

# Influence of the counterion on the coordinating properties of (2,2'-bipyridyl)bis(oxalato)chromate(III) anion: crystal structures and magnetic properties of $\text{AsPh}_4[\text{Cr}(\text{bipy})(\text{ox})_2]\cdot\text{H}_2\text{O}$ and $[\text{NaCr}(\text{bipy})(\text{ox})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$

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Two new chromium(III)-containing complexes of formula  $\text{AsPh}_4[\text{Cr}(\text{bipy})(\text{ox})_2]\cdot\text{H}_2\text{O}$  **1** and  $[\text{NaCr}(\text{bipy})(\text{ox})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  **2** (bipy = 2,2'-bipyridine and ox = oxalate dianion) have been synthesized and characterized by single-crystal X-ray diffraction. The structure of **1** consists of discrete  $[\text{Cr}(\text{bipy})(\text{ox})_2]^-$  mononuclear anions, tetraphenylarsonium cations and uncoordinated water molecules. The structure of **2** reveals a novel two-dimensional framework which is made up of oxalato-bridged bimetallic  $\text{Cr}^{\text{III}}-\text{Na}^{\text{I}}$  helical chains which are interconnected through centrosymmetric  $\text{Na}_2\text{O}_2$  units. Within the chain, a regular alternation of the metal ions is observed, the oxalate group acting as a bis(chelating) ligand. In addition to this coordination mode, two oxalates each act as monodentate ligands towards a sodium atom of a neighbouring chain thus leading to a sheetlike polymeric structure. The chromium environment is distorted octahedral in both complexes: two nitrogen atoms from a bidentate bipy ligand and four oxygen atoms from either two chelating (**1**) or two bis(chelating) (**2**) oxalate groups build the coordination polyhedron around the chromium atom. The Cr–N bond lengths [values in the ranges 2.077(3)–2.057(3) (**1**) and 2.067(4)–2.058(4) Å (**2**)] are somewhat longer than the Cr–O ones [values in the ranges 1.960(2)–1.946(2) (**1**) and 1.968(3)–1.949(3) Å (**2**)]. The sodium atom in **2** is also six-coordinated: a coordinated water molecule [2.371(5) and 2.325(4) Å for Na(1)–O(17) and Na(2)–O(18), respectively] and five oxygens from three oxalate groups [values of the Na–O (ox) bonds in the ranges 2.511(4)–2.331(4) and 2.481(4)–2.364(4) Å around Na(1) and Na(2), respectively] build a distorted octahedral  $\text{NaO}_6$  environment. The intralayer chromium–sodium and sodium–sodium distances through bridging oxalate in **2** vary in the ranges 5.657(4)–5.579(2) and 3.534(3)–3.497(4) Å, respectively. Variable-temperature magnetic susceptibility measurements of **1** and **2** reveal the occurrence of very weak antiferromagnetic interactions together with zero-field splitting effects in both compounds. The use of the  $[\text{Cr}(\text{bipy})(\text{ox})_2]^-$  unit as a ligand towards different univalent and divalent metal ions aimed at designing new heterobimetallic systems is analysed and discussed in the light of available structural data.

The adoption of the bis(chelating) coordination mode of the oxalato ligand (hereafter noted ox) in its metal complexes together with its remarkable ability to mediate magnetic interactions between paramagnetic centres which are bridged by it (intramolecular metal–metal separation larger than 5 Å) are the main factors responsible for the intensive magnetostructural investigations concerning the oxalato-bridged compounds.<sup>1–11</sup> From a synthetic viewpoint, the main difficulty to obtain discrete homometallic oxalato-bridged species is to avoid the formation of the very insoluble one-dimensional compounds. The use of suitable blocking ligands has been proved to be the best strategy in designing oxalato-bridged homodinuclear species  $\text{M}(\text{ox})\text{M}$  (M being a transition-metal ion). However, this is not an appropriate method to produce discrete oxalato-bridged heterometallic compounds,  $\text{M}(\text{ox})\text{M}'$ . In this case, the main problem the synthetic chemists are faced with is to avoid the formation of a mixture of the two homometallic  $[\text{M}(\text{ox})\text{M}]$  and  $[\text{M}'(\text{ox})\text{M}']$  species. This is easily done by using a stable mononuclear complex ligand which can function as a ligand to a second metal ion. Inert oxalato-containing chromium(III) complexes such as  $[\text{Cr}(\text{salen})(\text{ox})]^-$  [ $\text{H}_2\text{salen}$  = bis(salicylidene)-

ethylenediamine and  $[\text{Cr}(\text{ox})_3]^{3-}$  have proven to be suitable precursors in designing heterobimetallic di-<sup>12</sup> and tetra-nuclear<sup>13</sup> compounds as well as two-<sup>14–18</sup> and three-dimensional<sup>19,20</sup> multiproperty systems.

In this work we focus on the use of the bis(chelating) (2,2'-bipyridyl)bis(oxalato)chromate(III) anion as a building block in designing novel heterobimetallic supramolecular systems. The preparation, structural characterization and magnetic properties of the mononuclear compound  $\text{AsPh}_4[\text{Cr}(\text{bipy})(\text{ox})_2]\cdot\text{H}_2\text{O}$  **1** as well as that of the unprecedented sheetlike polymer of formula  $[\text{NaCr}(\text{bipy})(\text{ox})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  **2** are presented in this contribution.

## Experimental

### Materials

Chromium(III) chloride hexahydrate, 2,2'-bipyridine (bipy), sodium oxalate and tetraphenylarsonium chloride monohydrate were purchased from commercial sources and used as received. The complex  $\text{K}[\text{Cr}(\text{bipy})(\text{ox})_2]\cdot 4\text{H}_2\text{O}$  was synthesized

according to ref. 21. Elemental analysis (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain).

### Preparations

**AsPh<sub>4</sub>[Cr(bipy)(ox)<sub>2</sub>]-H<sub>2</sub>O 1.** An aqueous suspension (80 cm<sup>3</sup>) containing stoichiometric amounts of CrCl<sub>3</sub>·6H<sub>2</sub>O (2 mmol) and bipy (2 mmol) was refluxed during half an hour under continuous stirring. Na<sub>2</sub>ox (4 mmol) dissolved in the minimum amount of water was added to the resulting warm green solution and refluxing was continued until the solution turned red-violet (*ca.* 1 h). This solution was filtered and mixed with a concentrated aqueous solution of tetraphenylarsonium chloride (2 mmol). Compound **1** separates as a crystalline pink solid on standing at room temperature. It was filtered off, washed with the minimum amount of cold ethanol and diethyl ether and kept over calcium chloride. Hexagonal plates of **1** which were suitable for X-ray diffraction were obtained by slow evaporation of the remaining diluted solution (Found: C, 58.05; H, 3.75; N, 3.49. Calc. for C<sub>38</sub>H<sub>30</sub>AsCrN<sub>2</sub>O<sub>9</sub>: C, 58.11; H, 3.82; N, 3.57%). An alternative method which requires the previous synthesis of the green complex Cr(bipy)Cl<sub>3</sub>·dmf<sup>21</sup> and its reaction with potassium oxalate to yield the compound K[Cr(bipy)(ox)<sub>2</sub>]-4H<sub>2</sub>O can also be used. The exchange of the potassium cation by the tetraphenylarsonium one can be done in aqueous solution, the yield being quantitative, because of the lower solubility of the chromium complex as a tetraphenylarsonium salt in water.

**[NaCr(bipy)(ox)<sub>2</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O 2.** This compound was obtained as red parallelepipeds by slow evaporation of aqueous solutions (100 cm<sup>3</sup>) containing stoichiometric amounts of CrCl<sub>3</sub>·6H<sub>2</sub>O (2 mmol), bipy (2 mmol) and Na<sub>2</sub>ox (4 mmol) which were previously refluxed under stirring for 2 h. Because of the great solubility of **2** in water, crystals were formed when most of the solution was evaporated. Yield *ca.* 70% (Found: C, 36.38; H, 2.95; N, 5.97. Calc. for C<sub>14</sub>H<sub>14</sub>CrN<sub>2</sub>NaO<sub>11</sub>: C, 36.46; H, 3.04; N, 6.07%).

The most significant difference between the infrared spectra of the complexes **1** and **2** is the presence of two sharp and medium intensity peaks at 760 and 750 cm<sup>-1</sup> in the IR spectra of the former which correspond to the out-of-plane CH bending vibrations of the phenyl rings of the tetraphenylarsonium cation. In the 3500 cm<sup>-1</sup> region, a sharp and medium intensity doublet occurs in **1** (3560 and 3510 cm<sup>-1</sup>) whereas a strong and broad peak centered at 3450 cm<sup>-1</sup> is observed in **2**. These high-frequency features are consistent with the presence of water molecules of crystallization in **1** and both coordinated and uncoordinated water molecules linked by an extensive network of hydrogen bonds in **2**.<sup>22</sup> Finally, as far as the  $\nu_{\text{asym}}(\text{CO})$  stretching region of the IR spectra of **1** and **2** is concerned slight differences are also observed: a strong intensity doublet at 1710 and 1675 cm<sup>-1</sup> (**1**) and four strong peaks at 1715, 1710, 1690 and 1675 cm<sup>-1</sup> (**2**). The different coordination modes of oxalate in **1** (the two ox groups are chelating) and in **2** [the two ox ligands are bis(chelating) and in addition one of them has one oxygen atom that bridges two sodium atoms] account for these subtle spectroscopic changes (see the structural part below).

### Physical techniques

The infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–400 cm<sup>-1</sup> region. The magnetic susceptibility measurements were measured on polycrystalline samples in the temperature range 2.0–300 K with a Quantum Design SQUID susceptometer. It was calibrated with Hg[Co(NCS)<sub>4</sub>]. Diamagnetic corrections were estimated from Pascal's constants<sup>23</sup> as  $-387 \times 10^{-6}$  (**1**) and  $-212 \times 10^{-6}$  (**2**) cm<sup>3</sup> mol<sup>-1</sup>. The magnetic data were also

**Table 1** Summary of crystal data for AsPh<sub>4</sub>[Cr(bipy)(ox)<sub>2</sub>]-H<sub>2</sub>O **1** and [NaCr(bipy)(ox)<sub>2</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>38</sub> H <sub>30</sub> AsCrN <sub>2</sub> O <sub>9</sub>	C <sub>28</sub> H <sub>28</sub> Cr <sub>2</sub> N <sub>4</sub> Na <sub>2</sub> O <sub>22</sub>
<i>M</i>	785.56	921.52
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	14.489(3)	8.936(2)
<i>b</i> /Å	13.612(1)	12.472(2)
<i>c</i> /Å	18.377(4)	16.848(3)
<i>a</i> <sup>o</sup>		97.31(1)
<i>β</i> <sup>o</sup>	111.13(2)	90.88(1)
<i>γ</i> <sup>o</sup>		99.59(1)
<i>U</i> /Å <sup>3</sup>	3380.7(10)	1835.0(6)
<i>Z</i>	4	2
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.543	1.668
<i>F</i> (000)	1604	938
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	13.71	7.11
<i>R</i> <sup>a</sup>	0.037	0.043
<i>R</i> ' <sup>b</sup>	0.085	0.104
<i>w</i> <sup>c</sup>	$1/[\sigma^2(F_o^2) + (0.0404P)^2 + 3.2275P]$	$1/[\sigma^2(F_o^2) + (0.0667P)^2 + 2.8155P]$

<sup>a</sup>  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ . <sup>b</sup>  $R' = [\sum w(|F_o|^2 - |F_c|^2)/\sum w(|F_o|^2)]^{1/2}$ . <sup>c</sup>  $P = (F_o^2 + 2F_c^2)/3$ .

corrected for the temperature independent paramagnetism (t.i.p. =  $110 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> per chromium atom).

### Crystallography

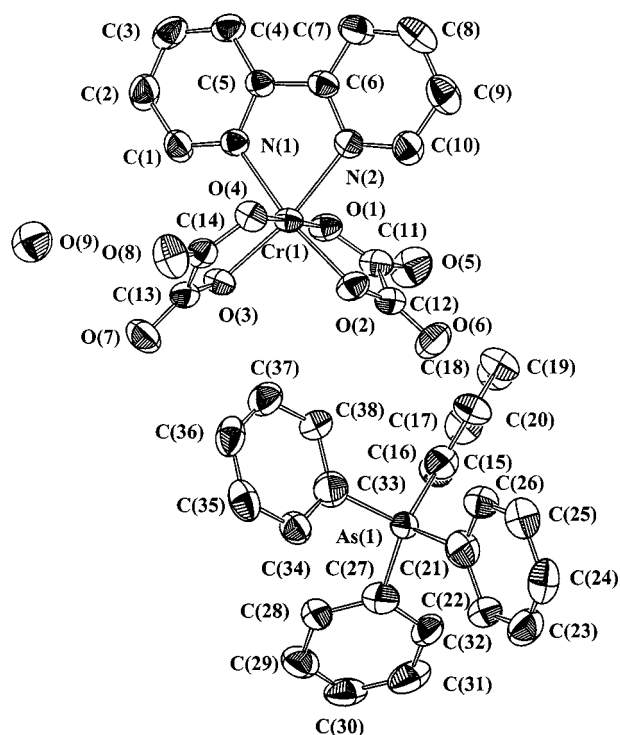
**Crystal data and data collection parameters.** Crystals of dimensions 0.1 × 0.2 × 0.1 (complex **1**) and 0.1 × 0.1 × 0.1 mm (**2**) were mounted on an Enraf-Nonius CAD-4 diffractometer and used for data collection. Intensity data were collected at 293 K by using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with the  $\omega$ - $2\theta$  scan method. The unit-cell parameters were determined from least-squares refinement on the setting angles from 25 centered reflections in the range  $12 < \theta < 20^\circ$ . No significant fluctuations were observed in the intensities of three standard reflections monitored periodically throughout data collection. Intensity data were corrected for Lorentz-polarization and absorption corrections. Of the 6187 (**1**) and 5180 (**2**) measured independent reflections in the range  $\theta$  1.51–24.97 (**1**) and 1.93–22.5° (**2**) with index ranges  $0 \leq h \leq 17$ ,  $0 \leq k \leq 16$  and  $-21 \leq l \leq 20$  (**1**) and  $0 \leq h \leq 9$ ,  $-13 \leq k \leq 13$  and  $-18 \leq l \leq 18$  (**2**), 5865 (**1**) and 4718 (**2**) were observed with  $I \geq 2\sigma(I)$  and used for the structure refinements. Crystal parameters and structure refinements are summarized in Table 1.

**Structure solution and refinement.** The structures of **1** and **2** were solved by standard Patterson methods and refined by the full-matrix least-squares method on *F*<sup>2</sup> for 470 (**1**) and 525 (**2**) refined parameters. The computations were performed with SHELXS 86 and SHELXL 93.<sup>24</sup> All non-hydrogen atoms were treated anisotropically. The hydrogen atoms of the waters of crystallization of complex **1** were located from a difference synthesis. These hydrogen atoms and those from the bipy ligand of complexes **1** and **2** were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The hydrogen atoms from the water molecules of complex **2** were neither found nor calculated. The final full-matrix least-squares refinements minimizing  $\sum w[(|F_o|)^2 - (|F_c|)^2]^2$  converged at the values of *R* and *R'* listed in Table 1. Values of *f*, *f'* and *f''* were taken from ref. 25. The residual maxima and minima in the final Fourier-difference maps were 0.387 and  $-0.339$  (**1**) and 0.415 and  $-0.235$  e Å<sup>-3</sup> (**2**). The values of the goodness-of-fit are 1.0 and 0.93 for **1** and **2**, respectively. The molecular plots were drawn with the ORTEP program.<sup>26</sup> Selected interatomic bond distances and angles are listed in Tables 2 (**2**) and 3 (**3**).

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**Table 2** Selected bond lengths (Å) and interbond angles (°) for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Cr(1)–N(1)	2.057(3)	Cr(1)–O(2)	1.960(2)
Cr(1)–N(2)	2.077(3)	Cr(1)–O(3)	1.946(2)
Cr(1)–O(1)	1.946(2)	Cr(1)–O(4)	1.954(2)
N(1)–Cr(1)–N(2)	78.71(10)	N(2)–Cr(1)–O(4)	89.83(10)
N(1)–Cr(1)–O(2)	169.73(10)	O(2)–Cr(1)–O(3)	95.00(10)
N(1)–Cr(1)–O(3)	93.22(10)	O(2)–Cr(1)–O(1)	82.68(9)
N(1)–Cr(1)–O(4)	90.36(10)	O(2)–Cr(1)–O(4)	96.14(10)
N(2)–Cr(1)–O(2)	91.00(10)	O(3)–Cr(1)–O(1)	95.88(9)
N(2)–Cr(1)–O(3)	93.90(10)	O(3)–Cr(1)–O(4)	82.74(9)
N(2)–Cr(1)–O(4)	168.97(10)	O(1)–Cr(1)–O(4)	178.12(9)
N(2)–Cr(1)–O(1)	91.71(10)		



**Fig. 1** Perspective view of compound **1** with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

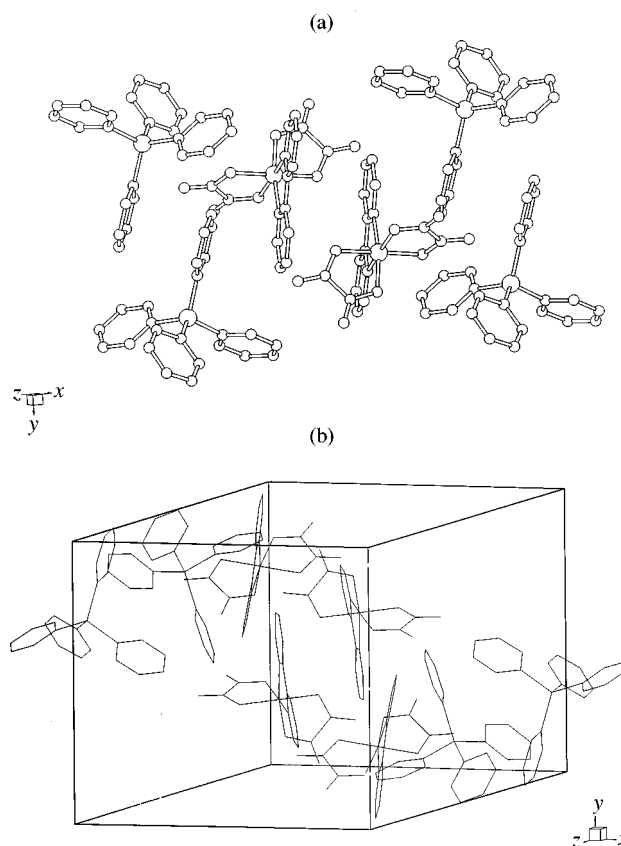
## Results and discussion

### Description of the structures

**AsPh<sub>4</sub>[Cr(bipy)(ox)<sub>2</sub>]·H<sub>2</sub>O 1.** The structure of complex **1** consists of tris(chelated) [Cr(bipy)(ox)<sub>2</sub>]<sup>−</sup> anions, tetraphenylarsonium cations and water molecules of crystallization which are linked through electrostatic forces, van der Waals interactions and hydrogen bonds. A perspective view of **1** with the atom numbering scheme is depicted in Fig. 1 and selected interatomic bond distances are listed in Table 2.

The chromium atom is coordinated to two nitrogen atoms of a chelating bipy group and to four oxygen atoms from two bidentate oxalato ligands in a distorted octahedral geometry. The main distortion of the octahedron arises from the short bite of the bipy and ox ligands [78.71(10), 82.68(9) and 82.74(9)° for N(1)–Cr(1)–N(2), O(1)–Cr(1)–O(2) and O(3)–Cr(1)–O(4), respectively]. The four Cr–O bond lengths are very close [values ranging between 1.960(2) and 1.946(2) Å] and they are somewhat longer than that reported for K<sub>3</sub>Cr(ox)<sub>3</sub>·3H<sub>2</sub>O [average Cr–O bond distance is 1.90 Å].<sup>27</sup> The Cr–N (bipy) bond lengths [2.077(3) and 2.057(3) Å] are significantly longer than the Cr–O (ox) but very close to that reported for bipy-containing chromium(III) complexes.<sup>20,28,29</sup>

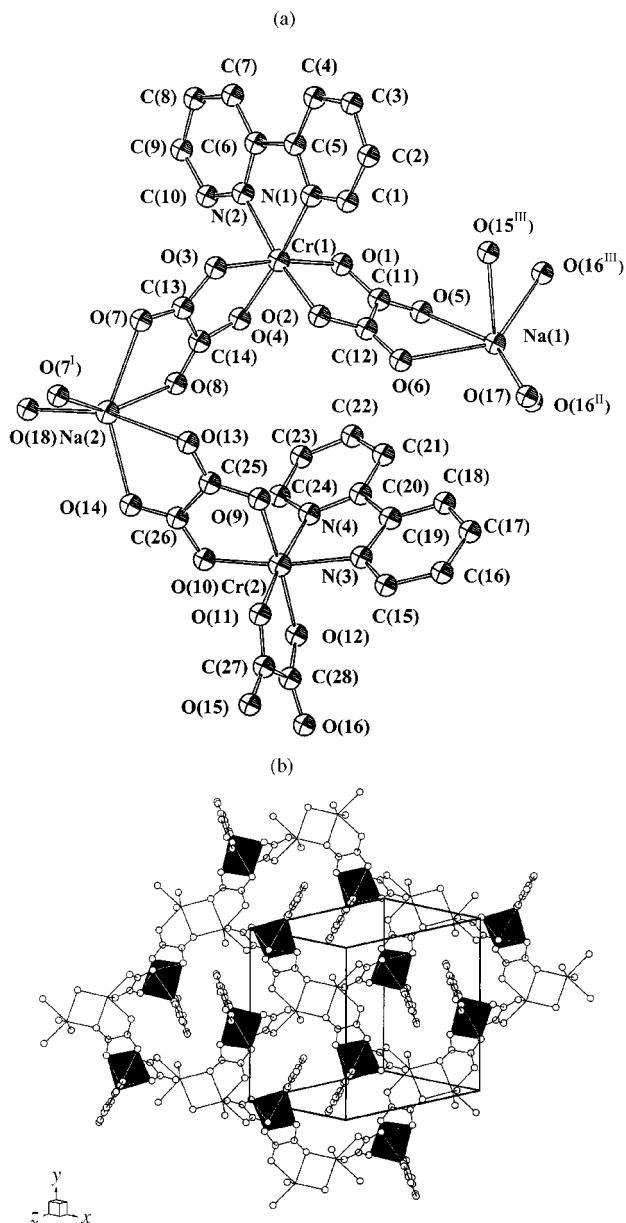
The bipy and ox ligands do not show significant deviations from planarity. The dihedral angle between the two chelating



**Fig. 2** (a) A view of the packing showing the  $\pi$ -interaction between phenyl groups of adjacent tetraphenylarsonium cations. (b) A view of the unit cell content of **1** showing the partial overlap between the bipy ligands of two adjacent [Cr(bipy)(ox)<sub>2</sub>]<sup>−</sup> mononuclear units.

oxalate groups is 87.41(9)° whereas those of bipy with the two oxalate ones are 88.37(9) and 88.97(10)°. Average carbon–carbon and –nitrogen bond lengths are close to those reported for uncoordinated 2,2′-bipyridine.<sup>30</sup> The average C–O bond distances of the ox ligand are 1.213(2) Å for the free bonds, and 1.296(2) Å for those bonded to the chromium atom. The smaller double bond character of the C–O bond in the latter accounts for this lengthening. The tetraphenylarsonium cation exhibits the expected tetrahedral shape and its bond lengths and bond angles are in agreement with those previously reported in other AsPh<sub>4</sub><sup>+</sup>-containing compounds.<sup>31</sup> Interestingly, a weak graphitic-like interaction is observed between two phenyl rings from adjacent tetraphenylarsonium cations [the distance between the two phenyl rings is 3.7(1) Å], the arsonium–arsonium separation being 7.8(1) Å [Fig. 2(a)]. This attractive interaction of phenyl groups in the offset-face-to-face conformation is commonly observed in supramolecular motifs.<sup>32</sup> In addition, the two bipy ligands of two neighbouring [Cr(bipy)(ox)<sub>2</sub>]<sup>−</sup> units [Fig. 2(b)] exhibit a weak but significant overlap [the separation between the two mean bipy planes is 3.7(1) Å]. The uncoordinated water molecule is hydrogen-bonded to one of the oxalate oxygens [the O(9)⋯O(8) separation is 2.947(6) Å and the O(9)–H(91)⋯O(8) angle is 169(5)°]. The shortest intermolecular chromium–chromium and chromium–arsonium separations are 7.189(5) and 7.585(6) Å, respectively.

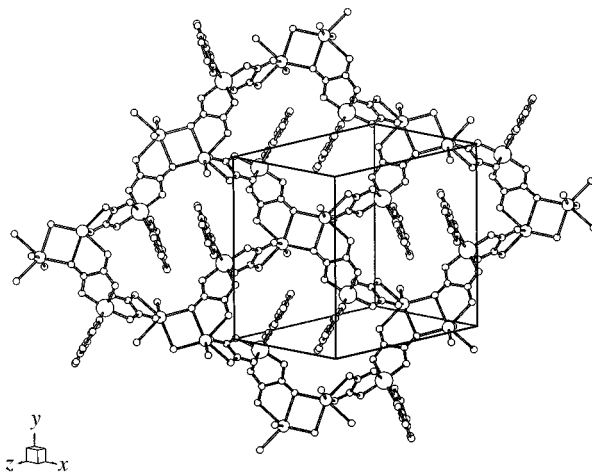
**[NaCr(bipy)(ox)<sub>2</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O 2.** Complex **2** exhibits a novel two-dimensional structure which is made up of bimetallic oxalato-bridged Cr<sup>III</sup>–Na<sup>I</sup> helical chains [Fig. 3(a)] which are linked through centrosymmetric Na<sub>2</sub>O<sub>2</sub> units to yield a sheetlike arrangement which is perpendicular to the [101] vector [Fig. 3(b)]. The Cr(1) and Cr(2) atoms in one helix have the same chirality and since the inversion centre is located in the middle



**Fig. 3** (a) Perspective view of the asymmetric unit of compound **2** with the atom numbering scheme (thermal ellipsoids are drawn at the 30% probability level). (b) Perspective drawing of a fragment of the resulting sheetlike polymer [black octahedra refer to chromium(III)]. Hydrogen atoms and uncoordinated water molecules have been omitted for clarity.

of the  $\text{Na}_2\text{O}_2$  units, the chromium atoms of neighbouring chains have opposite chirality. The infinite neutral sheets are eclipsed to each other and the intersheet separation is 8.357(4) Å. They are held together by an extensive hydrogen-bonding network involving both the coordinated and uncoordinated water molecules and half of the oxalate oxygen atoms [oxygen–oxygen distances ranging from 2.589(6) Å for O(5)⋯O(21) to 3.000(6) Å for O(7)⋯O(22)]. The stacking of the neutral sheets gives rise to channels of  $\text{Cr}_4\text{Na}_4$  octanuclear rings running along the  $x$  axis. These holes are filled by pairs of bipy ligands which overlap partially [the separation between the mean bipy planes is 3.5(1) Å] (Fig. 4). Within a sheet, four  $\text{Cr}_4\text{Na}_4$  rings and four tetranuclear  $\text{Cr}_2\text{Na}_2$  rhombuses alternate regularly around each octanuclear  $\text{Cr}_4\text{Na}_4$  ring with a two-fold axis which is perpendicular to the sheet and passes through the mid point between two opposite chromium atoms.

Two crystallographically independent chromium [Cr(1) and Cr(2)] and sodium [Na(1) and Na(2)] atoms are present in **2**. Both chromium atoms are six-coordinated in a distorted



**Fig. 4** A schematic drawing showing the partial overlap between the bipy ligands within the  $\text{Cr}_4\text{Na}_4$  cavity.

octahedral coordination assured by two bipy nitrogen atoms and four oxalate oxygens from two oxalato groups. Bond lengths and angles around Cr(1) and Cr(2) are very close and compare well with that observed in the related complex **1**, see Table 3. The sodium atoms are also six-coordinated with a water oxygen atom [2.371(5) and 2.325(4) Å for Na(1)–O(17) and Na(2)–O(18), respectively] and five oxalate oxygens [Na–O bonds varying in the ranges 2.511(4)–2.331(4) Å at Na(1) and 2.481(4)–2.325(4) Å at Na(2)] building a highly distorted octahedral surrounding. The values of the Cr–O (ox) bond distances are close to that reported in the anionic three-dimensional oxalato-bridged heterometallic  $[\text{Na}^{\text{MIII}}(\text{ox})_3]^{2-}$  networks [M = Fe, av. Na–O distance 2.318(2) Å]<sup>19</sup> (M = Cr, av. Na–O distance 2.333(11) Å).<sup>20</sup> The main distortions in the octahedral  $\text{NaO}_6$  moieties of **2** are associated to the large reductions from the ideal 90° value of some bond angles [66.92(12), 69.15(12), 60.70(12) and 69.61(12)° for O(5)–Na(1)–O(6), O(16<sup>III</sup>)–Na(1)–O(15<sup>III</sup>), O(7)–Na(2)–O(8) and O(14)–Na(2)–O(13), respectively].

As in complex **1**, the bipy ligand acts as a bidentate ligand and it does not exhibit significant deviations from planarity [the largest deviation from the mean plane is 0.090(5) Å at C(16)]. Two kinds of bridging oxalate ligands are present in compound **2**, one adopting only the bis(bidentate) coordination mode [O(1)C(11)O(5)O(2)C(12)O(6) and O(9)C(25)O(13)O(10)–C(26)O(14)] and the other [O(3)C(13)O(7)O(4)C(14)O(8) and O(11)C(27)O(15)O(12)C(28)O(16)] in addition to this coordination mode acts also as monodentate ligand through one of its four oxygen atom [O(7) and O(16)]. Because of these structural features, each chromium atom is surrounded by three five-membered chelate rings [from a bipy and two oxalate groups] whereas each sodium atom has around it two five- [from two oxalate groups] and one four-membered chelate rings [Na(2)–O(7)Na(2<sup>I</sup>)O(7<sup>I</sup>) and Na(1)O(16<sup>II</sup>)Na(1<sup>II</sup>)O(16<sup>III</sup>)] in addition to a coordinated water molecule. The  $\text{Na}_2\text{O}_2$  rings are planar with inversion centers standing at the mid point of the sodium–sodium distance. The oxalato ligands are also planar [the largest deviation is 0.103(2) Å at O(16)] and they form dihedral angles of 83.4(1) and 87.3(1)° at Cr(1) and Cr(2), respectively. The dihedral angles between the mean plane of bipy ligand and each oxalate group are 87.6(1) and 85.2(1)° [Cr(1)] and 88.4(1) and 81.4(1)° [Cr(2)].

The sodium–sodium separations within the  $\text{Na}_2\text{O}_2$  rings are 3.534(3) [Na(1)⋯Na(1<sup>II</sup>)] and 3.497(4) Å [Na(2)⋯Na(2<sup>I</sup>)] whereas the chromium–sodium distances through bridging oxalato groups are 5.614(3), 5.672(3), 5.657(4) and 5.579(2) Å for Cr(1)⋯Na(1), Cr(1)⋯Na(2), Cr(2)⋯Na(1<sup>III</sup>) and Cr(2)⋯Na(2), respectively. The shortest intersheet chromium–chromium distances are 8.056(4) [Cr(1)⋯Cr(1<sup>V</sup>);

**Table 3** Selected bond lengths (Å) and interbond angles (°) for complex **2** with e.s.d.s in parentheses\*

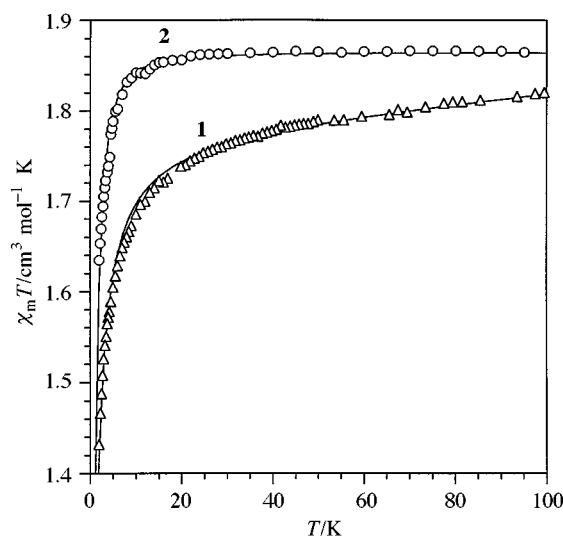
Chromium environment			
Cr(1)–N(1)	2.058(4)	Cr(2)–N(3)	2.064(4)
Cr(1)–N(2)	2.064(4)	Cr(2)–N(4)	2.067(4)
Cr(1)–O(1)	1.949(3)	Cr(2)–O(9)	1.962(3)
Cr(1)–O(2)	1.962(3)	Cr(2)–O(10)	1.961(3)
Cr(1)–O(3)	1.968(3)	Cr(2)–O(11)	1.957(3)
Cr(1)–O(4)	1.967(3)	Cr(2)–O(12)	1.958(3)
N(1)–Cr(1)–N(2)	79.2(2)	N(3)–Cr(2)–N(4)	78.2(2)
N(1)–Cr(1)–O(2)	92.15(14)	N(3)–Cr(2)–O(11)	95.8(2)
N(1)–Cr(1)–O(4)	174.03(14)	N(3)–Cr(2)–O(10)	169.6(2)
N(1)–Cr(1)–O(1)	92.98(14)	N(3)–Cr(2)–O(9)	92.30(14)
N(1)–Cr(1)–O(3)	92.74(14)	N(3)–Cr(2)–O(12)	90.11(14)
N(2)–Cr(1)–O(2)	171.20(14)	N(4)–Cr(2)–O(10)	92.5(2)
N(2)–Cr(1)–O(4)	96.95(14)	N(4)–Cr(2)–O(11)	173.9(2)
N(2)–Cr(1)–O(1)	95.41(13)	N(4)–Cr(2)–O(9)	88.7(2)
N(2)–Cr(1)–O(3)	91.09(13)	N(4)–Cr(2)–O(12)	96.16(14)
O(2)–Cr(1)–O(4)	91.81(13)	O(10)–Cr(2)–O(11)	93.56(14)
O(2)–Cr(1)–O(1)	83.48(13)	O(10)–Cr(2)–O(9)	82.73(13)
O(2)–Cr(1)–O(3)	90.79(13)	O(10)–Cr(2)–O(12)	95.59(13)
O(4)–Cr(1)–O(1)	91.90(13)	O(11)–Cr(2)–O(9)	92.31(13)
O(4)–Cr(1)–O(3)	82.74(13)	O(11)–Cr(2)–O(12)	82.97(13)
O(1)–Cr(1)–O(3)	172.04(13)	O(9)–Cr(2)–O(12)	174.90(14)
Sodium environment			
Na(1)–O(5)	2.505(4)	Na(2)–O(7)	2.422(4)
Na(1)–O(6)	2.479(4)	Na(2)–O(7 <sup>I</sup> )	2.364(4)
Na(1)–O(15 <sup>III</sup> )	2.380(4)	Na(2)–O(8)	2.445(4)
Na(1)–O(16 <sup>III</sup> )	2.331(4)	Na(2)–O(13)	2.481(4)
Na(1)–O(16 <sup>III</sup> )	2.511(4)	Na(2)–O(14)	2.367(4)
Na(1)–O(17)	2.371(5)	Na(2)–O(18)	2.325(4)
O(5)–Na(1)–O(6)	66.92(12)	O(7)–Na(2)–O(8)	60.70(12)
O(5)–Na(1)–O(17)	152.2(2)	O(7)–Na(2)–O(14)	146.39(14)
O(5)–Na(1)–O(16 <sup>III</sup> )	76.43(13)	O(7)–Na(2)–O(7 <sup>I</sup> )	80.86(13)
O(5)–Na(1)–O(15 <sup>III</sup> )	85.45(14)	O(7)–Na(2)–O(18)	111.5(2)
O(5)–Na(1)–O(16 <sup>III</sup> )	90.82(14)	O(7)–Na(2)–O(14)	146.39(14)
O(6)–Na(1)–O(17)	86.7(2)	O(8)–Na(2)–O(14)	87.04(14)
O(6)–Na(1)–O(16 <sup>III</sup> )	137.79(13)	O(8)–Na(2)–O(13)	150.46(13)
O(6)–Na(1)–O(15 <sup>III</sup> )	87.28(13)	O(8)–Na(2)–O(13)	84.02(13)
O(6)–Na(1)–O(16 <sup>III</sup> )	119.81(14)	O(8)–Na(2)–O(18)	100.4(2)
O(17)–Na(1)–O(16 <sup>III</sup> )	131.4(2)	O(14)–Na(2)–O(7 <sup>I</sup> )	118.19(14)
O(17)–Na(1)–O(15 <sup>III</sup> )	102.8(2)	O(14)–Na(2)–O(13)	69.61(12)
O(17)–Na(1)–O(16 <sup>III</sup> )	95.0(2)	O(14)–Na(2)–O(18)	95.9(2)
O(16 <sup>III</sup> )–Na(1)–O(15 <sup>III</sup> )	69.15(12)	O(7 <sup>I</sup> )–Na(2)–O(13)	89.77(13)
O(16 <sup>III</sup> )–Na(1)–O(16 <sup>III</sup> )	79.60(13)	O(7 <sup>I</sup> )–Na(2)–O(18)	92.38(14)
O(15 <sup>III</sup> )–Na(1)–O(16 <sup>III</sup> )	148.54(14)	O(13)–Na(2)–O(18)	164.5(2)
Na(1 <sup>II</sup> )–O(16)–Na(1 <sup>IV</sup> )	100.40(13)	Na(2)–O(7)–Na(2 <sup>I</sup> )	99.14(13)

\* Symmetry codes: I  $-x, -y + 1, -z + 1$ ; II  $-x + 1, -y + 1, -z$ ; III  $x, y - 1, z$ ; IV  $x, y + 1, z$ .

$V = 1 - x, -y, 1 - z$ ] and 8.357(4) [Cr(1)⋯Cr(1<sup>VI</sup>) and Cr(2)⋯Cr(2<sup>VI</sup>)]; VI  $1 - x, y, z$ ].

### Magnetic properties

The magnetic properties of complexes **1** and **2** in the form of the  $\chi_m T$  product versus  $T$  plot ( $\chi_m$  being the magnetic susceptibility per chromium atom) are shown in Fig. 5. Both curves are quite similar: the value of  $\chi_m T$  at room temperature is as expected for a magnetically isolated chromium(III) ion [ $\chi_m T = 1.86 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  (**1** and **2**); calculated value for a  $S = \frac{3}{2}$  state with  $g = 2.0$  is  $1.88 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ], remains practically constant as the temperature is lowered and finally decreases sharply in the very low temperature range [the values of  $\chi_m T$  at 2 K are 1.43 (**1**) and 1.63 (**2**)  $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ ]. No maximum of susceptibility is observed in the temperature range explored. The deviation from the Curie law at low temperatures for **1** and **2** is due to the zero-field splitting ( $D$ ) of the ground state of the Cr<sup>III</sup> ion and/or very weak chromium–chromium magnetic interactions. Keeping in mind the mononuclear nature of compound **1** and the great intra- and inter-sheet chromium–chromium separations in compound **2**, we have analysed their magnetic



**Fig. 5** Temperature dependence of  $\chi_m T$  for compounds **1** ( $\Delta$ ) and **2** ( $\circ$ ). The solid line is the best fit through the theoretical expression for a mononuclear chromium(III) complex with  $g$ ,  $D$  (zero-field splitting) and  $\theta$  (intermolecular interactions) as variable parameters (see text).

behaviour through the expression (1)<sup>33</sup> which is derived from

$$\chi_m = \frac{N\beta^2 g^2}{3k(T - \theta)} (\chi_{\parallel} + 2\chi_{\perp}) \quad (1)$$

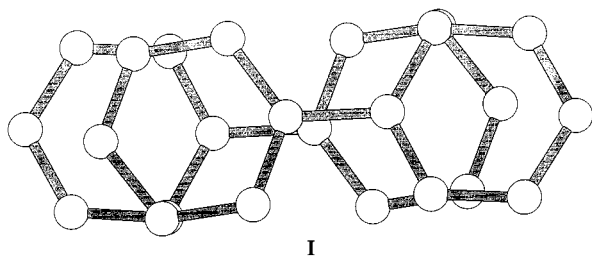
$$\chi_{\parallel} = \frac{1 + 9 \exp(-2D/kT)}{4[1 + \exp(-2D/kT)]} \quad (2)$$

$$\chi_{\perp} = \frac{4 + (3kT/D)[1 - \exp(-2D/kT)]}{4[1 + 2 \exp(-2D/kT)]} \quad (3)$$

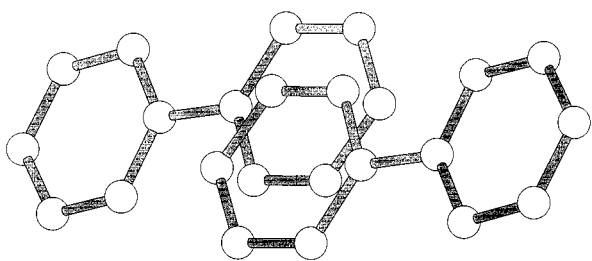
$$H = D[S_z^2 - 1/3S(S + 1)] \quad (4)$$

the Hamiltonian (4) with  $S = \frac{3}{2}$  and considering an axial crystal zero-field splitting.  $D$  and  $\theta$  correspond to the axial zero-field splitting parameter and the intermolecular interactions, respectively. Least-squares analysis of the susceptibility data led to  $|D| = 0.2 \text{ cm}^{-1}$ ,  $g = 1.97$ ,  $\theta = -0.5 \text{ cm}^{-1}$  and  $R = 1.6 \times 10^{-5}$  (**1**) and  $|D| = 1.6 \text{ cm}^{-1}$ ,  $g = 1.99$ ,  $\theta = -0.05 \text{ cm}^{-1}$  and  $R = 3.0 \times 10^{-5}$  (**2**).  $R$  is the agreement factor defined as  $\sum_i [(\chi_m T)_{\text{obs}}(i) - (\chi_m T)_{\text{calc}}(i)]^2 / [(\chi_m T)_{\text{obs}}(i)]^2$ . An excellent agreement between the experimental and theoretical curves is achieved as observed in Fig. 5. Although the  $|D|$  values obtained for chromium(III) in **1** and **2** are reasonable, it is clear that an accurate determination of  $D$  would require anisotropy magnetic measurements on single crystals but this is far from the aim of the present work. As far as the exchange coupling is concerned, the weak antiferromagnetic coupling which occurs in both compounds is as expected in agreement with their structures. In the case of **1**, we are dealing with paramagnetic [Cr(bipy)(ox)<sub>2</sub>]<sup>-</sup> mononuclear units and bulky diamagnetic tetraphenylarsonium cations which coexist in the unit cell, the intermolecular chromium–chromium distances being larger than 7.1 Å. The weak overlap between the terminal bipy groups (see **I** below) of two adjacent [Cr(bipy)(ox)<sub>2</sub>]<sup>-</sup> units [the separation between the two mean planes is 3.7(1) Å] most likely provides the exchange pathway for the small antiferromagnetic coupling observed. In this respect, a weak magnetic exchange across aromatic (pyrazolyl rings)  $\pi$ -stacking was reported recently.<sup>34</sup> The antiferromagnetic coupling in **2** is also very weak and it is about one order of magnitude less than that observed in **1**. Keeping in mind the large intersheet chromium–chromium separations in **2** (more than 8 Å) as well as the lack of both chemical bonds and bipy–bipy contacts between sheets in this compound, it is reasonable to assume the occurrence of only intrasheet

exchange pathways. In this context, two pathways are possible. One involves two bridging oxalato ligands and a sodium atom, the resulting Cr(1)⋯Cr(2) separation being 6.867(2) Å. The other one goes through the weak overlapping between the terminal bipy ligands [see **II** below and Fig. 3(b)] across the Cr<sub>4</sub>Na<sub>4</sub> cavity [7.238(2) and 7.195(2) Å for Cr(1)⋯Cr(I<sup>I</sup>) and Cr(2)⋯Cr(II), respectively]. Although the magnetic coupling between the chromium(III) ions through these extended pathways is expected to be very weak, the π nature of the metal centred magnetic orbitals allows us to rule out the first pathway and to keep the second one. In spite of the somewhat larger separation between the mean bipy planes in **2** [3.5(1) Å] when compared to that in **1** [3.7(1) Å], the overlapping is somewhat smaller in **2** [see **II**] and this would account for the smaller antiferromagnetic coupling in **2** versus **1**.



**I**



**II**

We would like to finish this contribution focusing on the design of novel molecular architectures by using stable [Cr(bipy)(ox)<sub>2</sub>]<sup>-</sup> mononuclear complexes as ligands. The nature of the counteranion to balance the negative charge of the [Cr(bipy)(ox)<sub>2</sub>]<sup>-</sup> anion plays a very important structural role. Non-coordinating and bulky cations such as tetraphenylarsonium allowed us to obtain the complex **1** where the chromium complex does not act as ligand. However in the presence of sodium cations, the two oxalato ligands of the chromium units act as ligands [one bis(bidentate) and the other simultaneously bis(bidentate) and monodentate] and a unprecedented sodium(I)-assisted heterometallic sheetlike structure (compound **2**) is obtained. The six-coordination of the sodium cation and charge balance considerations (four negative charges from two oxalate ligands versus four positive charges from univalent sodium and a trivalent chromium) seem to be determinant in the structure of **2**. In recent magnetostructural studies,<sup>28,29,35</sup> one of us has investigated the complexing ability of [Cr(bipy)(ox)<sub>2</sub>]<sup>-</sup> towards different metal ions such as Ba<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>. The reported heterometallic structures have in common the occurrence of the [Cr<sup>III</sup>(bipy)(ox)<sub>2</sub>] unit as expected because of the relative inertness of the chromium(III) compounds. A unique scaffold-like three-dimensional compound of formula [BaCr<sub>2</sub>(bipy)(ox)<sub>4</sub>(H<sub>2</sub>O)]<sub>n</sub>·nH<sub>2</sub>O was obtained in the case of Ba<sup>2+</sup>, the complexity of this structure arising from both occurrence of three different bridging modes of the oxalato ligand and the ten-coordination number adopted by the barium atom. In the case of silver(I), the structure of the resulting compound of formula [AgCr(bipy)(ox)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] consists of discrete tetranuclear cycles formed by two chromium and two silver atoms bridged by the oxalato ligands. The silver atom in this compound is five-

coordinate exhibiting a distorted trigonal bipyramidal geometry. Centrosymmetric trinuclear species of formula [M<sup>II</sup>Cr<sub>2</sub>(bipy)<sub>2</sub>(ox)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·nH<sub>2</sub>O with M = Cu (n = 3.5) or Co (n = 1) were obtained where the central metal ion M is six-coordinated by two *trans* water molecules and four oxalato oxygens from the two peripheral [Cr<sup>III</sup>(bipy)(ox)<sub>2</sub>] units. Finally, in the case of manganese(II), a novel chain compound of formula [MnCr<sub>2</sub>(bipy)<sub>2</sub>(ox)<sub>4</sub>]<sub>n</sub> is obtained, each chain being formed of diamond-shaped units sharing the manganese atoms. Eight oxalato oxygen atoms from four ox ligands build a flattened square antiprism geometry around each manganese atom.

The easy synthesis of these compounds {slow evaporation at room temperature of aqueous solutions containing the [Cr<sup>III</sup>(bipy)(ox)<sub>2</sub>] unit and the desired assembling cation} together with the variety and richness of the structures reported will yield a great number of interesting heterometallic systems in further studies.

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Paper 8/04990D