Oxalato-Bridged [$Cu^{II}Cr^{III}$] and [$Mn^{II}Cr^{III}$] Binuclear Complexes: Synthesis, Crystal Structures, Magnetic and EPR Investigations

Gabriela Marinescu,[a,b] Diana Visinescu,[a,b] Andrei Cucos,[a] Marius Andruh,*[a]
Yves Journaux,*[c] Victor Kravtsov,[d] Yurii A. Simonov,[d] and Janusz Lipkowski[e]

Dedicated to Professor Herbert W. Roesky

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Two new heterobinuclear complexes, [(bipy)(C_2O_4)Cr(μ-C_2O_4)Cu(Hfsaaep)(H_2O)]·2H_2O (**1**) and [(phen)(C_2O_4)Cr(μ-C_2O_4)Mn(phen)$_2$(N_3)]·H_2O (**2**) have been obtained by using bis(oxalato)chromium(III) anions, [Cr(AA)(C_2O_4)$_2$]$^-$, as building blocks [AA = 2,2′-bipyridine (bipy); 1,10-phenanthroline (phen)]. The crystal structures of the two complexes have been solved. These complexes comprise neutral oxalato-bridged Cr^{III}–Cu^{II} and Cr^{III}–Mn^{II} units. The [Cr(AA)(C_2O_4)$_2$]$^-$ anion acts as a bidentate ligand toward Cu^{II} in compound **1** and as a monodentate ligand toward Mn^{II} in compound **2**. The copper(II) ion in **1** exhibits a slightly distorted square bipyramidal stereochemistry, with the aqua ligand and one of the bridging oxalato oxygen atoms disposed in the apical positions [Cu(1)–O(1w) = 2.360(3) Å and Cu(1)–O(4) = 2.504(2) Å]. The second bridging oxalato oxygen atom [Cu(1)–O(2) = 2.0747(18) Å] and the *N*,*N*,*O*-type Hfsaaep ligand are located in the basal plane. The distance between the Cr^{III} and Cu^{II} ions across the bridging oxalate unit is 5.506 Å. The Mn^{II} ion in compound **2** is hexacoordinate (two chelating phen ligands, one oxalato bridging oxygen, and one terminal azido group). The intermolecular $Cr^{III}\cdots Mn^{II}$ distance is 5.257 Å. The magnetic properties of the two complexes have been investigated. The magnetic coupling between Cr^{III} and Cu^{II} in **1** was found to be ferromagnetic ($J = +1.4$ cm^{-1}). The nature of the ground state ($S = 2$) has been further confirmed by plotting the magnetization-versus-field curve. An antiferromagnetic interaction was found between Cr^{III} and Mn^{II} in compound **2** ($J = -1.9$ cm^{-1}). The magnetization-versus-field curve indicates the occurrence of a crossover between the Zeeman components: $M_S = -1$ (ground state $S = 1$), $M_S = -2$, from the first excited state ($S = 2$), and $M_S = -3$, from the second excited state. The EPR spectra of the two compounds are discussed.

Introduction

The ability of the oxalato anion to generate homo- and heteropolynuclear complexes with various nuclearities or dimensionalities is well known.[1] This chemistry has been stimulated mainly by the interesting magnetic properties exhibited by such compounds.[2] A plethora of oxalato-bridged homopolynuclear complexes has been characterized so far. These compounds are generally obtained through reactions involving a cationic complex, with potentially free coordination sites, and the oxalate anion. The presence of an ancillary ligand in the coordination sphere of the metallic ion, other than the water molecules, prevents the formation of the insoluble oxalates, and, moreover, influences the nuclearity, as well as the topology, of the metallic centers. As far as the heterometallic complexes are concerned, their synthesis raises an important point: the one-pot procedure, that is, the reaction of two different metal complexes with the oxalate anion, most frequently leads to mixtures of compounds and it is, therefore, inappropriate. To overcome this difficulty, an alternative synthetic approach has been developed: it employs anionic oxalato complexes as ligands toward the second metal ion ("complexes as ligands"; "building-block approach"). Particularly useful for the design of heterometallic systems are homoleptic and heteroleptic anionic complexes of chromium(III) containing potentially bridging oxalato groups. These sys-

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[a] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest,
Str. Dumbrava Rosie nr. 23, 020464 Bucharest, Romania
E-mail: marius.andruh@dnt.ro
[b] Institute of Physical Chemistry "I. G. Murgulescu", Romanian Academy,
Splaiul Independentei 202, 060021 Bucharest, Romania
[c] Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université de Paris-Sud,
Bât. 420,
91405 Orsay, France
E-mail: jour@icmo.u-psud.fr
[d] Institute of Applied Physics, Academy of Sciences of Moldova, Academy str. 5, 2028 Chisinau, R. Moldova
[e] Institute of Physical Chemistry, Polish Academy of Sciences, Str. Kasprzaka 44/52, 01−224 Warsaw, Poland

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tems are relatively stable towards substitution reactions and allow a good control over the reaction products. Three types of mononuclear chromium(III) oxalato complexes have been employed as building-blocks in obtaining heteropolynuclear systems: mono-oxalato, [$Cr(salen)(C_2O_4)]^-$ [H_2salen = *N*,*N′*-ethylenebis(salicylideneimine)][3] and [$Cr(acac)_2(C_2O_4)]^-$ (Hacac = acetylacetone),[4] bis(oxalato), [$Cr(AA)(C_2O_4)_2]^-$ [AA = 2,2′-bipyridine (bipy),[5] 1,10-phenanthroline (phen),[6] 2,2′-bipyrimidine (bpym),[7] and 2,2′-dipyridylamine (dpa)[8]], and tris(oxalato), [$Cr(C_2O_4)_3]^{3-}$, species.[9] While the homoleptic complex, [$Cr(C_2O_4)_3]^{3-}$, with three potentially bridging groups, is extensively used to generate two- or three-dimensional networks, the mono-oxalato species are appropriate for the synthesis of heterobinuclear complexes.

In a series of papers, it has been shown that bis-oxalato complexes of chromium(III), [$Cr(AA)(C_2O_4)_2]^-$ (AA = 2,2′-bipy, 1,10-phen, bpym, dpa), are extremely versatile building-blocks for the synthesis of heteropolynuclear complexes having a rich variety of structures.[5–8] The self-assembly processes between these species and mono- or dipositive hydrated cations led to two series of heteropolynuclear complexes: [$M^ICr(bipy)(C_2O_4)_2(H_2O)_x]\cdot yH_2O$ (M = K, Na, Ag) and [$M^{II}Cr_2(bipy)_2(C_2O_4)_4(H_2O)_n]\cdot mH_2O$ (M = Ba, Mn, Co, Ni, Cu). Within each series, completely different structures have been obtained, according to the coordination algorithm of the assembling cation. We have also shown that the structures of the heterometallic complexes can be further influenced by using ancillary ligands attached to the assembling cation. For example, the reaction between Mn^{2+}(aq), 2,2′-bipyridine, and [$Cr(phen)(C_2O_4)_2]^-$ in the presence of sodium oxalate led to a tetranuclear [$Cr^{III}-C_2O_4-Mn^{II}-C_2O_4$-$Mn^{II}-C_2O_4-Cr^{III}$] complex.[6]

In this paper we report two new heterobinuclear complexes, which have been obtained by using bis-oxalato building blocks and ancillary ligands attached to the second metal ion: [(bipy)(C_2O_4)Cr(μ-C_2O_4)Cu(Hfsaaep)(H_2O)]·$2H_2O$ {H_2fsaaep = 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid} and [(phen)(C_2O_4)Cr(μ-C_2O_4)Mn(phen)$_2$(N_3)]·H_2O.

Results and Discussion

The complexes reported here have been obtained through reactions involving the [$Cr(AA)(C_2O_4)_2]^-$ building blocks and cationic complex species of Cu^{II} and Mn^{II}.

The [CuCr] complex has been synthesized by reacting the bis-oxalato chromium precursor, [$NaCr(bipy)(C_2O_4)_2(H_2O)]\cdot 2H_2O$[5c] with the binuclear chloro-bridged copper(II) complex, [Cu(Hfsaaep)Cl]$_2$ {H_2fsaaep is a Schiff base ligand derived from 3-formylsalicylic acid: 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid}.[10] The chloro anion in the {Cu(hfsaaep)Cl} moiety was substituted by the [$Cr(bipy)(C_2O_4)_2]^-$ unit, resulting in a neutral [CuCr] heterobinuclear complex, **1**.

In the attempt to synthesize a $Mn^{II}_2Cr^{III}_2$ tetranuclear complex, with two different bridges connecting the metal ions (oxalato and azido), we have obtained a binuclear complex having an oxalato bridge between the two metal ions and a terminal azido ligand bound to manganese: [(phen)(C_2O_4)Cr(μ-C_2O_4)Mn(phen)$_2$(N_3)]·H_2O (**2**). The phen:Mn^{II} molar ratio has been chosen to be 1:1 to prevent the formation of the tris-chelated manganese complex.

Description of the Structures

[(Bipy)(C_2O_4)Cr(μ-C_2O_4)Cu(Hfsaaep)(H_2O)]·$2H_2O$ (1): The structure of **1** consists of neutral [CuCr] binuclear entities and uncoordinated water molecules (Figure 1). Crystal data, data collection parameters, and structure refinement details are given in Table 3. Selected bond lengths and angles are collected in Table 1. The [$Cr(bipy)(C_2O_4)_2]^-$ ion acts as a bidentate ligand toward the copper(II) ion, that is, one oxalato group acts simultaneously as a bidentate ligand toward chromium and copper. The distance between the Cr^{III} and Cu^{II} ions across the bridging oxalate is 5.506 Å. This distance is longer than those found in the trinuclear complex [$CuCr_2(bipy)_2(C_2O_4)_4(H_2O)_2]\cdot 1.5H_2O$ (Cu···Cr = 5.328 Å), where the two metal ions are bridged by a bis-chelating oxalato group,[5a] and in the binuclear [(bipy)$_2$Cu(μ-C_2O_4)Cr(C_2O_4)$_2$]$^+$ species (5.056 Å).[11] We recall that in the last compound,[11] the oxalato group behaves as a monodentate ligand toward the copper and its bridging mode differs from that found in complex **1**. The copper atom is coordinated by two oxygen atoms arising from the oxalato bridge, one phenolic oxygen and two nitrogen atoms arising from the organic ligand (one nitrogen atom from the azomethine group, and the other one from the pyridyl ring), and one aqua ligand. The coordination polyhedron of the copper atom may be described as a distorted square-based bipyramid. The apical positions are occupied by the aqua ligand [Cu(1)−O(1w) = 2.360(3) Å] and one oxygen atom from the bridging oxalato group, Cu(1)−O(4) = 2.504(2) Å. The phenolic group of the Schiff base ligand is deprotonated, while the carboxylic group is protonated. The strong intramolecular hydrogen bond,

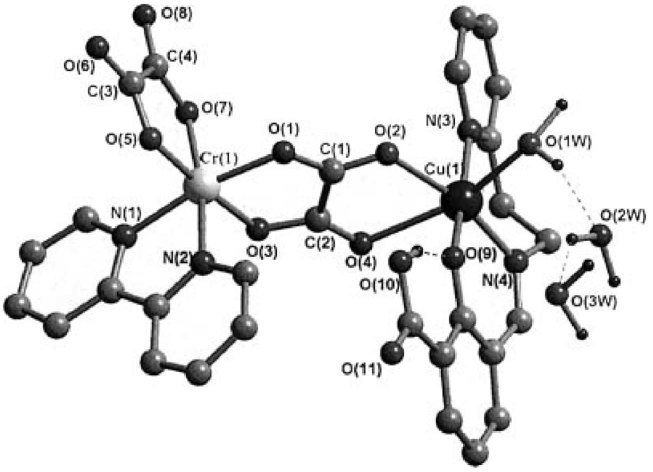

Figure 1. Perspective view of a molecule in crystal **1**, along with the atom numbering scheme

Table 1. Selected bond lengths (Å) and angles (°)

1		2	
Cu(1)−O(9)	1.9282(18)	Mn(1)−N(7)	2.1592(19)
Cu(1)−N(4)	1.971(2)	Mn(1)−O(4)	2.1883(15)
Cu(1)−N(3)	2.015(2)	Mn(1)−N(5)	2.2385(18)
Cu(1)−O(2)	2.0747(18)	Mn(1)−N(4)	2.2424(18)
Cu(1)−O(1 W)	2.360(3)	Mn(1)−N(3)	2.2937(18)
Cu(1)−O(4)	2.504(2)	Mn(1)−N(6)	2.2944(18)
Cr(1)−O(5)	1.939(2)	Cr(1)−O(5)	1.9300(15)
Cr(1)−O(7)	1.941(2)	Cr(1)−O(7)	1.9081(14)
Cr(1)−O(3)	1.9720(17)	Cr(1)−O(3)	1.9466(14)
Cr(1)−O(1)	1.9786(18)	Cr(1)−O(1)	2.0064(15)
Cr(1)−N(1)	2.057(2)	Cr(1)−N(1)	2.1344(18)
Cr(1)−N(2)	2.064(2)	Cr(1)−N(2)	2.0435(17)
		N(7)−N(8)	1.198(3)
		N(8)−N(9)	1.207(3)
O(9)−Cu(1)−N(4)	91.88(8)	N(7)−Mn(1)−O(4)	89.92(7)
O(9)−Cu(1)−N(3)	171.18(9)	N(7)−Mn(1)−N(5)	167.52(7)
N(4)−Cu(1)−N(3)	95.60(9)	O(4)−Mn(1)−N(5)	88.13(6)
O(9)−Cu(1)−O(2)	83.16(8)	N(7)−Mn(1)−N(4)	91.50(7)
N(4)−Cu(1)−O(2)	166.08(8)	O(4)−Mn(1)−N(4)	156.85(6)
N(3)−Cu(1)−O(2)	90.58(8)	N(5)−Mn(1)−N(4)	95.13(6)
O(9)−Cu(1)−O(1 W)	83.99(9)	N(7)−Mn(1)−N(3)	90.72(7)
N(4)−Cu(1)−O(1 W)	106.63(10)	O(4)−Mn(1)−N(3)	81.83(6)
N(3)−Cu(1)−O(1 W)	89.38(9)	N(5)−Mn(1)−N(3)	101.20(6)
O(2)−Cu(1)−O(1 W)	85.84(9)	N(4)−Mn(1)−N(3)	75.05(7)
O(9)−Cu(1)−O(4)	91.01(8)	N(7)−Mn(1)−N(6)	96.35(7)
N(4)−Cu(1)−O(4)	92.91(8)	O(4)−Mn(1)−N(6)	111.54(6)
N(3)−Cu(1)−O(4)	93.27(8)	N(5)−Mn(1)−N(6)	72.98(6)
O(2)−Cu(1)−O(4)	74.25(6)	N(4)−Mn(1)−N(6)	91.26(7)
O(1 W)−Cu(1)−O(4)	159.93(9)	N(3)−Mn(1)−N(6)	164.78(7)
O(5)−Cr(1)−O(7)	83.66(10)	O(5)−Cr(1)−O(7)	84.65(6)
O(5)−Cr(1)−O(3)	176.23(8)	O(5)−Cr(1)−O(3)	173.92(6)
O(7)−Cr(1)−O(3)	94.75(9)	O(7)−Cr(1)−O(3)	90.57(6)
O(5)−Cr(1)−O(1)	94.21(8)	O(5)−Cr(1)−O(1)	93.96(6)
O(7)−Cr(1)−O(1)	92.56(9)	O(7)−Cr(1)−O(1)	94.03(6)
O(3)−Cr(1)−O(1)	82.43(7)	O(3)−Cr(1)−O(1)	82.60(6)
O(5)−Cr(1)−N(1)	92.96(9)	O(5)−Cr(1)−N(1)	89.43(6)
O(7)−Cr(1)−N(1)	95.34(9)	O(7)−Cr(1)−N(1)	93.63(7)
O(3)−Cr(1)−N(1)	90.59(8)	O(3)−Cr(1)−N(1)	94.63(6)
O(1)−Cr(1)−N(1)	169.87(8)	O(1)−Cr(1)−N(1)	171.88(6)
O(5)−Cr(1)−N(2)	90.37(9)	O(5)−Cr(1)−N(2)	89.11(7)
O(7)−Cr(1)−N(2)	171.55(9)	O(7)−Cr(1)−N(2)	170.92(7)
O(3)−Cr(1)−N(2)	91.56(8)	O(3)−Cr(1)−N(2)	96.05(6)
O(1)−Cr(1)−N(2)	93.84(8)	O(1)−Cr(1)−N(2)	92.97(7)
N(1)−Cr(1)−N(2)	78.95(8)	N(1)−Cr(1)−N(2)	79.69(7)

O(10)−H···O(9) (Table 2), binds this moieties and contributes to their planar arrangement.

The chromium atom is coordinated by two bipy nitrogen and four oxygen atoms, adopting a distorted octahedral geometry. The short bites of the bipy [78.95(8)°] and oxalato ligands [82.43(7) and 83.65(10)°] are the main factors responsible for the distortion of the $[CrN_2O_4]$ chromophore. The Cr−N bond lengths [2.057(2) and 2.064(2) Å] are somewhat longer than the Cr−O(ox) ones (Table 1). The Cr−O bond lengths are slightly shorter for the terminal oxalato ligand [1.939(2) and 1.941(2) Å] than for the bridging one [1.9720(17) and 1.9786(18) Å]. Both Cu^{II} and Cr^{III} ions reside close to the plane of the bridging oxalato ligand and deviate from it by 0.209(3) and 0.018(3) Å, respectively.

The heterobinuclear [CuCr] entities are interconnected through hydrogen bonding interactions involving the two water molecules, the oxygen atoms from the terminal oxalato group, and the aqua ligand coordinated to copper, which results in infinite chains (Figure 2). The distances associated with these interactions are summarized in Table 2. The chains are interconnected in a layer parallel to the (*ab*) crystallographic plane by week π−π stacking interactions (3.57 Å) between pyridine moieties of Hfsaaep and bifurcated O(3 W)···O(7), O(3 W)···O(8) hydrogen bonds (Table 2). The water molecules and hydrophilic fragments of **1** dwell inside such layers, while the hydrophobic bipy entities point outside. The bipy ligands from neighboring layers are arranged in a parallel mode and mutually intercalate with alternating spacings of 3.44 and 3.59 Å (Figure 3). These π−π stacking interactions between the bipy ligands act as a 2-D zipper and join the layers in the direction of the *c* axis (Figure 3).

$[(Phen)(C_2O_4)Cr(\mu\text{-}C_2O_4)Mn(phen)_2(N_3)]\cdot H_2O$ (2): The crystal structure of **2** consists of neutral [MnCr] heterobinuclear entities and crystallization water molecules. The $[Cr(phen)(C_2O_4)_2]^-$ ion acts as a monodentate ligand through an oxalato oxygen atom toward the $[Mn(phen)_2(N_3)]^+$ moiety (Figure 4). The intramolecular Cr···Mn distance is 5.257 Å. Selected bond lengths and angles are gathered in Table 1. The parameters of the hydrogen bonds are listed in Table 2. The manganese(II) ion is hexacoordinated by four nitrogen atoms arising from the phen molecules, one from the azido ion, and by one oxygen atom from the bridging oxalato group. The Mn(1)−N(phen) distances are in the range 2.2385(18)−2.2944(18) Å, while the Mn(1)−N(azido) bond is shorter [2.1592(19) Å]. The Mn−O(oxalato) distance is 2.1883(15) Å. The azido group is almost linear (the N−N−N angle is 178.4(2)°]. The connection between Mn and the azido ligand is bent: the value of the Mn(1)−N(7)−N(8) angle is 117.20(15)°. The bite angles of the phen ligands are 75.05(7) and 72.98(6)°.

As far as the chromium environment is concerned, it exhibits the same characteristic features observed for other compounds containing the $\{Cr(phen)(C_2O_4)_2\}$ moiety.[6] The dihedral angles between the plane of the 1,10-phenanthroline ligand and the planes of the bridging and terminal oxalato groups are 71.72(3)° and 85.13(4)°, respectively. The dihedral angle between oxalato groups is 85.07(4)°.

The 1,10-phenanthroline ligands associated with N(1)/N(2) and N(5)/N(6) atoms are almost parallel in complex **2** and partially overlap. The corresponding dihedral angle [12.51(6)°] and the interplanar spacing of 3.44−4.01 Å in the overlapped area suggest the possibility of intramolecular π−π stacking interactions, which seems to be an interesting characteristic feature of this complex.

Several Mn^{II}−Cr^{III} oxalato-bridged complexes are known.[5a,6,9] To the best of our knowledge, this Mn^{II}−(μ-oxalato)−Cr^{III} binuclear complex is the first to be structurally characterized.

The intermolecular π−π stacking interactions play an important role in controlling the packing of compound **2** in the crystal. The phenanthroline ligands coordinated to the

Table 2. Hydrogen bonds in the structures of **1** and **2**

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	Angle (^{d}−H···A)
1				
O(10)−H(10)···O(9)	0.815(19)	1.72(2)	2.494(3)	159(4)
O(1 W)−H(1 W1)···O(2 W)	0.87(5)	1.89(5)	2.723(4)	160(5)
O(1 W)−H(2 W1)···O(8)#1	1.09(5)	2.04(5)	3.016(4)	146(4)
O(2 W)−H(1 W2)···O(3 W)	1.05(2)	1.97(5)	2.886(6)	143(5)
O(2 W)−H(2 W2)···O(6)#2	1.03(2)	2.06(4)	2.965(5)	145(5)
O(3 W)−H(1 W3)···O(6)#2	1.04(2)	1.93(5)	2.799(5)	139(6)
O(3 W)−H(2 W3)···O(8)#3	1.05(2)	2.42(5)	3.257(5)	136(5)
O(3 W)−H(2 W3)···O(7)#3	1.05(2)	2.36(5)	3.093(5)	126(4)
2				
O(1 W)−H(1 W)···N(9)	0.83(4)	2.16(4)	2.975(3)	164(4)
O(1 W)−H(2 W)···O(2)	0.84(4)	2.15(4)	2.939(3)	155(4)

Symmetry transformations used to generate equivalent atoms:
(#1) − *x* + *1*, −*y*, −*z*; (#2) *x*, *y* + *1*, z; (#3) *x* − *1*, *y* + *1*, *z*.

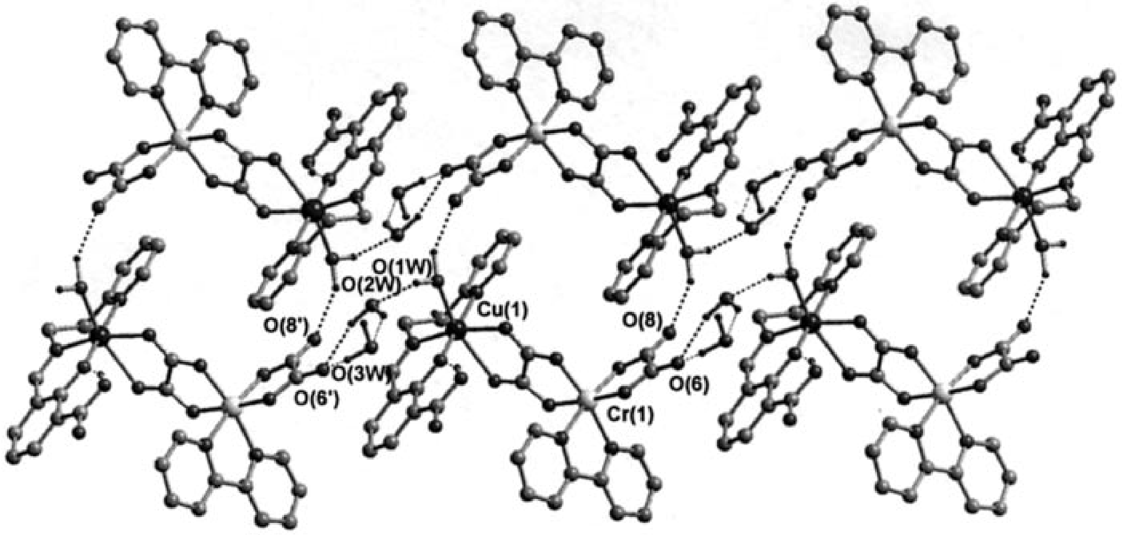

Figure 2. Hydrogen bonding interactions established between the [CuCr] units and the uncoordinated water molecules in crystal **1**

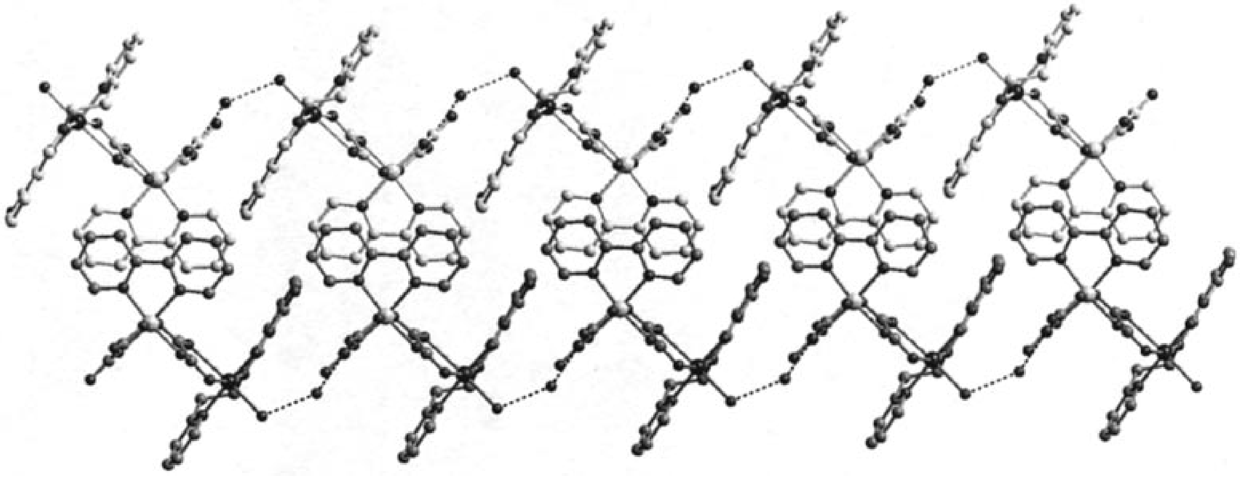

Figure 3. Packing diagram for compound **1**, showing the π−π stacking interactions between the bipy ligands

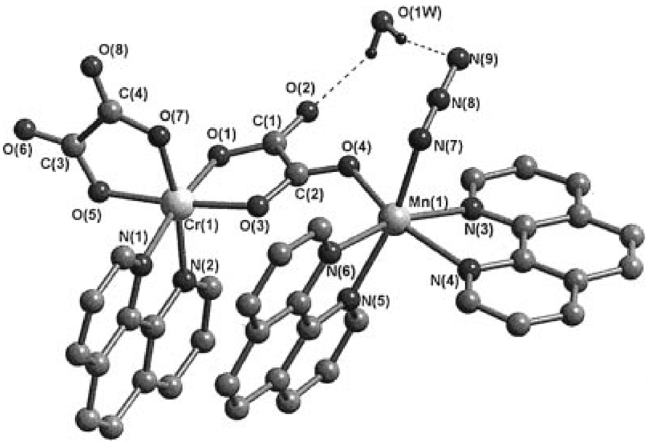

Figure 4. Molecular structure of the binuclear complex in crystal **2**

manganese ions, associated with the N(3) and N(4) atoms, are partially overlapped. The small separation between these phen molecules (3.38 Å), which are related by a center of symmetry, indicate the occurrence of strong π−π interactions (Figure 5). In addition, the phen molecules coordinated to chromium and manganese atoms belonging to two different binuclear units also interact through π−π stacking. The interplanar spacing in this case is in the range of 3.17−4.14 Å. The convolution of the stacking interactions between the phenanthroline molecules coordinated to Mn and Cr atoms results in well-defined layers, which parallel the (*bc*) crystallographic plane (Figure 5). The repeating motif consists of four [MnCr] binuclear units that are interconnected through the aromatic−aromatic interactions established between six phenanthroline moieties. The water molecules occupy the space between the layers.

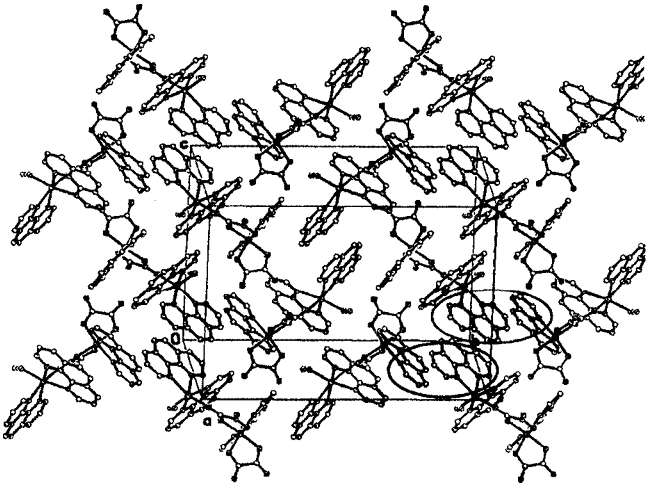

Figure 5. Packing diagram for compound **2**; the two pairs of phen ligands that interact through intermolecular π−π stacking are indicated by circles

Magnetic Properties

The cryomagnetic properties of compounds **1** and **2** deserve to be deeply investigated for two special reasons. (i) Although the bridging mode of the oxalato ligand in compound **1** has been observed with several other [CuCr] complexes,[11−13] the axial coordination of the oxalato oxygen atom to the square-pyramidal copper(II) ion in such compounds leads to the lack of any exchange interaction between Cr^{III} and Cu^{II} ions. In compound **1**, one of the oxygen atoms arising from the oxalato group is coordinated in the basal plane of the coordination polyhedron of copper and can efficiently mediate the exchange interaction between the $d_{x^2-y^2}$ magnetic orbital of Cu^{II} and the magnetic orbitals of Cr^{III}. (ii) The low nuclearity of compound **2** makes it a good candidate for studying the magnetic interactions in Mn^{II}−(μ-oxalato)−Cr^{III} complexes, because the data on such compounds is rather scarce. The plots of $\chi_M T$ versus T for compounds **1** and **2** are given in Figures 6 and 7.

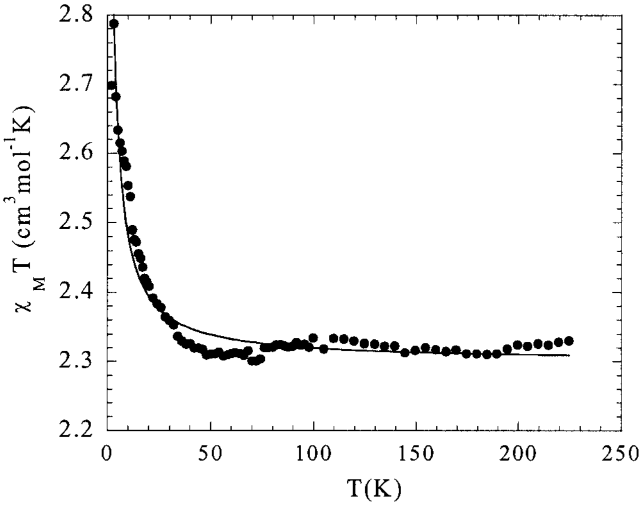

Figure 6. Plots of $\chi_M T$ vs. T for compound **1**; the solid line represents the curve of best fit

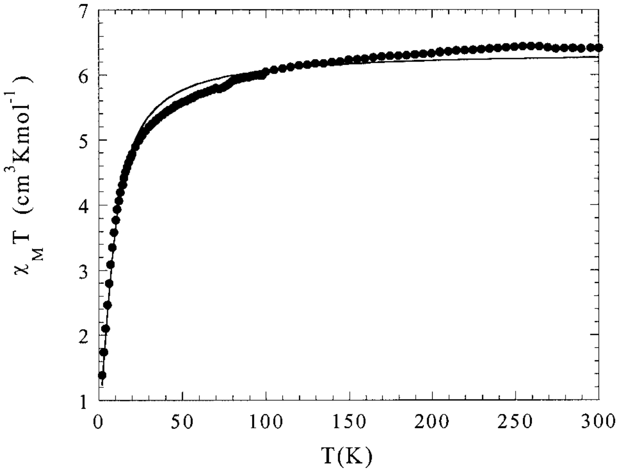

Figure 7. Plots of $\chi_M T$ vs. T for compound **2**; the solid line represents the curve of best fit

At 225 K the value of the $\chi_M T$ product for compound **1** is equal to 2.33 cm^3·mol^{-1}K, which corresponds to the expected value for a spin doublet and spin quadruplet isolated magnetically (the calculated value is 2.25 $cm^3 \cdot mol^{-1}K$, assuming, in a first approximation, $g_{Cu} = g_{Cr} = 2$). By decreasing the temperature, $\chi_M T$ remains constant down to 50 K and then it increases, reaching a value of 2.7 $cm^3 \cdot mol^{-1}K$ at 2 K. This behavior indicates a ferromagnetic intramolecular interaction. For the Cu^{II} ($S = 1/2$)$-$$Cr^{III}$ ($S = 3/2$) system, the energies of the low-lying spin states are obtained by using the isotropic spin Hamiltonian: $\boldsymbol{H} = -J\boldsymbol{S}_{Cu}\mathbf{S}_{Cr}$, which leads to Equation (1) describing the temperature dependence of the $\chi_M T$ product, where $g_1 = (5g_{Cr} - g_{Cu})/4$ and $g_2 = (3g_{Cr} + g_{Cu})/4$.

$$\chi_M T = \frac{2N\beta^2}{k}\frac{5g_2^2 + g_1^2 e^{-2J/kT}}{5 + 3e^{-2J/kT}} \tag{1}$$

Least-squares fitting to the data leads to the following values: $J = +1.4$ cm^{-1}; $g_{Cr} = 1.99$ (fixed); $g_{Cu} = 2.1$, with $R = 2.2 \times 10^{-4}$ {R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obsd.}(i) - (\chi_M T)_{calcd.}(i)]^2/\Sigma_i[(\chi_M T)_{obsd.}(i)]^2$}.

To confirm the nature of the ground state, we investigated the variation of the magnetization, M, with respect to the field, at 2 K (Figure 8). The $M = f(H)$ curve closely follows the Brillouin function for a $S = 2$ system, and it is situated above the Brillouin function constructed for two independent $S = 1/2$ and $S = 3/2$ systems.

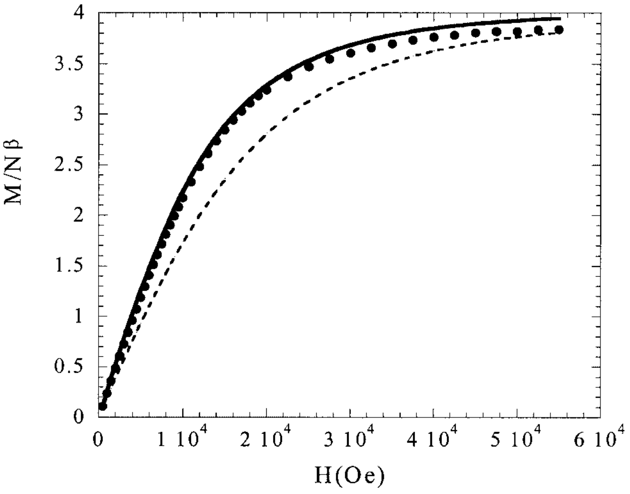

Figure 8. Magnetization-vs.-field curve for compound **1**; solid line: the Brillouin function for $S = 2$; dashed line: Brillouin functions for $S = 1/2$ and $S = 3/2$

Most of the μ-oxalato $Cr^{III}$$-$$Cu^{II}$ complexes reported in the literature[5a,11,13] show either no or antiferromagnetic interactions. Only **1** and the Cu^{II}-(μ-oxalato)-Cr^{III} complexes reported by Okawa et al.[3b][3c] show a ferromagnetic interaction. For the latter two compounds, the copper $d_{x^2-y^2}$ orbital interacts with the σ-type orbitals of the oxalato group; on the other hand, the t_{2g} metallic orbitals of the Cr^{III} ions interact with the π-type orbitals of the oxalato bridge, leading to the classical example of ferromagnetic coupling due to the strict orthogonality of the magnetic orbitals. For the other $Cr^{III}$$-$$Cu^{II}$ complexes described in the literature, the symmetry conditions are not fulfilled and the interaction is antiferromagnetic.

The value of the $\chi_M T$ product at room temperature for compound **2** is 6.41 $cm^3 \cdot mol^{-1}K$. This value corresponds to the one expected for two uncoupled Mn^{II} and Cr^{III} ions. Upon decreasing the temperature, $\chi_M T$ decreases, reaching a value of 1.38 $cm^3 \cdot mol^{-1}K$ at 2 K. This behavior indicates the occurrence of an antiferromagnetic coupling between Mn^{II} and Cr^{III}. The data were fitted using Equation (2), which gives the temperature dependence of the $\chi_M T$ product:

$$\chi_M T = \frac{2N\beta^2 g^2}{k}\frac{e^{-21J/4kT} + 5e^{-13J/4kT} + 14e^{-J/4kT} + 30e^{15J/4kT}}{3e^{-21J/4kT} + 5e^{-13J/4kT} + 7e^{-J/4kT} + 9e^{15J/4kT}} \tag{2}$$

Least-squares fitting leads to the following values: $J = -1.9$ cm^{-1} and $g = 2.01$, with $R = 5.6 \times 10^{-4}$. This value of the J parameter is close to the one found for a tetranuclear μ-oxalato $Mn^{II}$$-$$Cr^{III}$ complex ($J = -1.1$ cm^{-1}).[6]

The magnetization curve, $M = f(H)$, for compound **2**, recorded at 2 K (Figure 9), looks unusual: when increasing the field, instead of reaching the saturation corresponding to $S = 1$, M increases continuously to a value of 5 $N\beta$ at 6 T. This behavior can be explained by the crossover between the Zeeman components $M_S = -1$ (ground state $S = 1$), $M_S = -2$, from the first excited state ($S = 2$), and $M_S = -3$ from the second excited state (Figure 10). The crossover of the first two states occurs at $H = -2J/g\beta$, while that of the $M_S = -1$ and $M_S = -3$ occurs at $H = -3J/g\beta$. Least-squares fitting of the $M = f(H)$ curve, using a model taking into account all of the levels, leads to the following parameters: $J = -1.6$ cm^{-1} and $g = 1.99$. These values are in reasonable agreement with those found by the fitting of the magnetic susceptibility data.

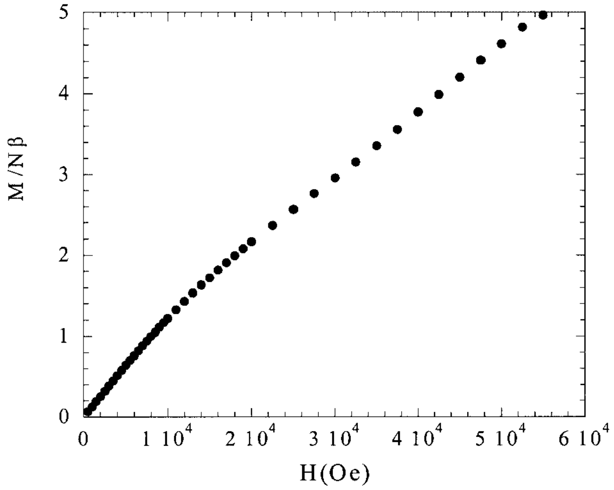

Figure 9. Magnetization-vs.-field curve for compound **2**

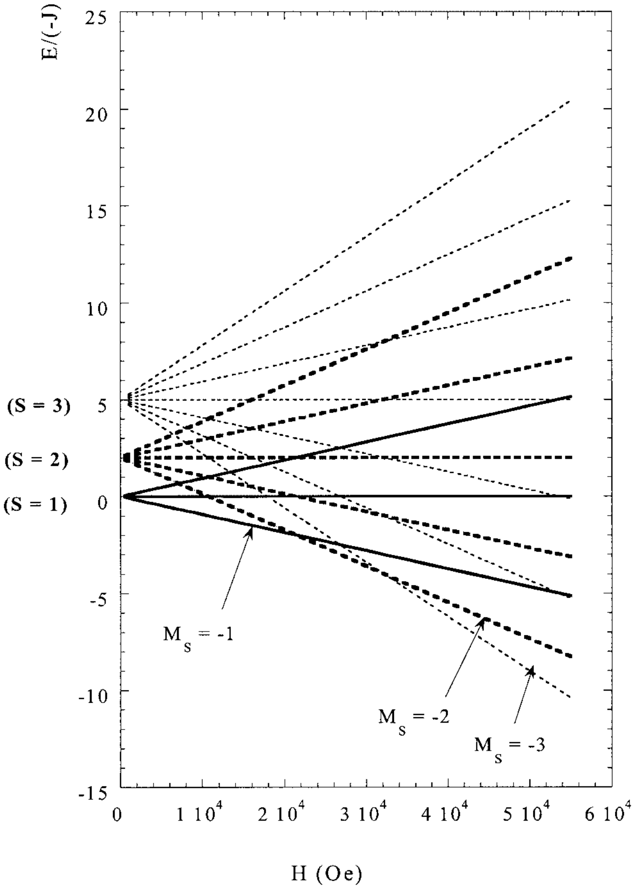

Figure 10. Energies of the lowest spin states ($S = 1$, $S = 2$, $S = 3$) as a function of the applied magnetic field for compound **2**

EPR Spectra

The X-band powder spectra for **1** were recorded between 5 K and room temperature. The spectrum at 5 K, depicted in Figure 11, exhibits features between 0 and 1100 mT. Upon increasing the temperature, the resonances detected at 5 K vary in their relative intensities, especially the signal around 320 mT, which, in contrast to the others signals, increases in intensity between 5 and 10 K. This behavior clearly indicates that this signal belongs to the excited triplet state. The EPR spectra of **1** are difficult to interpret because, even at 5 K, there are two EPR-active states and only one signal can be attributed without doubt to a precise state (triplet state). Moreover, these two states are separated only by 3.8 cm^{-1} and the strong exchange limit condition ($J >> D$) is probably not fulfilled and additional transitions could be observed. Nevertheless we tried to treat the triplet and the quintet states independently and, in a first step, we also assumed that the anisotropy of the two states comes from the zero field splitting of the chromium ion. Starting from the line at 320 mT, we tried to determine the D_1 value of the triplet state. Several possibilities can be considered to label this signal. The presence of high-field transition precludes the solutions that correspond to a small D_1 value. Furthermore, solutions with D_1 values > 1 cm^{-1} do not give satisfactory simulation. Only the solutions with D_1 values in the range from 0.6 to 0.68 cm^{-1} are able to reproduce the lines in the low- and high-field regions. The former value corresponds to axial symmetry and the latter to the rhombic one. The D_1 value of the triplet state is expected to be three-times larger than the D_2 value of the quintet state:[14a]

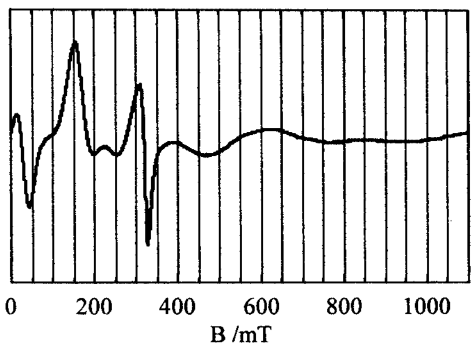

Figure 11. EPR spectrum for compound **1** at 5 K

$$D_1 = 3D_2 = \frac{3D_{Cr}}{2} \tag{3}$$

From this formula, we calculate the D_2 value using the previous range for the D_1 values and simulate the spectra of the quintet state. In all cases, the combined spectra of the simulated quintet- and triplet-states spectra do not correspond to the experimental one. In particular, the intense lines at 45 and 150 mT are not well reproduced. Only D_2 values close to 0.15 cm^{-1} are able to reproduce these lines. This finding clearly indicates that there is another contribution to the D values of the two states, namely the anisotropic exchange interaction. Taking this interaction into account, D_2 and D_1 are given by the following relationships:[14a]

$$D_1 = \frac{3D_{cr}}{2} - \frac{D_{CuCr}}{4} \tag{4}$$

$$D_2 = \frac{D_{Cr}}{2} + \frac{D_{CuCr}}{4} \tag{5}$$

These relationships show that the anisotropic exchange provides opposite contributions to the quintet and the triplet states, and this feature could explain why $D_2 < D_1/3$. Because of the large number of parameters to optimize (g_{Cu}, g_{Cr}, D_{Cr}, and D_{CuCr} tensors, and their orientations) we obtained only a rough agreement between our simulation and the experimental spectrum with D_{Cr} and D_{CuCr} values around 0.4 cm^{-1} and -0.15 cm^{-1}, respectively. Nevertheless, it seems impossible to get a good simulation without a noticeable value for the anisotropic exchange. It is well established that the anisotropic exchange in a pair is proportional to the exchange interaction in an excited state of the pair, where one ion is in its fundamental state and the other in an excited state.[14b,15] In **1**, because of the relative orientation of the magnetic orbitals in the excited state, for which one electron of the chromium ion is in the d_{xy} orbital, there is a strong overlap between this orbital and the $d_{x^2-y^2}$ of the copper ion. This large antiferromagnetic interaction in an excited state of **1** leads to an important value of the anisotropic exchange in **1**.

The X-band powder spectra for **2** were recorded at several temperatures. The spectrum at 5 K exhibits a broad band at $g = 2.0$ and features of lower intensity between 0 and 1180 mT. An increase of the temperature does not induce any noticeable changes in the spectrum. The absence of thermal variation precludes any thorough analysis of the X-band powder spectra of **2**. The compounds discussed here illustrate once more that $[Cr(AA)(C_2O_4)_2]^-$ ions are very useful and versatile building blocks in designing heterometallic complexes.

Experimental Section

General Remarks: All the chemicals used for the present study were purchased from commercial sources and used without further purification. $Na[Cr(bipy)(C_2O_4)_2(H_2O)]\cdot 2H_2O$ and $Ba[Cr_2(phen)_2(C_2O_4)_4(H_2O)]\cdot H_2O$ were prepared as outlined in the literature.[5c,16] $[Cu(Hfsaaep)Cl]_2$ has been obtained as already reported.[17]

$[(Bipy)(C_2O_4)Cr(\mu\text{-}C_2O_4)Cu(Hfsaaep)(H_2O)]\cdot 2H_2O$ (1): A solution of $[Cu(Hfsaaep)Cl]_2$ (1 mmol) in methanol/water (1:1, 10 mL) was added to an aqueous solution of $Na[Cr(bipy)(C_2O_4)_2(H_2O)]\cdot 2H_2O$ (1 mmol, 10 mL). Slow evaporation of the resultant solution led to dark-blue single crystals of $[Cu(Hfsaaep)(H_2O)Cr(bipy)(C_2O_4)_2]\cdot 2H_2O$. IR data (KBr): $\tilde{\nu}$ = 3474 m, 3113 w, 1691 s, 1680 vs, 1639 s, 1565 m, 1447 m, 1395 s, 1383 s, 1324 w, 1238 m, 1027 w, 889 w, 810 m, 771 m, 667 w, 547 m cm^{-1}.

$[(Phen)(C_2O_4)Cr(\mu\text{-}C_2O_4)Mn(phen)_2(N_3)]\cdot H_2O$ (2): A suspension of $[BaCr_2(phen)_2(C_2O_4)_4(H_2O)]\cdot H_2O$ (1 mmol) in water (50 mL) was reacted with a stoichiometric amount of $MnSO_4\cdot 4H_2O$ (1 mmol) dissolved in water (10 mL). The resulting mixture was stirred for 4 h to promote the complete precipitation of barium sulfate, which was removed by filtration. An ethanolic solution of 1,10-phenanthroline (2 mmol, 10 mL), an aqueous solution of $MnCl_2\cdot 4H_2O$ (1 mmol, 10 mL), and aqueous sodium azide (2 mmol, 10 mL) were added successively to the red solution. Slow evaporation of the resultant solution led to orange-red single crystals of $[(phen)(C_2O_4)Cr(\mu\text{-}C_2O_4)Mn(phen)_2(N_3)]\cdot H_2O$. IR data (KBr): $\tilde{\nu}$ = 3479 m, 2038 s, 1705 s, 1679 vs, 1647 s, 1512 m, 1404 s, 1346 s, 1250 s, 1213 w, 1140 w, 1101 w, 851 m, 802 m, 724 s, 640 w, 482 m, 401 w cm^{-1}.

Physical Techniques: The IR spectra (KBr pellets) were recorded with a BIO-RAD FTS 135 spectrophotometer. UV/Vis spectra (diffuse reflectance technique) were recorded using a UV4 (Unicam) spectrophotometer and employing MgO as a standard. Magnetic measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for the diamagnetic contributions of the sample holder. EPR spectra were recorded using a Bruker Elexsys 500 spectrometer at the X band.

X-ray Crystallographic Study: X-Ray diffraction measurements were performed at room temperature and at 150 K for **1** and **2**, respectively, with a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation and using φ and ω scans. Crystal data, data collection parameters, and structure refinement details are given in Table 3. Lattice parameters were determined by the least-squares method from 8414 (**1**) and 5830 (**2**) reflections. The structures were solved by direct methods and refined by full-matrix, least-squares techniques based on F^2. The non-hydrogen atoms were refined using anisotropic displacement parameters. In all cases, hydrogen atoms on carbon atoms were calculated and allowed to ride. The other hydrogen atoms were found from difference Fourier maps and refined isotropically. Calculations were performed using SHELX-97 crystallographic software package.[18]

Table 3. Crystallographic data, details of data collection, and structure refinement parameters for compounds **1** and **2**

Compound	1	2
Chemical formula	$C_{29}H_{27}CrCuN_4O_{14}$	$C_{40}H_{26}CrMnN_9O_9$
M (g mol^{-1})	771.09	883.64
Temperature (K)	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.9198(2)	9.84960(10)
b (Å)	12.8396(4)	23.4248(3)
c (Å)	16.6094(6)	16.2377(2)
α (°)	87.755(2)	90
β (°)	76.679(2)	106.1134(6)
γ (°)	73.419(19)	90
V (Å^3)	1574.54(8)	3599.26(7)
Z	2	4
$D_{calcd.}$ (g·cm^{-3})	1.626	1.631
μ (mm^{-1})	1.098	0.727
F(000)	788	1800
Goodness-of-fit on F^2	1.063	0.974
Final $R1$, wR_2 [$I > 2\sigma(I)$]	0.0461, 0.1104	0.0419, 0.0881
$R1$, wR_2 (all data)	0.0601, 0.1166	0.0626, 0.0943
Largest diff. peak and hole (e Å^{-3})	0.461 and −0.558	0.286 and −0.464

CCDC-206308 (for **1**) and -206309 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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