



First binuclear Cr(III)–Mn(III) oxalato-bridged complexes: Synthesis, crystal structures and magnetic properties

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ABSTRACT

Two Cr(III)–Mn(III) binuclear complexes, with the general formula $\{[Mn(H_2O)(valen)]\{Cr(AA)-(C_2O_4)_2\} \cdot 3H_2O$, have been obtained by assembling $[Mn((H_2O)(CH_3CN)(valen))]^+$ and $[Cr(AA)(C_2O_4)_2]^-$ ions [H_2valen is a bicompartamental Schiff-base proligand, resulting from the 2:1 condensation of 3-methoxy-salicylaldehyde with ethylenediamine; AA = 2,2'-bipyridine (bipy) **1**; 1,10-phenanthroline (phen) **2**]. In the two compounds the $[Cr(AA)(C_2O_4)_2]^-$ ions coordinate through one oxalato oxygen atom into one apical position of the manganese(III) ions, which exhibit an elongated octahedral stereochemistry. The other apical position is occupied by an aqua ligand. The intramolecular distances between the metal centers are 5.329 and 5.442 Å, for **1** and **2**, respectively. The packing of the molecules in the crystal (the interactions at the supramolecular level) are governed by the self-complementarity of the $\{Mn(valen)(H_2O)\}$ moieties. The aqua ligand of one moiety is hydrogen bonded to the oxygen atoms from the $\{O_2O_2\}$ compartment of a second complex yielding head-to-tail dimeric species. The magnetic properties of the two complexes have been investigated and reveal weak antiferromagnetic interactions mediated by the oxalato bridge ($2J = -2.12$, and -2.02 cm^{-1} for **1** and **2**, respectively). The zero-field-splitting effects for the two metal ions have been taken into account.

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1. Introduction

Heterometallic complexes, combining the peculiarities of different paramagnetic metal ions, are particularly interesting in the field of molecular magnetism [1]. Several synthetic strategies are currently employed in order to obtain heterometal complexes with various nuclearities/dimensionalities/spin topologies: (1) the use of compartmental ligands; (2) the building-block approach (complexes as ligands); (3) one-pot reactions, by mixing together the two metal ions as well as the bridging ligand. The first approach, relying upon polytopic ligands with dissymmetrical compartments, is particularly useful for obtaining oligonuclear complexes. The second one, consisting of self-assembly processes involving anionic building-blocks (complexes with potentially bridging ligands) and complex cations with accessible coordination sites, can lead either to discrete polymeric entities or to coordination polymers. The third approach is more delicate, since mixtures of homometallic polynuclear complexes can be formed.

The most representative building-blocks in designing heterometallic systems are: (a) bis-oxamato metal(II) complexes (M^{II} = copper, nickel, zinc) [2]; (b) tris-oxalato complexes [3]; (c)

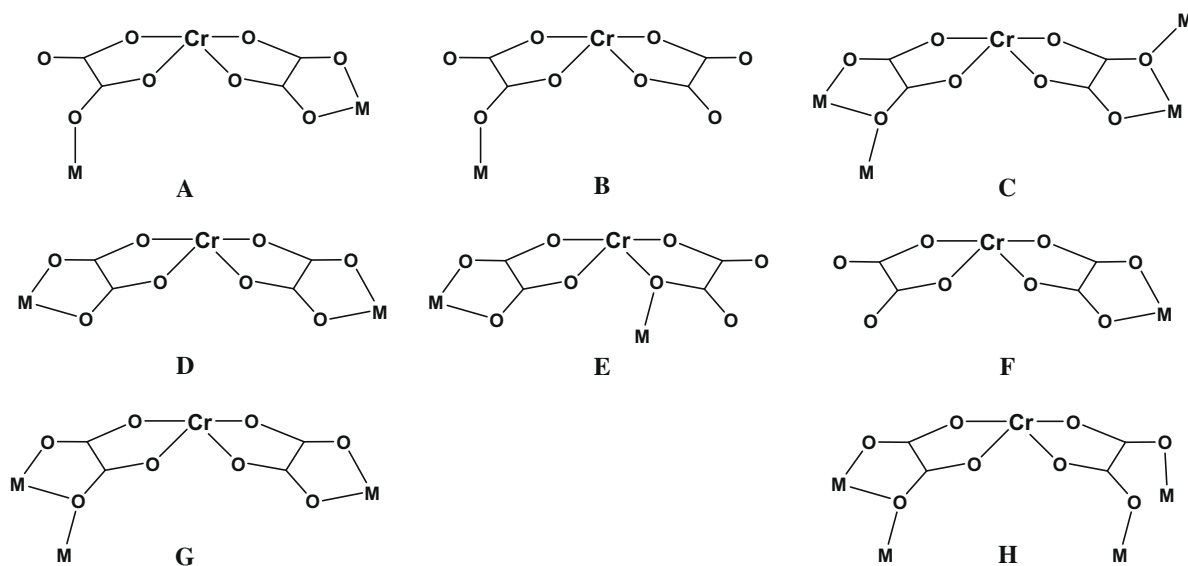
poly-cyano-complexes (both homo- and heteroleptic) [4]. As a general synthetic rule, coordination polymers are obtained by employing hydrated assembling cations, while discrete heterometallic entities are obtained by blocking several coordination sites of the assembling cations with ancillary ligands.

In most cases, the synthesis of heterometal oxalato-bridged complexes succeeds by following the building-block approach. Particularly useful for the design of such systems are homoleptic and heteroleptic anionic complexes of chromium(III) containing potentially bridging oxalato groups. They are relatively stable toward 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)) [5] and $[Cr(acac)_2(C_2O_4)]^-$ ($Hacac =$ acetylacetonate) [6], bis-oxalato, $[Cr(AA)(C_2O_4)_2]^-$ ($AA =$ 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2'-bipyrimidine (bpym), 2,2'-dipyridylamine (dpa) [7], and tris-oxalato, $[Cr(C_2O_4)_3]^{3-}$, species [8]. The homoleptic complex, $[Cr(C_2O_4)_3]^{3-}$, with three potentially bridging groups, is used to generate two- or three-dimensional networks, while the mono-oxalato species are appropriate for the synthesis of heterobinuclear complexes.

In a series of papers, we have shown that bis-oxalato complexes of chromium(III), $[Cr(AA)(C_2O_4)_2]^-$ ($AA =$ 2,2-bipy, 1,10-phen, as

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Scheme 1.

well as other diamines, such as dipyridylamine, 2,2'-bipyrimidine), are extremely versatile tectons for the synthesis of heteropolynuclear complexes [7]. They exhibit various coordination modes toward the second metal ion. Those already observed experimentally are depicted in Scheme 1. We also have shown that the auxiliary ligands attached to the assembling cations play a crucial role in the self-assembly process [7].

Manganese(III) complexes with salen type ligands are valuable starting materials for obtaining heterometallic Mn(III)–M(II/III) complexes [9]. The related ligands obtained from *o*-vanillin (H_2 valen being the simplest case) are largely used to obtain heterometal complexes, especially 3d–4f [10]. Others and we have shown that the second compartment, $O_2O'_2$, when it is not occupied by a second metal ion, can act as a hydrogen bond acceptor, directing the packing of the molecules in the crystal [11].

Here we present the first oxalato-bridged Mn(III)–Cr(III) complexes, which are obtained by employing $[Cr(AA)(C_2O_4)_2]^-$ building-blocks. As assembling cation we employ a manganese(III) complex, $[Mn(valen)(H_2O)(CH_3CN)]^+$ (H_2 valen is a bicompartamental Schiff-base proligand, resulting from the 2:1 condensation of 3-methoxysalicylaldehyde with ethylenediamine).

2. Experimental

2.1. Synthesis

The manganese precursor, $[Mn(valen)(H_2O)(CH_3CN)](ClO_4) \cdot CH_3CN$, has been obtained as already reported [11c]. The two chromium precursors were synthesized as described in previous papers [7c,d].

The two Mn(III)–Cr(III) compounds, $\{[Mn(H_2O)(valen)]\{Cr(bipy)(C_2O_4)_2\} \cdot 3H_2O$ **1** and $\{[Mn(H_2O)(valen)]\{Cr(phen)(C_2O_4)_2\} \cdot 3H_2O$ **2**, have been synthesized by the same procedure to a solution of $[Mn(valen)(H_2O)(CH_3CN)](ClO_4) \cdot CH_3CN$ (0.05 mmol) in 20 mL 1:1 CH_3CN/H_2O mixture, were added 20 mL solution of $AsPh_4[Cr(ox)_2(AA)]$ (0.05 mmol in 1:1 CH_3CN/H_2O mixture). The resulting brown solution was stirred for about 1.5 h and then filtered. The slow evaporation of the filtrate, at room temperature, yielded black crystals, suitable for X-ray diffraction. IR data (KBr, cm^{-1}): Compound **1**: 3413, 2926, 2854, 1719, 1680, 1620, 1551, 1468, 1439, 1398, 1358, 1302, 1254, 1220, 850, 807, 739, 723, 550. Compound **2**: 3415, 2927, 2853, 1711, 1684, 1645, 1620,

1552, 1468, 1439, 1398, 1358, 1302, 1254, 1220, 850, 807, 739, 723, 550.

2.2. Physical measurements

The IR spectra were recorded on KBr pellets with a Bio-Rad FTS 135 spectrophotometer in the 4000–400 cm^{-1} range. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 1.95–300 K temperature range in a 1000 Gauss applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.

2.3. X-ray crystallography

X-ray diffraction measurements were performed on Oxford Diffraction XCALIBUR diffractometer for **1**, and on a STOE IPDS II diffractometer for **2**, both operating with a $Mo K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) X-ray tube with a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package.

3. Results and discussion

3.1. Crystal structures

The two new Mn(III)–Cr(III) complexes, $\{[Mn(H_2O)(valen)]\{Cr(AA)(C_2O_4)_2\} \cdot 3H_2O$, have been obtained by reacting $[Mn(valen)(H_2O)(CH_3CN)](ClO_4) \cdot CH_3CN$ with $AsPh_4[Cr(AA)(C_2O_4)_2]$ ($AA = 2,2'$ bipyridine (bipy) **1**; 1,10-phenanthroline (phen) **2**). During the assembling process, the anionic chromium complex replaces the acetonitrile molecule coordinated into the apical position of the Mn(III) ion. Since their molecular structures are quite similar, they will be discussed together Table 1.

The crystallographic investigation of the two compounds reveals neutral binuclear $\{[Mn(H_2O)(valen)]\{Cr(AA)(C_2O_4)_2\} \cdot 3H_2O$ species along with crystallization water molecules. The $[Cr(AA)(C_2O_4)_2]^-$ ion acts as a monodentate ligand through an oxalato oxygen atom toward the $\{Mn(valen)(H_2O)\}$ moiety (Scheme 1 A, Fig. 1). The intramolecular Cr...Mn distances are as follows 5.329

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