensionality of the polymetallic systems.[13,14] The two chiral octahedra, Δ- and Λ-$[Cr(C_2O_4)_3]^{3-}$, generated with manganese(II) ions, a centrosymmetric 2D honeycombed layered structure of stoichiometry $[Mn^{II}Cr^{III}(C_2O_4)_2]_n{}^{n-}$.[14] On the other hand, oxalato-bridged 3D homometallic and heterometallic nonsymmetric networks, based on chiral building blocks of either Δ- or Λ-$[M(C_2O_4)_3]$ (M = Fe(II), Mn(II), Cr(III)) ions were recently reported.[15]

We have recently started a research program on the synthesis of heterometallic systems of interest to the field of materials science. We have chosen, as building blocks for the first study, $[Cr(bipy)(C_2O_4)_2]^-$. The choice of bipyridine was justified by the significant role these ligands can play on the overall structure, by means of aromatic stacking interactions. The new heteropolynuclear complexes were obtained by self-assembling the chromium(III) building blocks with different bivalent transition metal ions. The expected stoichiometry of the compounds, M(II):Cr(III) = 1:2, suggested the possibility for further use as raw materials for mixed oxides of spinel type.

We report here on the synthesis and crystal structures of two new heteropolynuclear complexes, $[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (**2**) and $[CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2]\cdot H_2O$ (**3**) as well as on the unprecedented 3D polymeric frame of their barium precursor, $[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n\cdot nH_2O$ (**1**).

Experimental Section

Synthesis. The chemicals were purchased from Aldrich and all the manipulations were performed using materials as received. Compound **1** was synthesized according to ref 16. Recrystallization from water produced red crystals suitable for X-ray crystallographic studies. Compounds **2** and **3** were obtained following the same general procedure: A suspension of **1** (0.5 mmol) in 50 mL of water reacted with a stoichiometric amount of $MnSO_4\cdot 4H_2O$ or $CoSO_4\cdot 7H_2O$, dissolved in 10 mL of water. The resulting mixture was stirred for 3 h to promote complete precipitation of barium sulfate, which was removed by filtration. Red-violet microcrystalline powders of **2** and **3** were obtained by slow concentration of the aqueous solutions. The solids were filtered off and washed with acetonitrile. Single crystals of **2** were obtained by slow diffusion of acetonitrile into the aqueous solution while those of **3** were obtained by recrystallization from water. The IR spectra of the single crystals were identical to those of the powders.

Table 1. Crystal Data for the Three Crystals

	1	2	3
chem formula	$[C_{28}H_{20}N_4O_{18}BaCr_2]_n$	$[C_{28}H_{16}N_4O_{16}MnCr_2]_n$	$C_{28}H_{22}N_4O_{19}CoCr_2$
fw	$(941.8)_n$	$(823.4)_n$	881.4
space group (No.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$C2/c$ (15)
a (Å)	15.949(11)	8.674(4)	20.505(5)
b (Å)	13.206(9)	13.416(8)	11.093(3)
c (Å)	16.957(12)	27.82(2)	17.346(4)
β (deg)	113.39(4)	107.30(3)	125.02(2)
V (Å^3)	3278(4)	3090(3)	3231.2(15)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.908	1.770	1.812
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
μ(Mo Kα) (cm^{-1})	19.3	11.8	12.63
T (°C)	21	21	21
R^a	0.029	0.056	0.061
$R_w{}^b$	0.027	0.049	0.049

[a] $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \sum w(|F_o - F_c|)/\sum(wF_o)$.

$[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (2). Yield: 95%. IR data (cm^{-1}): 1710 s, 1795 s, 1660 vs, 1600 m, 1500 w, 1450 m, 1410 s, 1320 w, 1280 m, 1180 w, 1160 w, 1110 w, 1060 w, 1040 w, 1025 w, 900 w, 810 m, 780 m, 730 m, 660 m, 650 w, 550 m, 480 m, 460 m, 410 m.

$[CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2]\cdot H_2O$ (3). Yield: 87%. IR data (cm^{-1}): 3420 m, 1720 s, 1590 s, 1640 vs, 1500 w, 1450 m, 1395 s, 1320 w, 1300 w, 1240 w, 1160 w, 1060 w, 1040 w, 900 w, 850 w, 810 m, 780 m, 730 m, 670 w, 650 w, 560 w, 540 m, 480 m, 460 m, 420 w.

Crystallographic Measurements and Structure Resolution. The crystals were selected after examination under a polarizing microscope for homogeneity. The data collection was made at room temperature on a Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation. The P3 programs were used for the data collection. The unit cell parameters were obtained by least-squares refinement of the angles 2θ (16−30°), ω, and χ for about 25 well-centered reflections. The data collections were made by the $\theta-2\theta$ scan technique, and three standard reflections were measured after every 97 reflections. The coordinates of the heavy atoms were determined from direct methods, and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structure was done by full-matrix least-squares analysis. A numerical absorption correction based on the equations of the crystal faces was done for crystals **1** and **2**. The molecule of lattice water is disordered equally on two positions for crystal **1**. The H atoms were fixed at their calculated positions (riding model) with $U_{iso} = 0.08$ Å^2. The calculations were done on a SHELXTL system.[17] The crystallographic data and experimental details are summarized in Table 1.

Other Measurements. The IR spectra (KBr pellets) were measured on a Perkin-Elmer 783 spectrometer. Diffuse reflectance electronic spectra were recorded with a Cary 5E spectrophotometer.

Results and Discussion

Our approach to design new Cr(III)−M(II) heteropolynuclear complexes consists in the reaction of the racemic Ba(II)−Cr(III) precursor with the appropriate transition metal(II) sulfate.

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(10) (a) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. (b) Deguenon, D.; Bernardinelli, G.; Tuchagues, J. P.; Castan, P. *Inorg. Chem.* **1990**, *29*, 3031. (c) Oshio, H.; Nagashima, U. *Inorg. Chem.* **1992**, *31*, 3295. (d) De Munno, G.; Ruiz, R.; Lloret, F.; Faus, J.; Sessoli, R.; Julve, M. *Inorg. Chem.* **1995**, *34*, 408 and references therein.

(11) (a) Ohba, M.; Tamaki, H.; Matsumoto, N.; Okawa, H.; Kida, S. *Chem. Lett.* **1991**, 1157. (b) Ohba, M.; Tamaki, H.; Matsumoto, N.; Okawa, H. *Inorg. Chem.* **1993**, *32*, 5385.

(12) (a) Zhong, Z. J.; Matsumoto, N.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 87. (b) Tamaki, H.; Zhang, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 6974.

(13) Farrell, R. P.; Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1995**, *34*, 157.

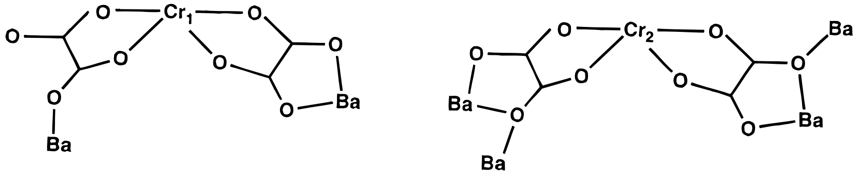
(14) Decurtins, S.; Schmalle, H. W.; Oswald, H. R.; Linden, A.; Ensling, J.; Gütlich, P.; Hauser, A. *Inorg. Chim. Acta* **1994**, *216*, 65.

(15) (a) Decurtins, S.; Schmalle, H. W.; Schneuwly, P.; Oswald, H. R. *Inorg. Chem.* **1993**, *32*, 1888. (b) Decurtins, S.; Schmalle, H. W.; Schneuwly, P.; Ensling, J.; Gütlich, P. *J. Am. Chem. Soc.* **1994**, *116*, 9521.

(16) Broomhead, J. A.; Dwyer, F. D. *Aust. J. Chem.* **1961**, *14*, 250.

(17) SHELXTL PLUS (PC version, 1990−1993). Siemens Analytical Instruments Inc., Madison, WI.

Chart 1



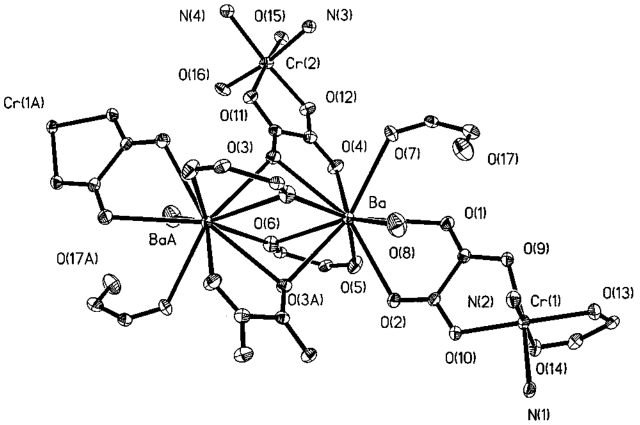


Figure 1. Labeled diagram of the environment of the Ba atoms in crystal **1**.

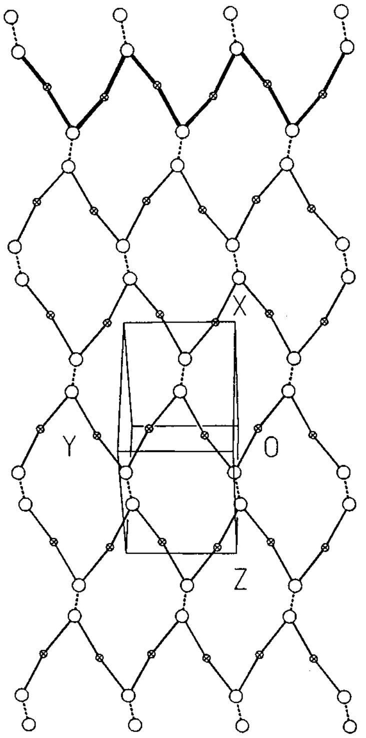


Figure 2. View of a chicken-wire sheet in $[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n\cdot nH_2O$ (**1**), showing only the Ba (white) and Cr(1) atoms. One chiral helix is shown in bold print.

$$Ba\{Cr(bipy)(C_2O_4)_2\}_2 + MSO_4 \rightarrow M\{Cr(bipy)(C_2O_4)_2\}_2 + BaSO_4$$

Following this straightforward synthetic route, different heterometallic systems with novel magnetic properties can be obtained in a nearly quantitative yield as well as high purity. The complexes $Ba[Cr(AA)(C_2O_4)_2]_2\cdot nH_2O$ (AA = 2,2′-bipyridine, 1,10-phenanthroline) have been used in the early 1960s as intermediates for the synthesis and resolution of (Δ,Λ)-$K[Cr(AA)(C_2O_4)_2]\cdot nH_2O$,[16] but their structures have not been reported so far.

Interesting structures for the Ba (**1**) and the Mn (**2**) compounds were anticipated, since barium ions can accept large coordination numbers, while the high-spin manganese(II) ions have no specific stereochemical preferences and could eventually accept large coordination numbers, up to 8. On the other hand, the cobalt analogue, **3**, could illustrate the key role played by the stereochemical requirements of the linking bivalent metal ion on the nuclearity and on the overall crystal structure of the heteropolynuclear systems, since coordination numbers larger than 6 are not likely for cobalt(II) ions. The molecular and crystal structures of the three compounds are, indeed, completely different, in spite of their similar stoichiometry and of the fact that the three comlexes have been synthesized in the same conditions. The $\{Cr(bipy)(C_2O_4)_2\}$ units are preserved, in agreement with the relative inertness of chromium(III) complexes.

The refined atomic coordinates of the three crystals are listed in Table 2. Selected bond distances and angles are collected in Table 3. The crystal structure of $[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n\cdot nH_2O$ (**1**) reveals a new type of scaffolding-like material with a unique neutral three-dimensional framework. The crystals belong to the centrosymmetric $P2_1/n$ space group. The Ba atoms are located on a general position, leading to two different crystallographic Cr atoms, which are involved in different types of bridges between the barium atoms. A labeled diagram of the environment of the Ba atoms is shown on Figure 1. The complexity of the structure arises from the simultaneous presence of three bridging modes of the oxalato groups. The two oxalato groups bound to Cr(1) exhibit two bridging modes, while those coordinated to Cr(2) are involved in only one type of bridging (Chart 1).

The free oxalato oxygen in the Cr(1) unit is intramolecularly hydrogen bonded to the aqua ligand (O···O distance = 2.776 Å) and also to a molecule of lattice water (O···O = 2.783 Å). The second lattice water molecule is hydrogen bonded to an oxalato O (distance = 2.918 Å) and to the aqua ligand (2.784 Å).

The barium ions have a coordination number of ten, being surrounded by nine oxalato oxygen atoms (Ba−O bonds range from 2.739(3) to 2.947(3) Å and are independent of the type of bonding) and one aqua ligand (2.801(3) Å). The Ba···Ba distance is quite short, 4.138(3) Å, and the center of inversion is located between the two Ba atoms, which can be described as forming a pillar. Each Ba atom is connected to two Cr(1) units almost in the same plane forming an infinite 2D chicken wire sheet (Figure 2). The Ba···Cr(1) distances are 5.974 and 6.236 Å. It is interesting to note that the Cr(1) units connecting the Ba atoms form a helix running along the *b* axis. All the Cr(1) atoms in one helix have the same chirality, and since the center of inversion is between the two Ba atoms (forming the pillar), the alternating helices within the chicken wire sheets have opposite chirality. One such helix is shown in bold printing on Figure 2. The sheets are linked together through the Ba pillars, where the two Ba atoms forming the pillar are connected by four oxalato bridges arising from four Cr(2) units. The four bridging Cr(2) units are at 107 and 73° to each other and form an elongated four-tipped star around the Ba···Ba pillar

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (Å^2 $\times$ 10^3)

atom	*x*	*y*	*z*	U_{eq}	atom	*x*	*y*	*z*	U_{eq}
$[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n \cdot nH_2O$ (**1**)									
Ba	4022(1)	5264(1)	491(1)	22(1)	C(4)	2911(2)	3299(3)	−1097(2)	28(1)
Cr(1)	3494(1)	8049(1)	3032(1)	24(1)	C(5)	2982(3)	3511(3)	1570(2)	33(1)
Cr(2)	2978(1)	1368(1)	−1686(1)	25(1)	C(6)	3219(3)	3896(3)	2497(2)	35(1)
O(1)	2816(2)	5804(2)	1345(2)	33(1)	C(7)	2678(2)	6380(2)	−1543(2)	28(1)
O(2)	3908(2)	7212(2)	993(2)	39(1)	C(8)	3415(2)	5939(2)	−1768(2)	26(1)
O(3)	4533(2)	3606(2)	−336(2)	30(1)	C(10)	4046(2)	10260(3)	3414(2)	32(1)
O(4)	2686(2)	4096(2)	−878(2)	39(1)	C(11)	4663(3)	11044(3)	3747(2)	40(1)
O(5)	2761(2)	6446(2)	−801(2)	40(1)	C(12)	5563(3)	10822(3)	4261(3)	45(1)
O(6)	4127(2)	5555(2)	−1190(2)	33(1)	C(13)	5825(3)	9829(3)	4453(2)	42(1)
O(7)	3529(2)	3599(2)	1231(2)	46(1)	C(14)	5177(2)	9064(3)	4110(2)	30(1)
O(8)	4909(2)	5504(3)	2274(2)	60(1)	C(15)	5368(2)	7988(3)	4298(2)	31(1)
O(9)	2936(2)	6761(2)	2479(2)	30(1)	C(16)	6207(3)	7617(3)	4846(3)	50(1)
O(10)	4032(2)	8037(2)	2183(1)	28(1)	C(17)	6301(3)	6577(3)	5006(3)	60(1)
O(11)	4087(2)	2142(2)	−1037(2)	28(1)	C(18)	5580(3)	5958(3)	4607(3)	55(1)
O(12)	2365(2)	2609(2)	−1572(2)	32(1)	C(19)	4747(3)	6358(3)	4057(3)	41(1)
O(13)	2816(2)	8097(2)	3776(2)	31(1)	C(20)	2677(3)	1246(3)	−22(2)	38(1)
O(14)	2446(2)	8826(2)	2263(2)	32(1)	C(21)	2851(3)	879(3)	793(2)	44(1)
O(15)	1805(2)	731(2)	−2240(1)	31(1)	C(22)	3396(3)	45(3)	1082(3)	43(1)
O(16)	3001(2)	1721(2)	−2795(1)	32(1)	C(23)	3747(3)	−423(3)	561(2)	35(1)
O(17)	3981(2)	4226(2)	2951(2)	55(1)	C(24)	3537(2)	−47(2)	−255(2)	26(1)
N(1)	4298(2)	9289(2)	3590(2)	27(1)	C(25)	3869(2)	−509(2)	−869(2)	27(1)
N(2)	4647(2)	7365(2)	3908(2)	30(1)	C(26)	4306(2)	−1435(3)	−731(2)	35(1)
N(3)	3018(2)	796(2)	−540(2)	28(1)	C(27)	4600(3)	−1802(3)	−1345(3)	40(1)
N(4)	3706(2)	39(2)	−1588(2)	27(1)	C(28)	4440(3)	−1243(3)	−2075(3)	42(1)
C(1)	3109(2)	6543(3)	1816(2)	26(1)	C(29)	3988(3)	−329(3)	−2177(2)	36(1)
C(2)	3738(2)	7313(2)	1632(2)	26(1)	Ow(1)	4366(3)	6815(4)	6403(4)	54(1)
C(3)	3943(2)	3015(2)	−789(2)	24(1)	Ow(2)	3400(4)	3725(4)	−3202(4)	59(1)
$[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (**2**)									
Mn	4628(2)	2606(1)	3758(1)	44(1)	C(4)	6761(9)	2109(7)	3120(3)	38(1)
Cr(1)	877(2)	2596(1)	5059(1)	36(1)	C(5)	11261(10)	3106(7)	3133(3)	37(1)
Cr(2)	8383(2)	2621(1)	2449(1)	34(1)	C(6)	11564(10)	2141(6)	2885(3)	37(1)
O(1)	4279(7)	3477(5)	4485(3)	54(1)	C(7)	−2305(9)	2149(7)	4643(4)	38(1)
O(2)	2952(7)	1690(5)	4057(3)	48(1)	C(8)	−2025(10)	3126(7)	4393(3)	38(1)
O(3)	4960(7)	3459(5)	3014(3)	52(1)	C(10)	6298(10)	992(7)	1848(4)	46(1)
O(4)	6339(7)	1719(5)	3459(2)	44(1)	C(11)	5436(10)	502(7)	1409(4)	56(1)
O(5)	2715(6)	3362(4)	4988(2)	41(1)	C(12)	5445(10)	891(7)	950(4)	58(1)
O(6)	1348(7)	1754(5)	4543(2)	40(1)	C(13)	6203(10)	1757(7)	930(4)	53(1)
O(7)	6518(6)	3379(4)	2508(2)	38(1)	C(14)	7057(9)	2218(6)	1384(3)	33(1)
O(8)	7850(7)	1740(4)	2935(2)	41(1)	C(15)	7937(9)	3147(7)	1402(3)	35(1)
O(9)	−1106(6)	1842(4)	4999(2)	38(1)	C(16)	8081(10)	3683(7)	986(4)	43(1)
O(10)	−567(7)	3468(4)	4570(2)	42(1)	C(17)	8941(10)	4543(7)	1058(4)	60(1)
O(11)	9835(7)	3447(5)	2968(2)	43(1)	C(18)	9675(10)	4885(7)	1539(4)	58(1)
O(12)	10352(7)	1848(5)	2514(2)	42(1)	C(19)	9479(10)	4361(7)	1939(4)	50(1)
O(13)	6351(7)	1756(5)	4502(3)	49(1)	C(20)	−132(11)	4234(7)	5647(4)	56(1)
O(14)	6895(7)	3513(4)	4056(2)	46(1)	C(21)	−172(11)	4741(7)	6081(4)	61(1)
O(15)	2354(7)	3500(5)	3464(2)	47(1)	C(22)	720(12)	4362(8)	6544(4)	68(1)
O(16)	2874(7)	1736(5)	3026(3)	55(1)	C(23)	1605(11)	3505(7)	6567(4)	58(1)
N(1)	7081(8)	1824(5)	1828(3)	35(1)	C(24)	1550(9)	3019(7)	6124(3)	39(1)
N(2)	8668(8)	3513(5)	1875(3)	30(1)	C(25)	2449(10)	2108(7)	6109(4)	42(1)
N(3)	721(8)	3389(5)	5670(3)	43(1)	C(26)	3366(10)	1611(7)	6531(4)	58(1)
N(4)	2269(8)	1757(5)	5638(3)	41(1)	C(27)	4180(10)	728(7)	6466(4)	62(1)
C(1)	3254(9)	3064(7)	4627(4)	40(1)	C(28)	4006(11)	386(8)	5992(4)	68(1)
C(2)	2479(9)	2088(7)	4379(3)	38(1)	C(29)	3011(11)	895(7)	5592(4)	54(1)
C(3)	6011(9)	3059(7)	2864(3)	38(1)					
$CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2 \cdot H_2O$ (**3**)									
Co	0	0	0	36(1)	C(2)	1525(5)	568(8)	1587(6)	25(3)
Cr	2589(1)	271(2)	3482(1)	27(1)	C(3)	2761(6)	2600(11)	4096(6)	37(3)
O(1)	−478(4)	828(6)	631(4)	52(3)	C(4)	1905(6)	2201(10)	3747(6)	37(3)
O(2)	1050(3)	1001(6)	796(4)	34(3)	C(5)	3371(6)	−302(10)	3040(7)	44(3)
O(3)	677(4)	−1133(6)	1227(4)	36(3)	C(6)	4482(6)	−675(10)	3221(7)	51(3)
O(4)	2184(3)	1022(6)	2250(4)	30(3)	C(7)	5008(6)	−1285(9)	4049(7)	40(3)
O(5)	1817(3)	−1029(6)	2672(4)	31(3)	C(8)	4793(6)	−1523(9)	4673(7)	36(3)
O(6)	1756(3)	1072(6)	3511(4)	37(3)	C(9)	4059(6)	−1128(9)	4422(6)	27(3)
O(7)	3193(3)	1721(6)	4117(4)	32(3)	C(10)	3760(5)	−1320(8)	5011(7)	26(3)
O(8)	2979(4)	3633(7)	4340(5)	53(3)	C(11)	4123(6)	−2028(9)	5802(7)	39(3)
O(9)	1436(4)	2914(7)	3711(5)	56(3)	C(12)	3753(6)	−2147(10)	6279(7)	44(3)
N(1)	3563(4)	−495(7)	3623(5)	26(3)	C(13)	3051(6)	−1533(9)	5955(7)	37(3)
N(2)	3065(4)	−705(7)	4703(5)	27(3)	C(14)	2744(6)	−808(9)	5191(7)	36(3)
C(1)	1305(6)	−645(8)	1831(7)	26(3)	OW	0	1302(14)	2500	97(4)

[a] U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(Figure 3), caused by the bridging mode exhibited by the oxalato ligands. The Ba pillars with the Cr(2) units form also an extended 2D structure. The Ba···Cr(2) distances are 6.132, 6.164, 6.252, and 6.587 Å. The Ba···Cr(2) planes are ap-

Table 3. Selected Bond Distances (Å) and Angles (deg)

$[BaCr_2(bipy)_2(C_2O_4)_4(H_2O)]_n \cdot nH_2O$ (**1**)							
Ba−O(1)	2.918(4)	Ba−O(2)	2.739(3)	Cr(1)−O(13)	1.961(3)	Cr(1)−O(14)	1.952(3)
Ba−O(3)	2.887(3)	Ba−O(4)	2.895(3)	Cr(1)−N(1)	2.063(3)	Cr(1)−N(2)	2.058(3)
Ba−O(5)	2.790(3)	Ba−O(6)	2.947(3)	Cr(2)−O(11)	1.959(3)	Cr(2)−O(12)	1.957(3)
Ba−O(7)	2.793(4)	Ba−O(8)	2.801(3)	Cr(2)−O(15)	1.977(3)	Cr(2)−O(16)	1.952(3)
Ba−O(3a)	2.845(3)	Ba−O(6a)	2.918(3)	Cr(2)−N(3)	2.063(3)	Cr(2)−N(4)	2.074(3)
Cr(1)−O(9)	1.976(3)	Cr(1)−O(10)	1.948(3)	Ba···Ba(a)	4.138(3)		
O(1)−Ba−O(2)	58.5(1)	O(1)−Ba−O(3)	142.7(1)	O(1)−Ba−O(3a)	129.4(1)	O(2)−Ba−O(3a)	72.0(1)
O(2)−Ba−O(3)	158.4(1)	O(1)−Ba−O(4)	96.2(1)	O(3)−Ba−O(3a)	87.6(1)	O(4)−Ba−O(3a)	124.8(1)
O(2)−Ba−O(4)	129.1(1)	O(3)−Ba−O(4)	57.7(1)	O(5)−Ba−O(3a)	89.5(1)	O(6)−Ba−O(3a)	58.9(1)
O(1)−Ba−O(5)	80.8(1)	O(2)−Ba−O(5)	66.6(1)	O(7)−Ba−O(3a)	146.8(1)	O(8)−Ba−O(3a)	87.7(1)
O(3)−Ba−O(5)	107.3(1)	O(4)−Ba−O(5)	66.2(1)	O(2)−Ba−O(6a)	113.8(1)	O(3)−Ba−O(6a)	58.7(1)
O(1)−Ba−O(6)	138.6(1)	O(2)−Ba−O(6)	102.4(1)	O(4)−Ba−O(6a)	115.6(1)	O(5)−Ba−O(6a)	145.5(1)
O(3)−Ba−O(6)	59.6(1)	O(4)−Ba−O(6)	66.4(1)	O(6)−Ba−O(6a)	90.2(1)	O(7)−Ba−O(6a)	86.9(1)
O(5)−Ba−O(6)	57.8(1)	O(1)−Ba−O(7)	67.2(1)	O(8)−Ba−O(6a)	66.9(1)	O(1)−Ba−O(6a)	130.5(1)
O(2)−Ba−O(7)	122.3(1)	O(3)−Ba−O(7)	78.8(1)	O(3a)−Ba−O(6a)	60.4(1)	Ba−O(1)−C(1)	111.2(2)
O(4)−Ba−O(7)	72.1(1)	O(5)−Ba−O(7)	123.3(1)	Ba−O(2)−C(2)	116.3(2)	Ba−O(3)−C(3)	119.4(2)
O(6)−Ba−O(7)	132.2(1)	O(1)−Ba−O(8)	65.6(1)	Ba−O(3)−Ba(a)	92.4(1)	C(3)−O(3)−Ba(a)	136.3(3)
O(2)−Ba−O(8)	68.0(1)	O(3)−Ba−O(8)	119.5(1)	Ba−O(4)−C(4)	119.5(2)	Ba−O(5)−C(7)	121.4(2)
O(4)−Ba−O(8)	145.3(1)	O(5)−Ba−O(8)	133.0(1)	Ba−O(6)−C(8)	115.0(3)	Ba−O(6)−Ba(a)	89.8(1)
O(6)−Ba−O(8)	146.2(1)	O(7)−Ba−O(8)	73.5(1)	C(8)−O(6)−Ba(a)	154.6(3)	Ba−O(7)−C(5)	131.7(2)
$[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (**2**)							
Mn−O(1)	2.430(8)	Mn−O(2)	2.244(7)	Cr(1)−O(9)	1.959(6)	Cr(1)−O(10)	1.944(6)
Mn−O(3)	2.457(8)	Mn−O(4)	2.245(7)	Cr(1)−N(3)	2.044(9)	Cr(1)−N(4)	2.040(7)
Mn−O(13)	2.444(6)	Mn−O(14)	2.251(6)	Cr(2)−O(7)	1.959(6)	Cr(2)−O(8)	1.953(7)
Mn−O(15)	2.245(6)	Mn−O(16)	2.446(7)	Cr(2)−O(11)	1.955(6)	Cr(2)−O(12)	1.960(6)
Cr(1)−O(5)	1.956(6)	Cr(1)−O(6)	1.962(7)	Cr(2)−N(1)	2.059(7)	Cr(2)−N(2)	2.068(8)
O(1)−Mn−O(2)	72.5(2)	O(1)−Mn−O(3)	123.5(2)	O(6)−Cr(1)−O(9)	90.5(3)	O(5)−Cr(1)−O(10)	89.3(3)
O(2)−Mn−O(3)	145.0(2)	O(1)−Mn−O(4)	145.3(2)	O(6)−Cr(1)−O(10)	93.7(3)	O(9)−Cr(1)−O(10)	83.4(2)
O(2)−Mn−O(4)	114.8(2)	O(3)−Mn−O(4)	71.2(2)	O(5)−Cr(1)−N(3)	93.9(3)	O(6)−Cr(1)−N(3)	171.0(3)
O(1)−Mn−O(13)	73.5(2)	O(2)−Mn−O(13)	74.4(2)	O(9)−Cr(1)−N(3)	93.8(3)	O(10)−Cr(1)−N(3)	94.6(3)
O(3)−Mn−O(13)	137.3(2)	O(4)−Mn−O(13)	76.2(2)	O(5)−Cr(1)−N(4)	93.5(3)	O(6)−Cr(1)−N(4)	93.2(3)
O(1)−Mn−O(14)	75.3(2)	O(2)−Mn−O(14)	138.7(2)	O(9)−Cr(1)−N(4)	94.6(3)	O(10)−Cr(1)−N(4)	172.8(3)
O(3)−Mn−O(14)	75.5(2)	O(4)−Mn−O(14)	79.7(2)	N(3)−Cr(1)−N(4)	78.5(3)	O(7)−Cr(2)−O(8)	83.4(3)
O(13)−Mn−O(14)	72.1(2)	O(1)−Mn−O(15)	74.5(2)	O(7)−Cr(2)−O(11)	90.6(3)	O(8)−Cr(2)−O(11)	93.7(3)
O(2)−Mn−O(15)	80.3(2)	O(3)−Mn−O(15)	75.8(2)	O(7)−Cr(2)−O(12)	170.3(3)	O(8)−Cr(2)−O(12)	89.7(3)
O(4)−Mn−O(15)	138.9(2)	O(13)−Mn−O(15)	143.9(3)	O(11)−Cr(2)−O(12)	83.1(3)	O(7)−Cr(2)−N(1)	94.6(3)
O(14)−Mn−O(15)	115.0(2)	O(1)−Mn−O(16)	136.2(2)	O(8)−Cr(2)−N(1)	94.8(3)	O(11)−Cr(2)−N(1)	170.6(3)
O(2)−Mn−O(16)	74.7(2)	O(3)−Mn−O(16)	73.7(2)	O(12)−Cr(2)−N(1)	92.8(3)	O(7)−Cr(2)−N(2)	93.2(3)
O(4)−Mn−O(16)	75.8(2)	O(13)−Mn−O(16)	123.7(2)	O(8)−Cr(2)−N(2)	172.9(2)	O(11)−Cr(2)−N(2)	92.5(3)
O(14)−Mn−O(16)	145.4(3)	O(15)−Mn−O(16)	71.9(2)	O(12)−Cr(2)−N(2)	94.4(3)	N(1)−Cr(2)−N(2)	79.3(3)
O(5)−Cr(1)−O(6)	82.9(3)	O(5)−Cr(1)−O(9)	169.8(3)				
$CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2 \cdot H_2O$ (**3**)							
Co−O(1)	2.057(9)	Co−O(2)	2.089(6)	O(3)−C(1)	1.226(10)	O(4)−C(2)	1.272(9)
Co−O(3)	2.155(6)	Cr−O(4)	1.977(7)	O(5)−C(1)	1.286(10)	O(6)−C(4)	1.299(13)
Cr−O(5)	2.002(6)	Cr−O(6)	1.951(8)	O(7)−C(3)	1.304(14)	O(8)−C(3)	1.215(14)
Cr−O(7)	1.941(6)	Cr−N(1)	2.053(9)	O(9)−C(4)	1.217(15)		
Cr−N(2)	2.058(8)	O(2)−C(2)	1.236(10)				
O(1)−Co−O(2)	92.0(3)	O(1)−Co−O(3)	88.2(3)	O(5)−Cr−O(7)	170.2(2)	O(5)−Cr−N(1)	96.2(3)
O(1)−Co−O(2a)	88.0(3)	O(1)−Co−O(3a)	91.8(3)	O(5)−Cr−N(2)	93.4(3)	O(6)−Cr−O(7)	83.8(3)
O(2)−Co−O(3)	79.7(2)	O(2)−Co−O(3a)	100.3(2)	O(6)−Cr−N(1)	172.8(3)	O(6)−Cr−N(2)	96.8(4)
O(4)−Cr−O(5)	82.7(3)	O(4)−Cr−O(6)	90.3(3)	O(7)−Cr−N(1)	90.9(3)	O(7)−Cr−N(2)	94.6(3)
O(4)−Cr−O(7)	90.0(3)	O(4)−Cr−N(1)	94.6(3)	N(1)−Cr−N(2)	78.7(4)		
O(4)−Cr−N(2)	171.9(3)	O(5)−Cr−O(6)	89.7(3)				

proximately perpendicular to the Ba···Cr(1) sheets, resulting in a unique and quite remarkable infinite three-dimensional material (Figure 4).

The crystal structure of the manganese compound is very different. The asymmetric unit consists of heterotrinuclear species of formula $MnCr_2(C_2O_4)_4(bipy)_2$. The coordination number of the manganese atom is 8, exhibiting a flattened square antiprism geometry. This high coordination number is in accordance with the fact that the high-spin d^5 configuration, with no crystal field stabilization energy, does not have a great preference for any particular stereochemistry. However, coordination numbers of 7 or 8 for Mn(II) are still unusual.[18] Four of the Mn−O bond distances vary from 2.244(7) to 2.251(6) Å, while four others are much longer, ranging from 2.430(8) to 2.457(8) Å. The longer bonds are equally distributed, two on top of the antiprism, two on the bottom and each oxalato ligand is bonded to Mn by a long and a short bond. All these values are higher than those found in $\{[PPh_4][MnCr(C_2O_4)_3]\}_n$ (average 2.132 Å), a two-dimensional network containing hexacoordinated Mn(II) bonded to three oxalato groups.[14] The chelate angles O−Mn−O angles range from 71.2(2) to 80.3(2)°, while the other angles are much larger (114.8(2)−145.4(3)°). Since all the chelates are formed from one atom at the top of the square antiprism and one at the bottom, the antiprism is quite flattened. The crystal consists of infinite heterobimetallic chains parallel to the *a* axis (Figure 5). Each chain is formed of diamond-shaped units sharing the manganese atoms, while the two other

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(18) (a) Hagen, K. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 764. (b) Andruh, M.; Hübner, K.; Noltemeyer, M.; Roesky, H. W. *Z. Naturforsch.* **1993**, *48B*, 591.

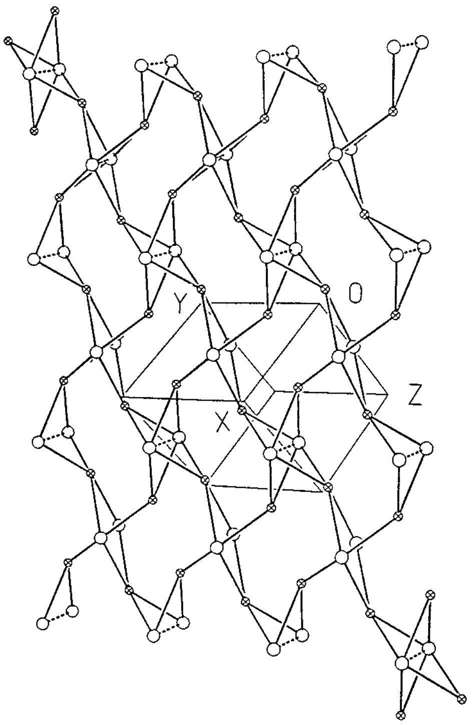

Figure 3. Connection of barium atoms in **1** through the Cr(2) bridging units.

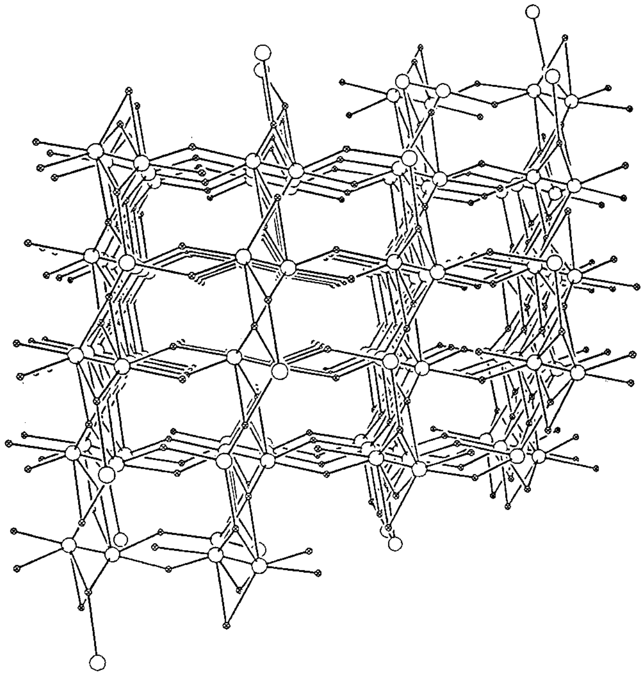

Figure 4. Perspective view of **1** along the *b* axis, showing only the barium and chromium atoms.

corners are occupied by chromium atoms. The Mn···Cr distances are: 5.533, 5.543, 5.555, and 5.573 Å. All the chromium centers in a chain have the same chirality, either Δ or Λ. Consequently, each chain is chiral and the centers of inversion are located between the chains. The square antiprism geometry of the manganese atoms results from similar chiralities of the chromium bricks. Molecular models have shown that it is not possible to obtain such a chain containing the two Cr diastereoisomers. The alternation of chains with opposite chirality and the interpenetration through stacking bipyridine molecules lead to achiral layers parallel to the *ac* plane. This compound nicely illustrates the role of the aromatic stacking interactions as a useful crystal engineering tool for increasing the dimensionality of the overall structure.[19]

The structure of $CoCr_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(bipy)_2(H_2O)_2 \cdot H_2O$ (**3**) consists of discrete {$CoCr_2$} entities (Figure 6). To the best of our knowledge, this is the first structurally characterized oxalato-bridged Cr(III)−Co(II) complex. The cobalt atom is located on an inversion center. The Cr···Co distance is 5.288 Å. There are two types of oxalato groups: bridging and terminal. The cobalt atom is surrounded by four oxygen atoms from the two bridging oxalato and two aqua ligands, exhibiting a distorted octahedral stereochemistry. The $Co-OH_2$ distances are 2.057(9) Å while the Co−O(oxalato) bonds are 2.089(6) and 2.155(6) Å. The chelate angles O(2)−Co−O(3) are 79.7(2)°, while the angles O(2)−Co−O(3a) are larger (100.3(2)°) than normal, as expected. The chromium sites have opposite chiralities. The Cr−O bond distances are slightly shorter for the terminal oxalato ligand (1.941(6) and 1.951(8) Å) than for the bridging ligand (1.977(7) and 2.002(6) Å), while the Cr−N bonds are 2.053(9) and 2.058(8) Å. The chelate angle N(1)−Cr−N(2) is 78.7(4)°, while the other two oxalato chelate angles are slightly larger (82.7(3) and 83.8(3)°). Therefore the chelate angle of the bridging oxalato ligand is slightly larger for the Cr(III) ring than for the Co(II) ring. The C−O bonds of the bridging ligand are significantly different, with average values of 1.279(10) Å for those bonded to Cr, and 1.231(10) Å for those bonded to Co. For comparison, the average C−O bond of the terminal oxalato ligand are 1.216(15) Å for the free bonds, and 1.302(14) Å for those bonded to Cr.

The molecule of solvent is located on a 2-fold axis. The crystal is stabilized by hydrogen bonds involving the water molecules and the oxalato ligands. The aqua ligands are intermolecularly hydrogen bonded to two O of the oxalato ligands with distances O(1)···O(8) = 2.694 Å) and O(1)···O(2) = 2.879 Å. The free molecule of water is hydrogen bonded to the aqua ligands (OW···O(1) = 2.847 Å) and to O(6) (OW···O(6) = 2.976 Å).

The diffuse reflectance spectra of the three compounds have been recorded. As expected, the characteristic d−d bands of the *cis*-$[CrN_2O_4]$ chromophore are observed in the spectra of all the compounds ($\nu_2 \approx 390$ nm, $\nu_1 = 520-540$ nm). The "ruby" lines[20] (spin-forbidden quartet-doublet transitions) are also observed for all three complexes, as low-intensity narrow bands located at ~710 and ~720 nm. Compound **3** shows an additional band near ~1000 nm which can be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition of the pseudo-octahedral high spin $[CoO_6]$ chromophore. The d−d bands of the $[MnO_8]$ chromophore, due to spin-forbidden transitions, are all too weak to be observed or are obscured by the d−d bands of chromium(III).

The first electronic transition for *cis*-$[Cr(III)N_2O_4]$ chromophores gives directly the value of the 10*Dq* parameter.[20] This value for the Cr(III) moiety in **2** is 18 400 cm^{-1}, slightly lower than the one found in **3** (19 000 cm^{-1}). A possible explanation for this difference could be the fact that a bridging oxalato group causes a weaker field than a terminal one. In compound **2**, both oxalato groups are bridging, whereas in **3** two types of binding (bridging and terminal) are present. The crystallographic results have shown that the Cr−O bonds of the terminal oxalate (average 1.946(7) Å) are slightly stronger than those of the bridging ligand (average 1.990(7) Å). The corresponding mean 10*Dq* value for the *cis*-$[Cr(III)N_2O_4]$ chromophores in the barium derivative is 19 160 cm^{-1}.

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(19) Wesolek, M.; Meyer, D.; Osborn, J. A.; De Cian, A.; Fischer, J.; Derory, A.; Legoll, P.; Drillon, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1592.

(20) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, Oxford, England, New York, and Toronto, Canada, 1984.

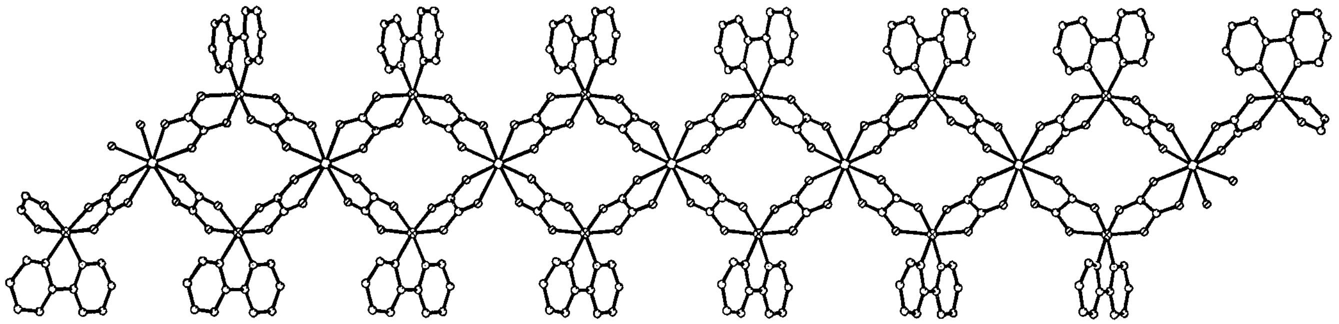

Figure 5. View of one enantiomeric chain in $[MnCr_2(bipy)_2(\mu\text{-}C_2O_4)_4]_n$ (**2**).

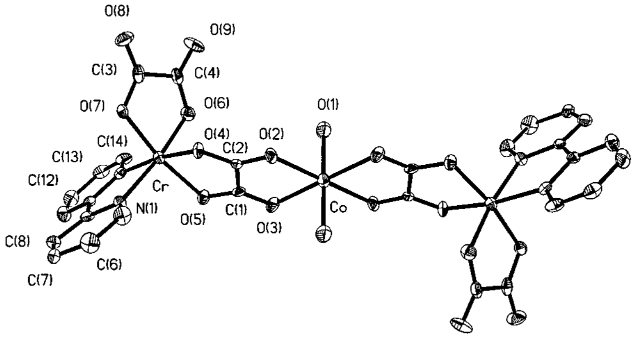

Figure 6. Labeled diagram of $CoCr_2(bipy)_2(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2\cdot H_2O$ (**3**) (the free water molecule and the H atoms are not shown).

The complete investigations of the magnetic and spectroscopic properties of these compounds and of other related compounds are underway, and the results will be published later. The structures described above show the versatility of the $[Cr(bipy)(C_2O_4)_2]^-$ building blocks to generate interesting self-assembling frameworks. The stereochemical requirements of the assembling ions (Ba(II), Mn(II), Co(II)) play a decisive role in the structure of the material. Moreover, some connectivity rules of different metal ions into supramolecular architectures[6–8] can be derived and used in designing new heterometallic systems with expected properties: (i) compounds of high dimensionality with the formula $Ln(II)\{Cr(bipy)(C_2O_4)_2\}_2(H_2O)_n$ may be anticipated when replacing barium ions with large bivalent rare-earth metal ions; (ii) discrete entities with low nuclearities will more likely crystallize by replacing barium ions with bivalent transition-metal ions which prefer an octahedral coordination geometry (for instance Ni(II), Fe(II), or Cu(II) ions).[21] The good aqueous solubility of complexes **2** and **3** allows for further chemistry. Actually, the $[Cr(bipy)(C_2O_4)_2]^-$ anion behaves like any other metal-free anion (*e.g.* SO_4^{2-}, NO_3^-, $MeCOO^-$, etc.) which can accomplish different coordination functions ("free", monodentate, bridging, etc.). Our MA_2 systems (M = Mn, Co; A = $[Cr(bipy)(C_2O_4)_2]^-$) can assume the role of a starting material in coordination chemistry, in the same way as other soluble M(II) salts.

Supporting Information Available: The supplementary material includes lists of crystallographic data and details of the X-ray diffraction studies, anisotropic temperature factors, bond distances and angles, and hydrogen coordinates (16 pages).

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(21) Rochon, F. D.; Andruh, M.; Melanson, R. To be submitted for publication.