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Heterometallic M_2Cr_4 (M^{II} = Sr, Pb) Clusters Assembled by Tris(μ-aqua) Bridges

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Three heterometallic compounds formulated as $[CaCr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2{\cdot}6H_2O]2H_2O$ (**I**) $[M_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]14H_2O$, [M = Sr^{2+} (**II**) Pb^{2+} (**III**), H_3nta = nitrilotriacetic acid] were prepared and structurally characterised. In all three compounds a common core [Cr(μ-OH)(μ-OAc)Cr] containing two different bridging ligands, hydroxido and acetato groups, is present. In **I**, Ca^{2+} counterions link the dinuclear chromium units together through outer carboxylate oxygen atoms and a hydrogen-bonded network, whereas in **II** and **III** the nuclearity is extended by the presence of three bridging water molecules linking together two Sr^{2+} or Pb^{2+} counterions, which results in hexanuclear M_2Cr_4 clusters. The temperature dependence of the magnetic susceptibilities of **I**–**III**, which were fitted with an isotropic Hamiltonian, yielded antiferromagnetic interaction parameters (*J*) for **I**–**III** close to $-14\ cm^{-1}$.

Introduction

Hydroxido-bridged chromium(III) complexes have been widely investigated from magnetic, spectroscopic and structural points of view.[1–3] Recently, a lot of polynuclear chromium complexes that have more that one type of bridging units, such as fluorido, hydroxido, alcoxido, or oxido, together with one or more carboxylato or carbonato bridges, have been reported.[4–13] These ligand environments frequently generated higher nuclearity compounds or 2D or 3D polymers. For example, complexes with nuclearities equal or larger than two include cores such as $[Cr_2(OH)]$,[4] $[Cr_2(OH)_2]$,[5] $[Cr_3O]$,[6] $[Cr_3(OH)_2]$,[7] $[Cr_4S]$,[8a] $[Cr_4O]$,[8b] $[Cr_4O_2]$,[9] $[Cr_4(OH)_4]$,[10] $[Cr_8F_8]$,[11] $[Cr_8(OH)_8]$,[12a] $[Cr_8(OH)_{12}]$,[12b] $[Cr_8O_4]$,[12a] $[Cr_{12}O_9(OH)_3]$,[13a] and $[Cr_{12}O_{12}]$.[13b]

The variety of bridging ligands gives clusters with diverse stereochemistries and generates a large interest in the characterisation of chromium–chromium magnetic interactions.[14] Here we report the synthesis and magnetic properties of one trinuclear $CaCr_2$ (**I**) and two original hexanuclear M_2Cr_4 [M = Sr^{2+}, (**II**) Pb^{2+}, (**III**)] complexes with identical chromium(III) dimeric units $[(nta)Cr(\mu\text{-}OH)(\mu\text{-}OAc)Cr(nta)]^{2-}$ formed by one hydroxido and one carboxylato bridging ligands (H_3nta is nitilotriacetic acid). An unusual feature in **II** and **III** is that the hexanuclear heterometallic complexes are assembled by tris μ-aqua bridges $\{[Cr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2]M(\mu\text{-}H_2O)_3M[Cr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2]\}$.

Results and Discussion

For the synthesis of hydroxido-bridged chromium coordination compounds we used the well-known property of chromium to hydrolyze,[15] especially in the presence of carboxylic ligands that have a large affinity for chromium(III) ions. Heterometallic complexes **I**–**III** were prepared by using a step-by-step method (Scheme 1). In the first step, $M_3(nta)_2$ was obtained by interaction between nitrilotriacetic acid (H_3nta) and MCO_3 in water (see Experimental Section). The next step included the synthesis of chromium complex A (Scheme 1) by an exchange reaction between $CrCl_3{\cdot}6H_2O$ and $M_3(nta)_2$.[16a] As it was previously demonstrated[16b] that complex A is present in solution, we did not try to isolate it. Depending on the pH of the solution, an equilibrium between the aqua and hydroxido complexes (Scheme 1, A, B, C) occurs, as shown by spectral (UV/Vis, ^2H NMR) and (potentiometric investigations or just pH-dependencies) pH-metric investigations of different Co^{III}– and Cr^{III}–nta complexes.[5] Furthermore, we proved earlier

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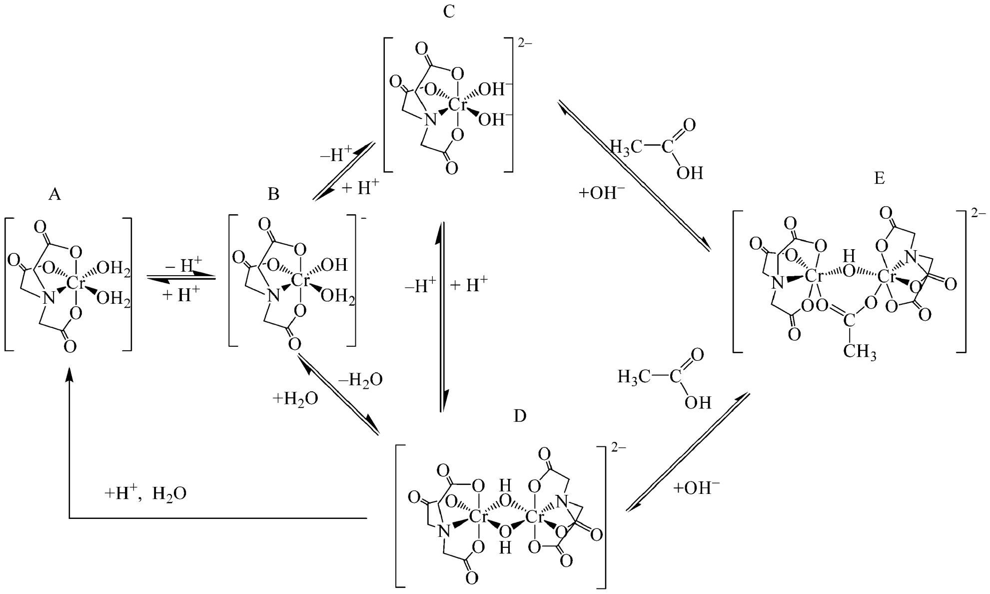

Scheme 1.

that a dimerisation reaction yielding compound D (Scheme 1) was achieved with the use of $M(OH)_2$ solutions.[17] Finally, one of the bridging hydroxy groups was substituted by interaction with acetic acid (E). This dimeric anionic unit with two different bridges was used to prepare compounds **I**–**III** that involve the Ca^{2+}, Sr^{2+} and Pb^{2+} cations, respectively.

According to the X-ray structural study, compound **I** can be formulated as $[CaCr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2\cdot 6H_2O]$, and it is solvated by six water molecules. The formation of a $CaCr_2$ trinuclear structure results from an association between the binuclear $[Cr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2]^{2-}$ and $[Ca(H_2O)_6]^{2+}$ complex ions through one carboxylate group of the nta ligand, which exhibits a μ-O,O′ bridging functionality (Figure 1a). Two chromium atoms are linked by one hydroxido and one carboxylato bridging ligand, and the Cr1···Cr2 separation is equal to 3.540(1) Å. The Cr···Ca separations are much larger: 6.122(1) and 8.833(1) Å for Cr(1) and Cr(2), respectively. The crystal structure of compound **I** can be characterised as a 2D network sustained by multiple H-bonds (Figure 1b). All possibilities for the formation of H-bonds in the crystal are completely realised. In this case, oxygen atoms of the carboxylate groups act as acceptors, whereas water molecules and μ-OH groups act as donors of protons.

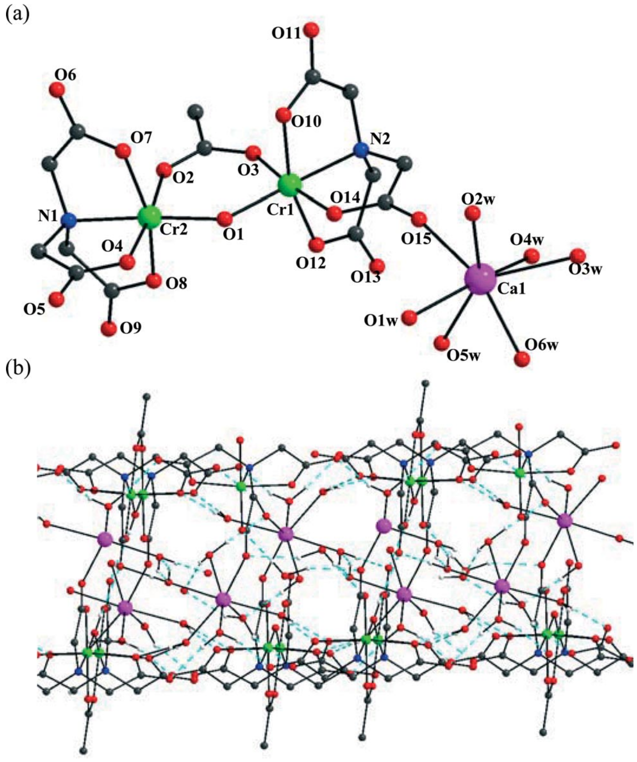

Figure 1. (a) Structure of trinuclear Cr_2Ca compound **I**; (b) 2D layer in the structure of **I** (hydrogen atoms not involved in hydrogen bonds are omitted for clarity).

Single-crystal X-ray studies demonstrated that compounds **II** and **III** are isostructural. As an example, the structure of $[Sr_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]\cdot 14H_2O$ (**II**) is presented Figure 2. Unlike **I**, the molecular crystal **II** is made of hexanuclear Sr_2Cr_4 complexes (Figure 2a) and solvated water molecules. Each chromium atom is coordinated by one amine nitrogen and three carboxylate oxygen atoms of the deprotonated nta^{3-} ligand. The octahedral geometry is completed by one hydroxido and one acetato bridging ligand (Table S2). The fact that merits our attention is that in both the $CaCr_2$ [structure (**I**)] and Sr_2Cr_4 [structure (**II**)] entities, the $[Cr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2]^{2-}$ unit has an appropriate stereochemical orientation of the carboxylate groups to coordinate the Sr (or Pb for structure **III**) atom. At the same time, compared to **I**, the nuclearity of compound **II** is increased by three bridging water molecules, which results in a hexanuclear Sr_2Cr_4 cluster. In this case, the dimeric chromium anions can be considered as a tetradentate compartmental ligand coordinated to the Sr^{2+} (Pb^{2+}) ions through the oxygen atoms, as shown in Figure 2a. The Sr–Ow (or Pb–Ow) bonds and the Sr1OwSr2 (or Pb1OwPb2) angles involving the oxygen atoms from the water molecules are all equivalent. From this structural consideration and also from charge-balance considerations, it is clear that the three bridging molecules present in structures **II** and **III** are water molecules. The Cr···Cr separations of 3.479(1) Å for Cr(1)···Cr(2) and 3.485(1) Å for Cr(3)···Cr(4) are very similar to that found for the $CaCr_2$ compound (**I**). In contrast, the average value of the shortest Sr···Cr distances within the hexanuclear cluster is equal to 4.440(3) Å, which is much shorter in comparison with the same distance in **I** [6.122(1) Å]. This is explained by the tetradentate coordination of the $[Cr_2(\mu\text{-OH})(\mu\text{-OAc})(nta)_2]^{2-}$ ligand to the strontium atom in compound **II**. The crystal structure of compound **II** is also governed by the extended system of multiple intermolecular H-bonds involving all coordinated and solvated water molecules, which leads to the formation of a 3D architecture (Figure 3b).

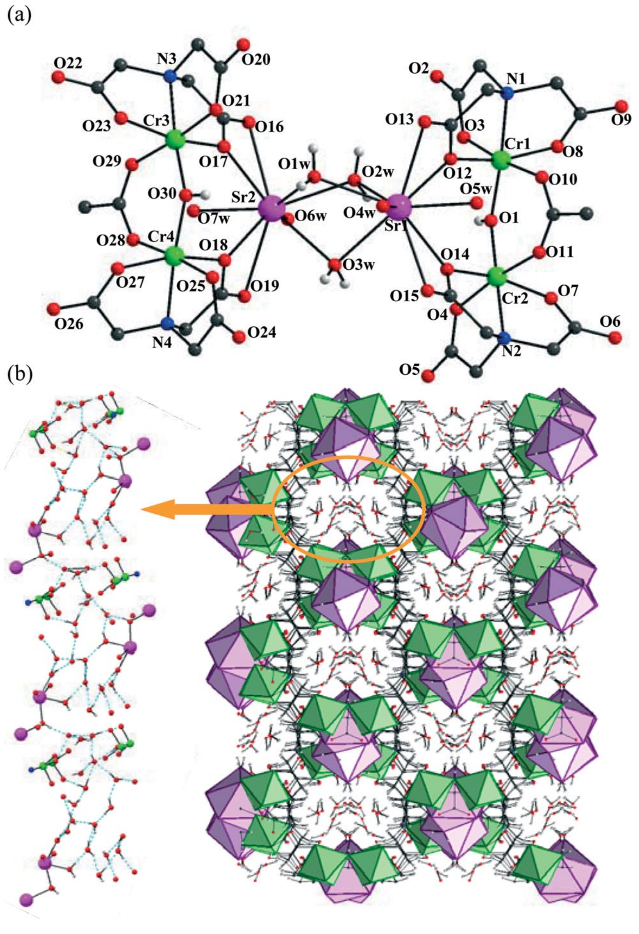

Figure 2. (a) Molecular structure of the hexanuclear $[Sr_2Cr_4(\mu\text{-OH})_2(\mu\text{-OAc})_2(nta)_4 7H_2O]\cdot 14H_2O$ (**II**) complex; (b) hydrogen-bonding network implied in the packing of compound **II**.

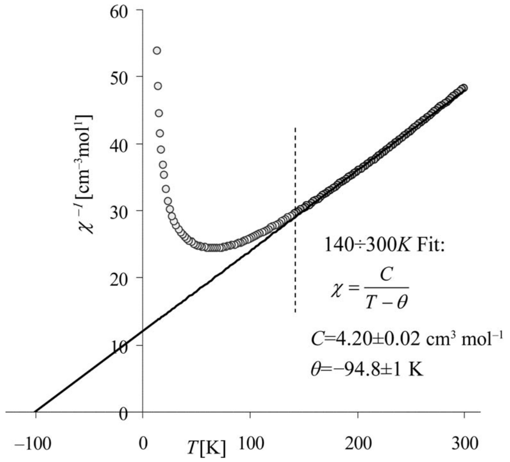

Figure 3. Inverse molar susceptibility $[\chi_M(T)]^{-1}$ vs. temperature T for **I** ($CaCr_2$).

The main difference between compounds **I**, **II** and **III** comes from the structural properties of the cations, especially their ionic radii (Ca^{2+} Sr^{2+} Pb^{2+})[18] and their coordination numbers. So, Ca^{2+} with an ionic radius of 0.99 Å prefers coordination numbers of 6–7, whereas Sr^{2+} and Pb^{2+} prefer coordination numbers of 7–9 owing to their larger ionic radii (1.12 Å for Sr and 1.19 Å for Pb).[18]

In our case, the chromium complex acts as a tetradentate compartmental ligand with four oxygen donor atoms, which is selective to ionic radii around 1.1–1.2 Å. We also obtained complexes with barium and magnesium ions that possess larger (1.35 Å) and smaller (0.72 Å) ionic radii.[18] According to their chemical analyses and IR spectra, we can assume the presence of similar chromium building blocks in these compounds. Unfortunately, we were not able to grow crystals suitable for X-ray analysis.

The magnetic behaviour of compounds **I**–**III** was studied in the 2–300 K temperature range. The data were corrected for diamagnetic contributions of the ligands estimated from Pascal's constants. As an example, the magnetic behaviour of trinuclear calcium chromium compound **I** is shown in Figure 3 in the form of a Curie–Weiss plot of the thermal variation of the $(\chi_M)^{-1}$ susceptibility.

For one mole of chromium atoms with spins $S = 3/2$ and $g = 2.0$ the expected constant C is equal to $1.88\,cm^3\,K\,mol^{-1}$, so that the theoretical Curie constant is $3.76\,cm^3\,K\,mol^{-1}$ for **I**. The calculated value obtained from the fitting of the experimental data in the 140–300 K temperature range is slightly larger [$4.20(2)\,cm^3\,K\,mol^{-1}$], which is in agreement with the presence of an antiferromagnetic interaction. This behaviour is also confirmed by the evolution of $(\chi_M)^{-1}$ in the low-temperature range.

For the hexanuclear heterometallic Sr_2Cr_4 compound, $\chi_M T$ is equal to $6.41\,cm^3\,K\,mol^{-1}$ at 300 K, a value smaller than the one expected for two uncoupled metal ($S = 3/2$) ions ($7.504\,cm^3\,K\,mol^{-1}$) in the $^4A_{2g}$ ground state (Figure 4). Lowering the temperature induces $\chi_M T$ to decrease to $0.019\,cm^3\,K\,mol^{-1}$ at 2 K. That corresponds to an $S = 0$ spin state, which results from antiferromagnetic coupling. Taking into consideration the structural information, the magnetic data for **II** and **III** can be presented as a sum of two isolated dimers.

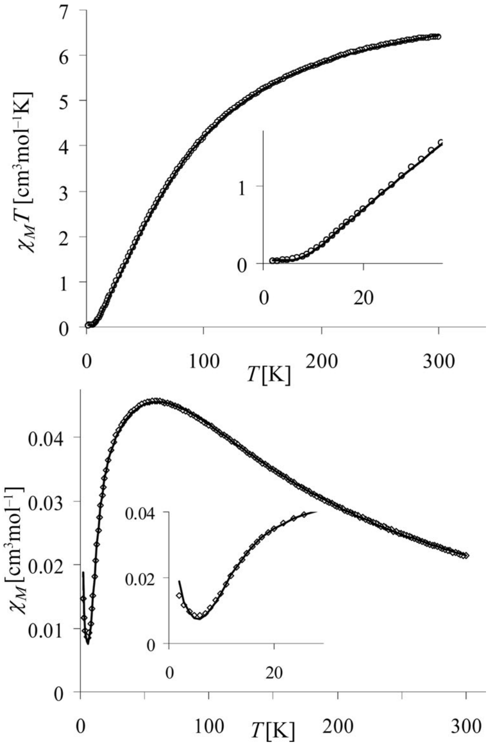

Figure 4. Plots of $\chi_M T$ and χ_M vs. temperature for **II** (Sr_2Cr_4). The solid lines represent the best fit corresponding to the model described in the text.

Therefore, quantitative analysis was performed on the basis of classical HDVV formalism derived from the isotropic Hamiltonian[19] $H_d = -2JS_1S_2$. The data were fit in the simultaneous $\chi_M T(T)$ and $\chi_M(T)$ thermal dependences including temperature independent paramagnetism (*TIP*), impurity contribution (ρ) and intermolecular interaction (zj) according to the expressions:

$$\chi_d(T) = \frac{Ng^2\mu_B^2}{kT} \cdot \frac{2e^{\left(\frac{2J}{kT}\right)} + 10e^{\left(\frac{6J}{kT}\right)} + 28e^{\left(\frac{12J}{kT}\right)}}{1 + 3e^{\left(\frac{2J}{kT}\right)} + 5e^{\left(\frac{6J}{kT}\right)} + 7e^{\left(\frac{12J}{kT}\right)}}$$

$$\chi_M(T) = n \cdot \frac{\chi_d(T)}{\left(1 - \frac{\chi_d(T)zj}{Ng^2\mu_B^2}\right)} \cdot (1-\rho) + \rho \cdot \frac{Ng^2\mu_B^2}{3kT} \cdot S(S+1) + TIP$$

where n = 1 for **I** and n = 2 for **II** and **III**. The results of the best fits, presented in Table 1, (Figures S1 and S2, see Supporting Information) correspond to antiferromagnetic interactions J around -14 cm^{-1}. This value is very close to the ones obtained in chromium dimers containing two μ-OH bridges. In contrast to previous results, the data are perfectly fitted without use of biquadratic exchange parameters.

The J values obtained for **I**–**III** are in agreement with the literature values reported for similar bridging units.[4,17]

Experimental Section

Materials: All starting materials and solvents were purchased from Aldrich and used without further purification.

Physical Measurements: IR spectra (KBr pellets) were recorded with a GX system 2000 Perkin–Elmer spectrophotometer. Magnetic susceptibility data (2–300 K) were collected on powdered samples with a Quantum Design MPMS SQUID susceptometer. Diamagnetic corrections were applied using Pascal's constants.[20]

Preparation of Complexes

[(Hexaaquacalcium){μ-hydroxy-μ-acetato-*O,O′*-bis[nitrilotriacetatochromium(III)]}] Dihydrate [$\{Ca(H_2O)_6\}\{Cr_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)(nta)_2\}$]·$2H_2O$ (I): Water (50 mL) was added to a mixture of H_3nta (0.38 g, 2 mmol) and dispersed $CaCO_3$ (0.6 g, 6 mmol). After complete $CaCO_3$ dissolution, $CrCl_3\cdot6H_2O$ (0.52 g, 2 mmol) in water (15 mL) was added to the initial solution (the temperature was maintained at about 95 °C). After heating for 1 h, the pH of the solution was adjusted to 5.0–5.5 with acetic acid (1 M). The reaction mixture was filtered and concentrated to a volume of 15 mL. Crystals were separated by filtration after one week and washed with cold water, ethanol and ether. Yield: 74%. $C_{14}H_{32}CaCr_2N_2O_{23}$ (740.47): calcd. C 22.71, H 4.36, Cr 14.04, N 3.78; found C 23.53, H 3.90, Cr 13.90, N 3.17. IR (KBr): $\tilde{\nu}$ = 3312 (m, br.) ν(OH), 1630 (s) $\nu_{as}(CO_2)$, 1560 (s), 1466 (m) $\nu_s(CO_2)$, 1377 (s), 1335 (m), 1278 (m) $\rho_\omega(CH_2)$, 1212 (m), 1094 (m) ν(CN), 1016 (m), 936 (m) ν(CC), 910 (s) δ(CrOH), 749 (s) $\delta(CO_2)$, 599 (vs) $\rho_\omega(CO_2)$ cm^{-1}.

[{Tris(μ-aqua)bis(diaquastrontium)}bis{μ-hydroxy-μ-acetato-*O,O′*-bis(nitrilotriacetatochromium(III))}] Tetradecahydrate [$\{(H_2O)_2Sr(\mu\text{-}H_2O)_3Sr(H_2O)_2\}\{Cr_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)(nta)_2\}_2$]·$14H_2O$ (II): Compound **II** was obtained by a synthetic procedure analogous to that of **I**. Yield: 38%. $C_{28}H_{74}Cr_4N_4O_{51}Sr_2$ (1666.11): calcd. C 20.18, H 4.48, Cr 12.48, N 3.36; found C 20.53, H 3.78, Cr 13.90, N 3.06. IR (KBr): $\tilde{\nu}$ 3387 (m, br.) ν(OH), 1624 (vs) $\nu_{as}(CO_2)$, 1560 (vs), 1466 $\nu_s(CO_2)$, 1379 (s), 1341, 1277 (m) $\rho_\omega(CH_2)$, 1204, 1095 ν(CN), 1004, 958 ν(CC), 938, 911 δ(CrOH), 748 (s) $\delta(CO_2)$, 663 (s) $\rho_\omega(CO_2)$, 619 (s) cm^{-1}.

[{Tris(μ-aqua)bis(diaqualead(II))}bis{μ-hydroxy-μ-acetato-*O,O′*-bis(nitrilotriacetatochromium(III))}] Tetradecahydrate [$\{(H_2O)_2Pb(\mu\text{-}H_2O)_3Pb(H_2O)_2\}\{Cr_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)(nta)_2\}_2$]·$14H_2O$ (III): $(NH_4)_2SO_4$ (0.132 g, 1 mmol) was stirred with **II** (0.833 g, 0.5 mmol). The reaction mixture was filtered and added to $Pb(NO_3)_2$ (0.331 g, 1 mmol). After 24 h, red crystals were obtained. Yield: 45%. $C_{28}H_{74}Cr_4N_4O_{51}Pb_2$ (1905.27): calcd. C 17.65, H 3.91, Cr 10.92, N 2.94, Pb 21.75; found C 18.23, H 3.57, Cr 11.07, N 3.00, Pb 22.27. IR (KBr): $\tilde{\nu}$ 3383 (m, br.) ν(OH), 1699 (s) $\nu_{as}(CO_2)$, 1551 (s), 1465 (m) $\nu_s(CO_2)$, 1388 (s), 1203 (w) $\rho_\omega(CH_2)$, 1094 (m)

Table 1. Magnetic data for compounds **I**–**III**.

	J [cm^{-1}]	zj [cm^{-1}]	g	C [cm^3 K mol^{-1}]	$\Theta(K)$	*TIP*	ρ	R
I ($CaCr_2$)	–14.2(3)	–0.005(2)	2.01(3)	4.20(1)	–95(1)	5×10^{-5}	0.012	$1{,}3 \times 10^{-4}$
II (Sr_2Cr_4)	–13.31(1)	–0.008(1)	2.00(1)	8.35(3)	–87(1)	3.1×10^{-4}	0.005	5×10^{-5}
III (Pb_2Cr_4)	–14.75(2)	–0.004(2)	2.00(2)	8.35(3)	–100(1)	3.1×10^{-4}	0.019	9×10^{-5}

Table 2. Crystallographic data collection and structure determinations for complexes **I**–**III**.

Compound	**I**	**II**	**III**
Formula	$C_{14}H_{32}CaCr_2N_2O_{23}$	$C_{28}H_{74}Cr_4Sr_2N_4O_{51}$	$C_{28}H_{74}Cr_4Pb_2N_4O_{51}$
Formula weight	740.47	1666.11	1905.27
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a [Å]	11.0158(3)	13.7878(4)	13.8428(5)
b [Å]	11.7105(3)	16.1023(5)	16.0624(6)
c [Å]	13.5750(4)	27.0316(8)	26.8937(9)
α [°]	110.744(2)	90	90
β [°]	95.038(1)	100.871(2)	101.103(2)
γ [°]	116.989(1)	90	90
V [Å^3]	1392.88(7)	5893.7(3)	5867.8(4)
Z, $\rho_{\text{calcd.}}$ [g cm^{-3}]	2, 1.766	4, 1.884	4, 2.157
λ [Å]	0.71073	0.71073	0.71073
T [K]	180	180	180
μ(Mo-K_α) [cm^{-1}]	1.065	2.636	6.559
GOOF for F^2	1.033	1.004	1.006
R [$I > 2\sigma(I)$][a]	0.0247	0.0296	0.0245
wR (all data)[b]	0.0667	0.0733	0.0595
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ [e Å^3]	0.406 and –0.631	0.943 and –0.503	1.611 and –1.603

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

ν(CN), 1002 (m), 957 ν(CC), 936 (m), 911 (s) δ(CrOH), 741 (s) δ(CO_2), 664 (s) ρ_ω(CO_2), 616 (s).

Substances **I**–**III** are soluble in water, slightly soluble in DMSO and DMF and insoluble in ethanol and acetone.

X-ray Structure Determination: The X-ray data for **I**, **II** and **III** were collected with a STOE Imaging Plate Diffractometer System (IPDS) equipped with an Oxford Cryosystems cooling system and by using graphite monochromated Mo-K_α X-rays (λ = 0.71073 Å). Data were collected[21a] by using ϕ rotation movement with the crystal-to-detector distance equal to 60 mm (ϕ = 0.0–270°, $\Delta\phi$ = 1.5°). All the structures were solved by direct methods by using SHELXS-97[21b] and refined by full-matrix least-squares on F_o^2 with SHELXL-97[21c] with anisotropic displacement parameters for non-hydrogen atoms. All the hydrogen atoms were obtained from difference Fourier syntheses. Positional parameters of H(water) atoms were verified by the geometric parameters of the corresponding hydrogen bonds and included in the refinement in the riding-model approximation with U_{iso} = 1.2 U (atom of attachment). Scattering factors were taken from the standard compilation.[21d] The molecular plots were obtained by using the ZORTEP program. Sixteen-electron absorption corrections were introduced by semiempirical methods based on equivalent reflections by using the program MULTISCAN.[21f] The final full-matrix least-squares refinement, minimizing $[\Sigma_w(|F_o^2| - |F_c^2|)^2]^2$, converged at the values of R and wR listed in Table 2, together with the main crystallographic parameters. CCDC-667926 (for **I**), -667927 (for **II**) and -667928 (for **III**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Magnetic susceptibility data for **I** and **III** in terms of $\chi_M T$ and χ_M vs. T plots; selected bond lengths for **I**, **II** and **III**

Acknowledgments

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