



Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 65th anniversary

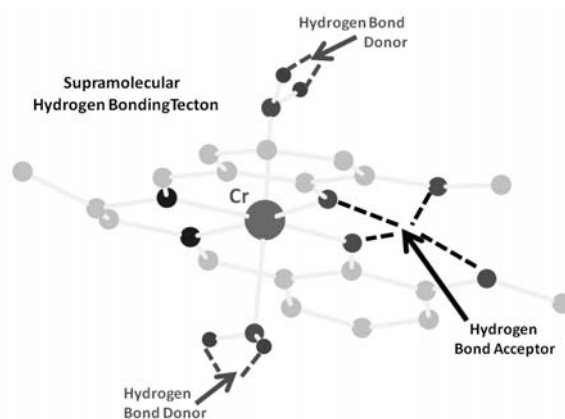
SUPRAMOLECULAR HOMOMETALLIC Cr(III) SYSTEMS RESULTING FROM SECOND COORDINATION SPHERE INTERACTIONS

Vlad IUCHA, Ruxandra GHEORGHE,* Augustin M. MADALAN and Marius ANDRUH*

Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest,
23 Dumbrova Roşie Street, 020464 Bucharest, Roumania

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Three new complexes of chromium(III) have been synthesized and crystallographically characterized: $[\text{LCr}(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot (18\text{-C-6}) \cdot \text{H}_2\text{O}$ **1**, $[\text{LCr}(\text{H}_2\text{O})_2][\text{Cr}(\text{ox})_2(2,2'\text{-bipy})] \cdot 2\text{H}_2\text{O}$ **2**, $[\text{LCr}(\text{H}_2\text{O})(\text{NCS})]$ **3**, where H_2L is a bicompartimental Schiff base ligand derived from the 2:1 condensation of 3-methoxysalicylaldehyde with 1,2-diaminopropane (18-C-6: 18-crown-6; ox^{2-} : the oxalate anion; 2,2'-bipy: 2,2'-bipyridyl). The crystal packing of these complexes is governed by second coordination sphere interactions. The complex species are self-complementary: one aqua ligand from one complex is hosted into the free compartment (O_2O^2) of a similar complex. Supramolecular chromium(III) dimers result in the case of complex **1**, which interconnects through hydrogen bonds with the 18-C-6 molecules, generating a supramolecular chain. In case of compound **2**, a 2D net is built on the hydrogen bonding interactions established between the dimers, $[\text{Cr}(\text{ox})_2(2,2'\text{-bipy})]^-$ anions and crystallization water molecules. The crystal packing of **3** affords supramolecular Cr(III) dimers.



INTRODUCTION

In recent years great effort has been devoted to the self-assembly of organic and inorganic molecules in the solid state, thus extending the range of new solids with desirable chemical and physical properties.¹ Most of the strategies employed in designing inorganic-organic networks rely on the strong directionality of coordination bonds and hydrogen bond interactions,² affording various types of polymeric networks.³ The non-covalent interactions between coordinated ligands

and other neutral or charged species, which generate the second coordination sphere, are systematically investigated in the frame of metallocsupramolecular chemistry.⁴ The second coordination sphere interactions made possible the creation of “simple” supramolecular systems built on the interaction of crown ethers and macropolycyclic ethers, employed as host receptors, and metal complexes containing hydrogen-bond donor groups (*e.g.* NH_3 , H_2O), as guests,^{4,5} but also of more complex architectures, such as rotaxanes.⁶

* Corresponding authors: ruxandra.gheorghe@g.unibuc.ro or marius.andruh@dnt.ro

Schiff-base ligands derived from 3-methoxysalicylaldehyde and various diamines have a very rich coordination chemistry.⁷ They act mainly as compartmental ligands, allowing a straightforward synthesis of heterobinuclear 3d-4f complexes.⁸ The 3d metal is hosted in the N₂O₂ compartment, while the oxophilic lanthanide cation occupies the larger O₂O'₂ site. It has also been shown that these ligands are able to accommodate two different 3d transition metals as well.⁹ Mononuclear complexes, with a metal ion hosted in the N₂O₂ compartment, show an interesting property: the second compartment, O₂O'₂, can act as a good receptor toward hydrogen bond donors.^{7a,10}

A very simple hydrogen bond donor is the water molecule. The crystal investigation of a mononuclear nickel(II) complex with a Schiff base ligand derived from *o*-methoxysalicylaldehyde and 2,2-dimethyl-1,3-propylenediamine reveals that the crystallization water molecule is hosted into the O₂O'₂ compartment.¹¹ The second compartment of the mononuclear complexes can also be a receptor for an aqua ligand arising from another complex, generating various supercomplexes.¹² If the metal ion within the mononuclear complex coordinates one or two aqua ligands onto its apical positions, the complex species are self-complementary: one aqua ligand from one complex can be hosted into the free compartment O₂O'₂ of a similar complex.¹³ There are also reports of several supramolecular systems built on mononuclear copper(II) complexes (with a Schiff base ligand obtained from the condensation of *o*-salicylaldehyde with ethylenediamine), acting as receptors, and bis-protonated diamines as guests.¹⁴

In this paper we report on new supramolecular solid-state architectures resulted from second coordination sphere interactions involving chromium(III) mononuclear complexes.

EXPERIMENTAL

Synthesis

Chemicals were purchased from commercial sources and all manipulations were performed using materials as received. (NEt₄)₂[Co(NCS)₄] and K[Cr(ox)₂(2,2'-bipy)] were synthesized as outlined in the literature.¹⁵

The cationic precursor [LCr(H₂O)₂]Cl was prepared adapting the synthesis reported in ref. 16. To a solution of chromium(III) chloride hexahydrate (1 mmol, 0.27 g) in methanol-water (9/1) were added 3-methoxysalicylaldehyde (2 mmol, 0.3 g) and 1,2-diaminopropane (1 mmol, 0.74 g). After the mixture was refluxed for about 30 minutes, sodium carbonate (0.6 mmol, 0.64 g) was gradually added, followed

by reflux for 4 hours. Concentrating the solution yielded a reddish brown precipitate. IR data (KBr, cm⁻¹): 3305l, 2968w, 1611vs, 1547m, 1457m, 1369m, 1253s, 1216s, 1075w, 965w, 860w, 737m, 436w.

[LCr(H₂O)₂](ClO₄)·(18-C-6)·H₂O **1**: a methanol solution (50 mL) of [LCr(H₂O)₂]Cl (0.1 mmol, 0.05 g) is mixed with solid 18-crown-6 (0.15 mmol, 0.04 g) and Cu(ClO₄)₂·6H₂O (0.1 mmol, 0.04 g). A brown-reddish suspension is readily formed and filtered. The filtrate yielded brown-reddish single-crystals of **2**. IR data (KBr, cm⁻¹): 3394l, 2910w, 1622s, 1551m, 1445m, 1353w, 1253s, 1222s, 1108vs, 962w, 861w, 783m, 636w, 448vw.

[LCr(H₂O)₂][Cr(ox)₂(2,2'-bipy)]·2H₂O **2**: two solutions of [LCr(H₂O)₂]Cl (0.1 mmol, 0.05 g), in 20 mL 1:1 acetonitrile/water, and K[Cr(ox)₂(2,2'-bipy)] (0.1 mmol, 0.03 g), in water (10 mL), were mixed together. Orange single-crystals of **3** were obtained after the slow evaporation of the resulting brown-reddish solution. IR data (KBr, cm⁻¹): 3480l, 1720vs,l, 1621vs, 1445s, 1373vs, 1303m, 1253m, 1219m, 740m, 548w, 454w.

[LCr(H₂O)(NCS)] **3** was obtained as follows: an acetonitrile-methanol (1/1) (20 mL) of [LCr(H₂O)₂]Cl (0.1 mmol, 0.05 g) was added to an acetonitrile solution (20 mL) of (NEt₄)₂[Co(NCS)₄] (0.1 mmol, 0.053 g). After 3 days of slowly evaporating, the green solution gave reddish single crystals of **1** which were filtered off. IR data (KBr, cm⁻¹): 3225 ml, 2972wl, 2080s, 1627vs, 1620vs, 1545m, 1439 vs-l, 1320m, 1284m, 1243s, 1217s, 1072s, 1039m, 964m, 854m, 730vs, 647m, 443m.

Physical measurements

The IR spectrum (KBr) pellets was recorded on a Bruker Tensor 37 spectrophotometer in the 4000 - 250 cm⁻¹ region. The UV-Vis spectrum (diffuse reflectance technique) was recorded with a Jasco V-670 spectrophotometer.

Crystal structure determination

Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent, as described above. Data were collected at 293 K on a STOE IPDS II diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F². The non-H atoms were refined with anisotropic displacement parameters. Drawings of the molecule were performed with the program Diamond 2. CCDC reference numbers: 933294, 933295 and 933296.

RESULTS AND DISCUSSION

The compartmental ligand, H₂L, used in this work is the Schiff base derived from 3-methoxysalicylaldehyde and 1,2-diaminopropane. In reaction with chromium(III) chloride, it affords a mononuclear chromium(III) complex, where the metal ion displays an octahedral stereochemistry, with the organic ligand forming the equatorial plane and two aqua ligands occupying the apical

positions. This complex possesses an outer $O_2O'_2$ binding site, which could accommodate a second metal ion or act as a hydrogen bond acceptor (receptor). Exploiting the accessible coordination sites of this complex would make it a favorable starting material for the design of novel solid-state architectures. Aiming to obtain such systems, we have investigated the self-assembly processes involving the $[LCr(H_2O)_2]Cl$ complex and: (i) $Cu(ClO_4)_2$ in the presence of 18-crown-6; (ii) $K[Cr(ox)_2(2,2'-bipy)]$; (iii) $(NEt_4)_2[Co(NCS)_4]$. The reactions led to highly crystalline products, whose crystallographic investigation reveals the formation of three new complexes. Two of them are mononuclear, $[LCr(H_2O)_2](ClO_4) \cdot (18-C-6) \cdot H_2O$ **1** and $[LCr(H_2O)(NCS)]$ **3**, while the third one is a cation-anion type complex system, $[LCr(H_2O)_2][Cr(ox)_2(2,2'-bipy)] \cdot 2H_2O$ **2**.

The IR spectra of all three compounds clearly show the characteristic bands of the organic compartmental ligand: $\nu(C=N)$, $\sim 1620\text{ cm}^{-1}$; $\nu(C=C)$, $\sim 1450\text{ cm}^{-1}$; $\nu(C-O)$, $\sim 1325\text{ cm}^{-1}$; $\nu_{as}(C-O-C)$, $\sim 1250\text{ cm}^{-1}$; $\nu_s(C-O-C)$, $\sim 1220\text{ cm}^{-1}$.

The IR analysis of compound **1** also reveals the presence of the perchlorate anion, with bands at 1108 and 626 cm^{-1} , and of the 18-crown-6 molecule (the strong band centered at 1108 cm^{-1} and the medium large one at around 2910 cm^{-1} that

can also be assigned to vibrations of the C-O and, respectively, C-H bonds from 18-crown-6).

The IR spectrum of compound **2** contains bands generated by the presence of oxalate [$\nu_{as}(CO)$, $1720, 1687, 1621\text{ cm}^{-1}$; $\nu_s(CO)$, $1445, 1373, 1219\text{ cm}^{-1}$, $\delta(OCO)$ 809 cm^{-1}] and 2,2'-bipyridyl ligands [$\nu(CH)$, 777 cm^{-1}].

The band located at 2080 cm^{-1} in the IR spectrum of compound **3** accounts for the presence of the isothiocyanate ligand.

The solid state electronic spectra of **1** ÷ **3** exhibit a large band located at approximately 480 nm , with a shoulder at 550 nm . Considering a *pseudo*-octahedral stereochemistry for the chromium(III) ion, these bands can be assigned to the ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4A_2 \rightarrow {}^4T_2$ electronic transitions.

Description of structures

Relevant crystallographic and structure refinement data for systems **1-3**, as well as selected bond distances and angles, are collected in Tables 1 and 2, respectively.

Compound $[LCr(H_2O)_2](ClO_4) \cdot (18-C-6) \cdot (H_2O)$ **1** crystallizes in a *P121/c1* space group as a monocation $[LCr(H_2O)_2]^+$, along with a perchlorate counter anion, a 18-crown-6 molecule and crystallization water molecule (Fig. 1).

Table 1

Crystallographic data and structure refinement

	1	2	3
Empirical formula	$C_{25}H_{36}ClCrN_2O_{14}$	$C_{33}H_{34}Cr_2N_4O_{16}$	$C_{22}H_{20}CrN_3O_5S$
M (g mol ⁻¹)	676.01	846.64	490.47
Crystal system	<i>Monoclinic</i>	<i>Triclinic</i>	<i>Monoclinic</i>
Space group	<i>P 1 21/n 1</i>	<i>P-1</i>	<i>C 1 2/c 1</i>
Temperature, (K)	293(2)	293(2)	293(2)
Wavelength, (Å)	0.71073	0.71073	0.71073
a (Å)	11.6640(12)	11.5245(12)	21.3272(15)
b (Å)	16.1119(16)	12.1866(13)	13.5462(12)
c (Å)	17.0031(17)	15.0474(16)	18.7352(14)
α (°)		69.499(8)	
β (°)	106.947(8)	67.845(8)	123.492(5)
γ (°)		87.460(8)	
V (Å ³)	3056.6(5)	1823.9(3)	4513.9(6)
Z	4	2	8
D_{calc} (g cm ⁻³)	1.469	1.542	1.443
μ (mm ⁻¹)	0.532	0.675	0.638
$F(000)$	1412	872	2024
Goodness of fit on F^2	0.980	0.939	1.082
Final $R1, wR_2$ [$I > 2\sigma(I)$]	0.0765, 0.0765	0.0684, 0.1286	0.0685, 0.1372
$R1, wR_2$ (all data)	0.1736, 0.1850	0.1492, 0.1506	0.1217, 0.1568
Largest diff. peak and hole (eÅ ⁻³)	0.237, -0.253	1.065, -0.586	0.403, -0.355

Table 2
Selected bond lengths (Å) and interbond angles (°)

	1	2	3
Cr(1) - O(2)	1.926(3)	Cr(1) - O(2)	1.914(2)
Cr(1) - O(3)	1.919(3)	Cr(1) - O(3)	1.923(2)
Cr(1) - O(5)	2.025(5)	Cr(1) - O(5)	2.022(2)
Cr(1) - O(6)	2.002(5)	Cr(1) - O(6)	2.009(3)
Cr(1) - N(1)	1.995(4)	Cr(1) - N(1)	2.006(3)
Cr(1) - N(2)	1.999(4)	Cr(1) - N(2)	1.990(3)
O(2)-Cr(1)-O(3)	94.34(12)	Cr(2) - O(7)	1.964(3)
O(3)-Cr(1)-N(2)	91.59(15)	Cr(2) - O(8)	1.963(3)
N(2)-Cr(1)-O(6)	89.60(18)	Cr(2) - O(11)	1.938(2)
N(1)-Cr(1)-O(6)	88.72(18)	Cr(2) - O(12)	1.948(3)
O(6)-Cr(1)-O(3)	90.06(16)	Cr(2) - N(3)	2.054(3)
O(6)-Cr(1)-O(2)	90.11(15)	Cr(2) - N(4)	2.062(3)
O(5)-Cr(1)-O(2)	91.27(17)	O(2)-Cr(1)-O(3)	94.27(10)
O(5)-Cr(1)-O(3)	91.30(18)	O(3)-Cr(1)-N(2)	91.50(12)
O(5)-Cr(1)-N(1)	89.8(2)	N(2)-Cr(1)-O(6)	88.30(13)
O(5)-Cr(1)-N(2)	88.9(2)	N(1)-Cr(1)-O(6)	89.82(14)
N(1)-Cr(1)-O(2)	91.20(15)	O(6)-Cr(1)-O(3)	90.68(12)
N(1)-Cr(1)-N(2)	82.87(17)	O(6)-Cr(1)-O(2)	90.81(12)
		O(5)-Cr(1)-O(2)	90.39(11)
		O(5)-Cr(1)-O(3)	88.80(10)
		O(5)-Cr(1)-N(1)	90.58(13)
		O(5)-Cr(1)-N(2)	90.55(12)
		N(1)-Cr(1)-O(2)	91.47(12)
		N(1)-Cr(1)-N(2)	82.77(14)
		O(12)-Cr(2)-O(11)	83.84(11)
		O(11)-Cr(2)-N(3)	88.51(11)
		O(8)-Cr(2)-N(3)	93.20(12)
		O(8)-Cr(2)-O(12)	95.30(12)
		O(7)-Cr(2)-O(8)	82.16(11)
		O(7)-Cr(2)-O(12)	93.50(13)
		O(7)-Cr(2)-O(11)	91.54(12)
		O(7)-Cr(2)-N(3)	94.74(13)
		N(4)-Cr(2)-N(3)	78.47(13)
		N(4)-Cr(2)-O(8)	95.41(12)
		N(4)-Cr(2)-O(12)	93.59(13)
		N(4)-Cr(2)-O(11)	90.99(12)

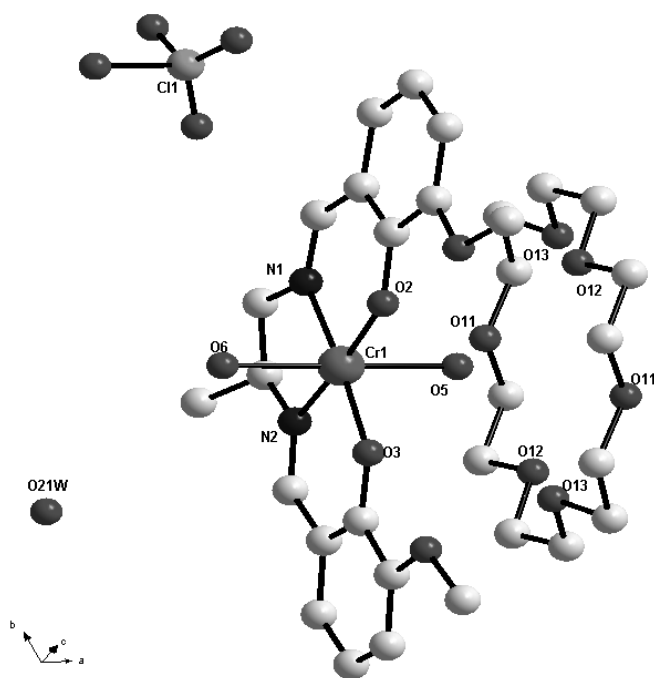


Fig. 1 – View of the molecular structure of **1**.

The chromium(III) is hosted in the inner $[N_2O_2]$ compartment of the Schiff base ligand, exhibiting an elongated octahedral geometry, with a $[N_2O_2]$ macrocycle basal donor set and two aqua ligands occupying the apical positions. The bond distances in the equatorial plane are as follows: Cr1 – O2 = 1.926(3) Å; Cr1 – O3 = 1.919(3) Å; Cr1 – N1 = 1.995(4) Å; Cr1 – N2 = 1.999(4) Å, while the axial distances are Cr1 – O5 = 2.025(5) Å and Cr1 – O6 = 2.002(5) Å. The analysis of the packing diagram reveals the formation of a hydrogen bonded supramolecular chain-like structure. The two apical water molecules involve the cationic complex in two different supramolecular hydrogen bonding

interactions. On one hand there is the formation of dimeric supercomplexes: the aqua ligand (O6) is hydrogen bonded to the oxygen atoms from the free compartment of the neighbouring one (the value of the O...O distances varies between 2.74 and 3.11 Å). The intra-dimer Cr...Cr distance is 4.61 Å. The interconnexion of these dimeric supercomplexes into a supramolecular chain is achieved through the second axial aqua ligand (O5) which is involved in hydrogen bonding interactions with the oxygen atoms belonging to the crown ether molecule (O5...O12 = 2.75 Å; O5...O13 = 2.82 Å) (Fig. 2).

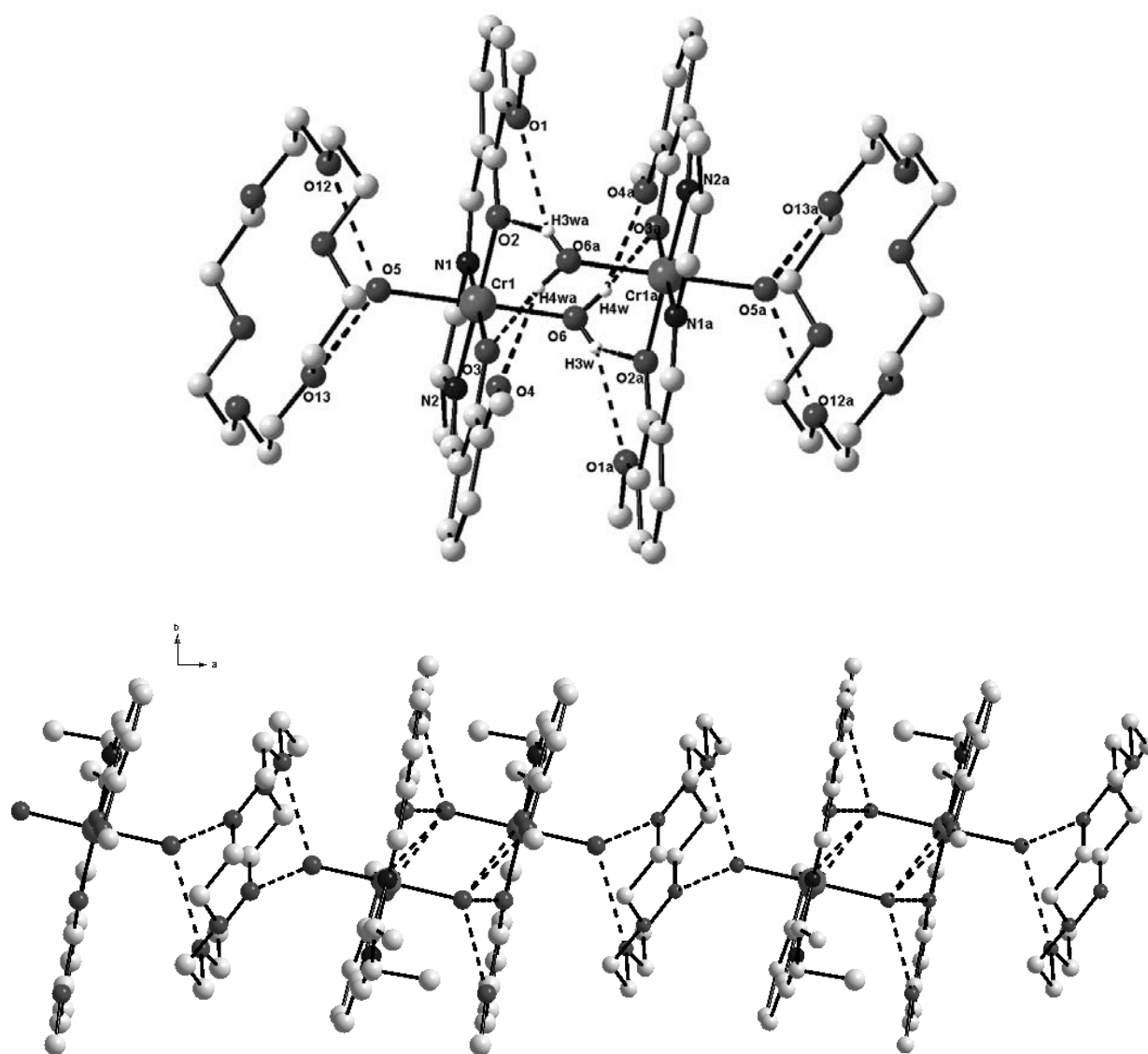


Fig. 2 – (a) Detail of the packing diagram in crystal **1**; (b) representation of the formation of a supramolecular chain in crystal **1** through hydrogen bonds.

The X-ray analysis of **1** shows that the use of $\text{Cu}(\text{ClO}_4)_2$, as a starting material, was only a source of counter-anions, perchlorate, as the copper(II) ion is not a component of the crystalline product.

The unit cell of $[\text{LCr}(\text{H}_2\text{O})_2][\text{Cr}(\text{ox})_2(2,2'\text{-bipy})]\cdot 2\text{H}_2\text{O}$ **2** includes distinct cationic, $[\text{LCr}(\text{H}_2\text{O})_2]^+$, and anionic, $[\text{Cr}(\text{ox})_2(2,2'\text{-bipy})]^-$, units and crystallization water molecules (Fig. 3). It crystallizes in a *P-1* space group.

The $[\text{LCr}(\text{H}_2\text{O})_2]^+$ moiety preserves the same structural features of compound **1**. The chromium(III) ion has an elongated octahedral geometry, where the values of the basal bond distances are $\text{Cr1} - \text{O2} = 1.914(2) \text{ \AA}$, $\text{Cr1} - \text{O3} = 1.923(2) \text{ \AA}$, $\text{Cr1} - \text{N1} = 2.006(3) \text{ \AA}$, $\text{Cr1} - \text{N2} = 1.990(3) \text{ \AA}$, and the ones established between Cr1 and the apical water molecules are $\text{Cr1} - \text{O5} = 2.022(2) \text{ \AA}$, $\text{Cr1} - \text{O6} = 2.009(3) \text{ \AA}$.

The chromium(III) ion in the $[\text{Cr}(\text{ox})_2(2,2'\text{-bipy})]^-$ entity adopts an octahedral geometry, coordinating two bidentate chelating oxalate

ligands and one chelating 2,2'-bipyridine. The Cr - N bond lengths, $2.054(3)$ și $2.062(3) \text{ \AA}$, are slight higher than the Cr - O ones, $1.938(2) \div 1.964(3) \text{ \AA}$.

On a closer look at the crystallin packing of system **2**, we notice the self-complementarity between two $[\text{LCr}(\text{H}_2\text{O})_2]^+$ neighbouring complexes, as in the previous case (Fig. 4). One of the apical water molecules coordinated to a chromium(III) ion is hydrogen bonded to the phenoxo and methoxy oxygen atoms from a $[\text{O}_2\text{O}'_2]$ site belonging to the other $[\text{LCr}(\text{H}_2\text{O})_2]^+$ moiety. The distances involved in these interactions vary between 2.76 and 3.09 \AA . The second apical water molecule establishes a hydrogen bond with an oxygen atom of an oxalato ligand (distance $\text{O}\cdots\text{O} = 2.72 \text{ \AA}$) and another one with a crystallization water molecule (distance $\text{O}\cdots\text{O} = 2.704 \text{ \AA}$). The $[\text{Cr}(\text{ox})_2(2,2'\text{-bipy})]^-$ ion are involved in a complex system of hydrogen bonds with the crystallization water molecules through their terminal oxygen atoms (Fig. 5).

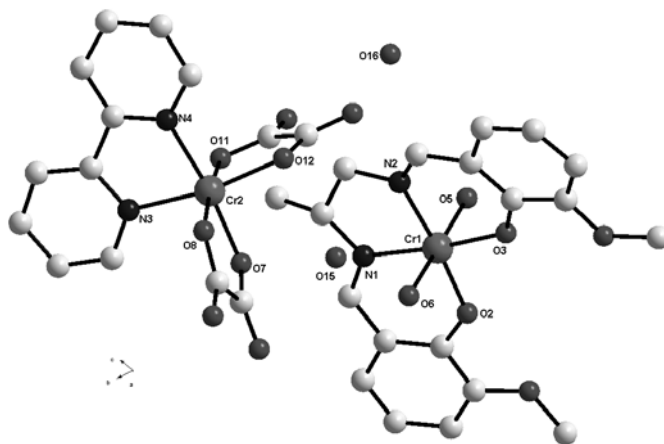


Fig. 3 – Crystal structure of **2**.

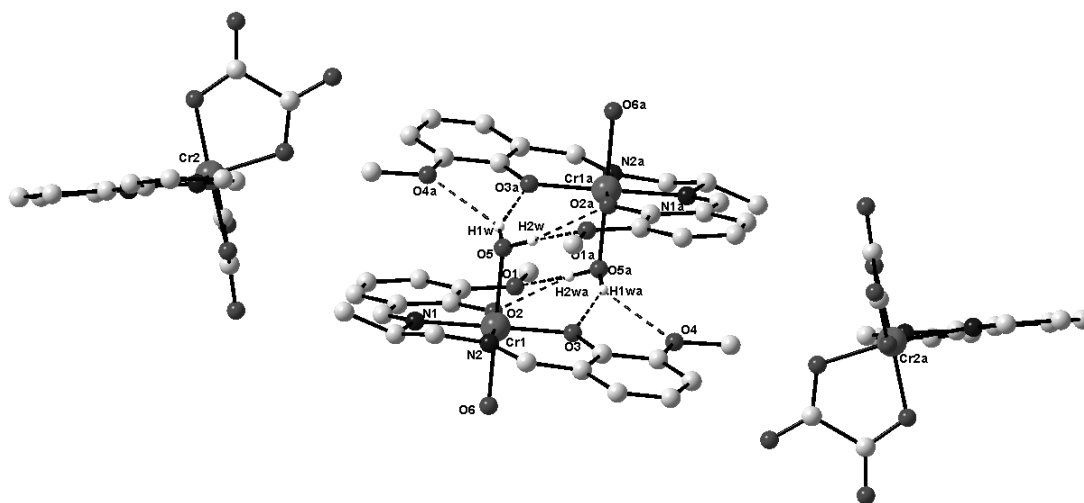


Fig. 4 – Formation of supramolecular hydrogen-bonded chromium(III) dimers.

The structural determination of $[\text{LCr}(\text{H}_2\text{O})(\text{NCS})]\cdot\text{CH}_3\text{CN}$ **3** evidences a mononuclear Cr(III) complex. The organic ligand L^{2-} forms the equatorial plane of the octahedral chromium(III) ion, whereas the apical positions are occupied by the aqua ligand and the NCS^- ion coordinated through nitrogen (Fig. 6a). It crystallizes along a acetonitrile molecule, in a $C1$ $2/c1$ space group.

The bond distances are as follows: Cr1 – N1 = 2.000(2) Å; Cr1 – N2 = 1.999(2) Å; Cr1 – O2 = 1.9169(19) Å; Cr1 – O3 = 1.9152(18) Å (for the equatorial plane), Cr1 – O5 = 2.041(2) Å (chromium – apical water molecule) and Cr1 – N3 = 1.994(3) Å (chromium – apical isothiocyanate).

The same self-complementarity as in case of compound **1** is also present in the supramolecular architecture of system **2**, generating dimeric

supercomplexes (Fig. 6b): the apical water molecule from one complex is hydrogen bonded to the oxygen atoms from the free $[\text{O}_2\text{O}'_2]$ compartment of a neighbouring complex. The value of the distances $\text{O}\cdots\text{O}$ involved in these interactions vary between 2.77 and 3.04 Å.

The structure of compound **3** reveals once more the decomposition of the $(\text{NEt}_4)_2[\text{Co}(\text{NCS})_4]$ building-block during a chemical process (see our previous results in Ref. 17). This time, it only generates the presence of a terminal isothiocyanato ligand, the cobalt(II) ions not being present in the structure of the final crystalline product.

The geometrical parameters associated to the hydrogen bonds sustaining the supramolecular dimeric moieties in compounds **1** - **3** are gathered in Table 3.

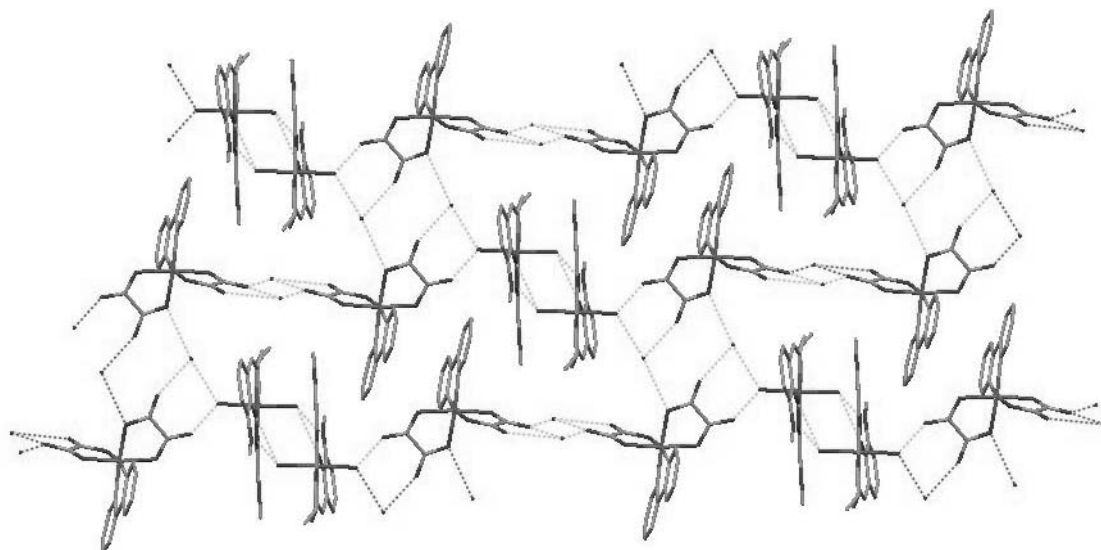


Fig. 5 – Crystallin packing diagram for compound **2**.

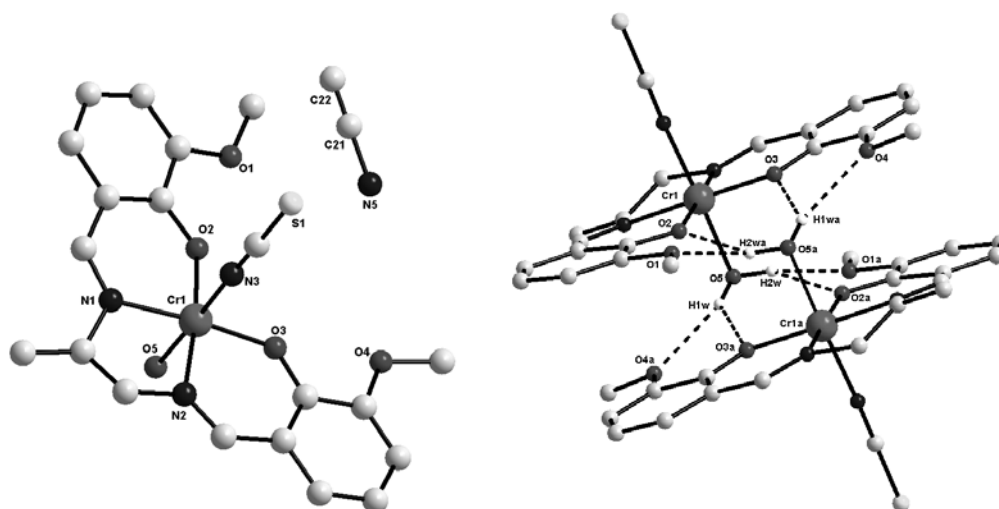


Fig. 6 – (a) Crystal structure of complex **3** and (b) formation of a supramolecular hydrogen-bonded dimer in crystal **3**.

Table 3

Geometrical parameters associated to the hydrogen bonds sustaining the supramolecular dimeric moieties in compounds **1 - 3**

D-H...A	D...A (Å)	D-H...A (deg)
Compound 1		
O6 - H3w ... O1a	2.375	150.12
O6 - H3w ... O2a	2.099	139.20
O6 - H4w ... O3a	2.030	150.01
O6 - H4w ... O4a	2.473	134.61
Compound 2		
O5 - H1w ... O3a	1.990	151.59
O5 - H1w ... O4a	2.241	137.35
O5 - H2w ... O1a	2.295	153.97
O5 - H2w ... O2a	2.165	135.18
Compound 3		
O5 - H1w ... O3a	2.082	138.76
O5 - H1w ... O4a	2.241	144.88
O5 - H2w ... O1a	2.271	140.59
O5 - H2w ... O2a	2.082	139.92

The examples presented herein sustain the idea that mononuclear complexes belonging to the [M(valX)] family (valX²⁻ being a compartmental ligand derived from *o*-vanillin and a diamine) can efficiently act as receptors (hydrogen bond acceptors) for water molecules from complementary species (substrate). The packing is driven by the ability of the empty O₂O'₂ site to act as a hydrogen bond acceptor. In all three cases, supramolecular Cr(III)-Cr(III) dimers are formed on the basis of the self-complementarity of the [LCr(H₂O)₂]⁺ unit. Compound **1** can be described as a supramolecular chain of dimers, as the hydrogen bonds further interconnect the [Cr₂] supramolecular tectons through 18-crown-6 molecules. In **2**, the same [Cr₂] dimers and the [Cr(ox)₂(2,2'-bipy)] units are "knotted" together into a hydrogen bonded bidimensional network. The structure of system **3** is made of hydrogen bonded supramolecular dimers, [L(SCN)Cr(OH)₂] ... (H₂O)Cr(NCS)L]. The composition of the co-crystallization products is the result of the interactions occurring at the second coordination sphere level of the complex species which are involved.

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