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2,2′-Oxydiacetato-bridged complexes containing Sm(III) and bivalent cations. Synthesis, structure, magnetic properties and chemical speciation

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Abstract

Heterometallic compounds containing Sm(III), bivalent cations M (M = Cu, Ni, Co, Mn, Ca, Mg), and 2′,2′-oxydiacetate (oda) as connecting ligand have been prepared and characterized. The complexes can be formulated as $[Sm_2M_3(oda)_6] \cdot xH_2O$. The structure of $[Sm_2Cu_3(oda)_6(H_2O)_6]$ shows the presence of the Sm(III) coordinated by six carboxy and three ether oxygen atoms, and the Cu(II) cation bonded to four carboxy oxygens and two molecules of water. An open 3D framework is observed, containing large hexagonal channels. At room temperature, the polynuclear complexes behave as built by magnetically isolated paramagnetic ions, but at low temperatures, very weak antiferromagnetic interactions M – M are predominant. The chemical systems were also investigated in solution (25.0 °C, $I = 0.5$ M Me_4NCl) by potentiometry. The same kind of polynuclear species have been found.

Keywords: Lanthanide; 2,2′-Oxydiacetate; Polynuclear complexes; Carboxylato bridge

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1. Introduction

During the last ten years, heterobimetallic complexes containing Cu(II) and lanthanide ions (Ln) bridged by carboxylic acids have been reported and studied [1–13]. Other examples, though scarce, include analogous complexes containing other metals instead of copper [14–16]. In such compounds, metal ions are connected by carboxylato bridges resulting in different structural architectures, from discrete bimetallic complexes to extended 3D arrays. Besides the fascinating structural diversities, these compounds show potential applications in different fields. They are appropriate models to study the nature of magnetic interactions between lanthanides and d-transition metal ions, and they could be useful materials in separation, catalysis, gas storage and molecular recognition [17–19]. A very recent and excellent review accounts for this kind of polynuclear complexes [20].

Among the potential carboxylato bridges, oda (2,2′-oxydiacetate) has proved to bridge Ln(III) and Cu(II) with the formation of very interesting structures [1–7]. In these structures, the Ln metal ion is nine coordinated, being surrounded by nine oxygen atoms from three oda ligands. Copper atoms are six coordinated by six oxygen atoms, four from $[Ln(oda)_3]$ units (through a μ-COO bridge), and two from water molecules. The structures $[Ln_2Cu_3(oda)_6] \cdot 3H_2O$

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(Ln = Gd, Nd), $[Ln_2Cu_3(oda)_6(H_2O)_6] \cdot 12H_2O$ (Ln = Dy, Ho, Y, Gd, Eu, Nd, Pr), $[Ln_2Cu_3(oda)_6(H_2O)_6]$ (Ln = Nd, Er, Yb), and $[Ln_2Cu_3(\mu_2\text{-}H_2O)(oda)_6(H_2O)_3] \cdot 3H_2O$ (Ln = La, Ce) have been reported. Analogous complexes with Sm, Tb, Tm and Lu have not been studied. The most interesting point in the structures is the formation of a 3D network containing large hexagonal channels of nearly 6Å diameter. The channels contain the lattice water molecules. This type of structures is very interesting for many applications. As catalysts for example, they can provide appropriate binding and activation of the reacting molecules, as well as stabilization of reaction intermediates and transition states.

Up to now, the studies on these heteropolynuclear complexes have been mostly focused on lanthanide-copper compounds at solid state. No reports can be found on the possibility to prepare analogous complexes with other M(II) transition metals. Moreover, it would be very interesting to know if such polynuclear species can also exist in aqueous solution. If so, the complexes would be potential homogeneous catalysts for many processes.

With this in mind, we decided to investigate the Sm(III)-oda-M(II) (M = Cu, Mn, Ni, Fe, Co, Ca, Zn, Cd, Be, Mg, Pb) and Sm(III)-oda-VO^{2+} systems, both at solid state and in solution. Samarium has not been previously studied, neither in solution nor at solid state, and provides a new example to further investigate this interesting series. Chemical speciation of these systems at 25.0 °C, $I = 0.5$ M Me_4NCl is reported for the first time. In addition, a few systems containing M′(III) cations (M′ = Fe, Al) are included in this work. We also report susceptibility measurements of the magnetically relevant heteropolynuclear species.

2. Experimental

2.1. Materials and methods

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. $Sm(NO_3)_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$, $BeSO_4 \cdot 4H_2O$, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$, $CoCl_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and an aqueous commercial 48% solution of $VOCl_2$, were used as metal sources. 2,2′-Oxydiacetic acid solutions were prepared by weighing the Fluka reagent.

The infrared spectra, as KBr pellets, were obtained from a Bomen MB 102 FT-IR spectrophotometer. Elemental analysis (C, H) was performed on a Carlo Erba EA 1108 instrument. Thermal analysis was performed on a Shimadzu TGA-50 instrument with a TA 50I interface, using a platinum cell and nitrogen atmosphere. Experimental conditions were 0.5 °C min^{-1} temperature ramp rate and 50 mL min^{-1} nitrogen flow rate.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[Sm_2 Cu_3(oda)_6] \cdot 18H_2O$(**1**)

$Cu(NO_3)_2 \cdot 3H_2O$ (0.36 g, 1.5 mmol) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.44 g, 1.0 mmol) were dissolved in 10 mL of water. 2,2′-Oxydiacetic acid (0.40 g, 3.0 mmol) was dissolved in another 10 mL water, and the pH value was adjusted to 7.0 with ammonium hydroxide. Both solutions were mixed, and a clear blue solution was obtained. After a few minutes a microcrystalline pale blue solid was obtained, and separated by filtration, washed with water (3 × 2 mL), and dried with acetone (2 × 2 mL) and diethylether (3 × 2 mL). The mother liquour was allowed to evaporate slowly for 4–5 days in order to obtain suitable crystals for X-ray diffraction. Yield 60–70%. *Anal.* Calc. for $C_{24}H_{60}O_{48}Cu_3Sm_2$: C, 17.9; H, 3.8. Found: C, 19.8; H, 4.2%. IR peaks associated to the oda ligand appear at: 1605, 1439, and 1124 cm^{-1}. The TGA diagram shows a weight loss of 19.6% in the range 50–100 °C which corresponds to the loss of all water molecules, calc. 20.2%. Decomposition point, 216 °C.

2.2.2. Synthesis of $[Sm_2Ni_3 (oda)_6] \cdot 18H_2O$(**2**)

$Ni(NO_3)_2 \cdot 6H_2O$ (0.44 g, 1.5 mmol) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.44 g, 1.0 mmol) were dissolved in 10 mL of water. 2,2′-Oxydiacetic acid (0.40 g, 3.0 mmol) was dissolved in another 10 mL water, and the pH value was adjusted to 7.0 with ammonium hydroxide. Both solutions were mixed, and a clear green solution was obtained. The solution was allowed to evaporate slowly at room temperature for 4–5 days. A pale green solid was filtered, washed with water (3 × 2 mL), and dried with acetone (2 × 2 mL) and diethylether (3 × 2 mL). Yield 35–40%. *Anal.* Calc. for $C_{24}H_{60}O_{48}Ni_3Sm_2$: C, 18.1; H, 3.8. Found: C, 18.0; H, 4.0%. IR peaks associated to the oda ligand appear at: 1618, 1438, and 1125 cm^{-1}. The TGA diagram shows a weight loss of 20.4% in the range 50–220 °C which corresponds to the loss of all water molecules, calc. 20.3%. Decomposition point, 296 °C.

2.2.3. Synthesis of $[Sm_2 Co_3(oda)_6] \cdot 18H_2O$(**3**)

This compound was obtained as **2**, starting from $Co(NO_3)_2 \cdot 6H_2O$ (0.44 g, 1.5 mmol). A microcrystalline pink solid was collected after 4–5 days. Yield 40–45%. *Anal.* Calc. for $C_{24}H_{60}O_{48}Co_3Sm_2$: C, 18.1; H, 3.8. Found: C, 17.9; H, 4.1%. IR peaks associated to the oda ligand appear at: 1608, 1438, and 1125 cm^{-1}. The TGA diagram shows a weight loss of 20.5% in the range 50–160 °C which corresponds to the loss of all water molecules, calc. 20.4%. Decomposition point, 237 °C.

2.2.4. Synthesis of $[Sm_2 Mn_3(oda)_6] \cdot 9H_2O$(**4**)

This compound was obtained as **2**, starting from $Mn(NO_3)_2 \cdot 4H_2O$ (0.38 g, 1.5 mmol). Cubic pale yellow crystals were collected after 4–5 days. Yield 40–45%. *Anal.* Calc. for $C_{24}H_{42}O_{39}Mn_3Sm_2$: C, 20.3; H, 3.0. Found: C, 20.2; H, 3.1%. IR peaks associated to the oda ligand