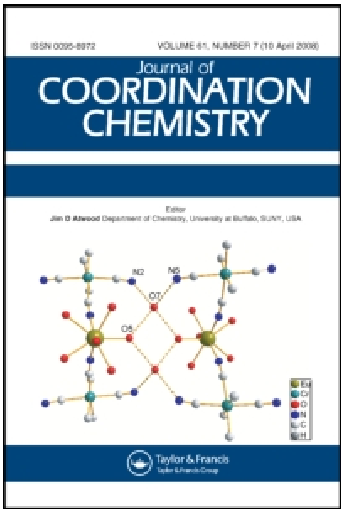

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

An oxo-centered carboxylate-bridged trinuclear complex: synthesis, crystal structure, and magnetic properties of $[Cr_3(\mu_3\text{-}O)(HL)_2(H_2O)_3](ClO_4)_3$

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To cite this Article Gao, Feng-Xian , Gu, Wen , Yang, Yong-Sheng , Ma, Xiao-Fang , Qian, Jing and Yan, Shi-Ping(2008) 'An oxo-centered carboxylate-bridged trinuclear complex: synthesis, crystal structure, and magnetic properties of $[Cr_3(\mu_3\text{-}O)(HL)_2(H_2O)_3](ClO_4)_3$', Journal of Coordination Chemistry, 61: 9, 1455 — 1461
To link to this Article: DOI: 10.1080/00958970701583946
URL: http://dx.doi.org/10.1080/00958970701583946

Journal of Coordination Chemistry
Vol. 61, No. 9, 10 May 2008, 1455–1461

An oxo-centered carboxylate-bridged trinuclear complex: synthesis, crystal structure, and magnetic properties of $[Cr_3(\mu_3\text{-}O)(HL)_2(H_2O)_3](ClO_4)_3$

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(*Received 29 January 2007; in final form 11 June 2007*)

A new complex $[Cr_3(\mu_3\text{-}O)(HL)_2(H_2O)_3](ClO_4)_3$, L = 1,4,7-triazacyclononane-*N*,*N′*,*N″*-tripropionate(tacntp), has been synthesized and structurally characterized. The complex crystallizes in the orthorhombic, space group *Pccn*, with unit cell parameters $a = 18.245(3)$ Å, $b = 18.955(3)$ Å, $c = 27.806(4)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. The complex has a trimetallic structure with three metal ions at the corners of a nearly equilateral triangle and the center occupied by a triply-bridging oxygen. Variable-temperature magnetic susceptibility indicates that the total spin value of the ground state is 3/2.

Keywords: Chromium; Crystal structure; tacntp; Magnetic property

1. Introduction

Magnetic exchange interactions in polynuclear assemblies and more specifically for molecules which possess high-spin ground states are of interest [1]. Oxo-centered carboxylate-bridged complexes, $[M_3O(RCOO)_6(L)_3]^+$ (M: metal atom; RCOOH: carboxylic acid; L: terminal ligand (water, methanol, pyridine (Py), piperidine (Pip), etc.)), represent one of the most intensely studied classes of polynuclear compounds [2a]. In 1970, the first accurate structure was reported for $[Cr_3O(O_2CCH_3)_6(H_2O)C_3]Cl \cdot 6H_2O$ [2b]. In such compounds all three metal atoms are M(III); in 1972, the first example of a compound having L other than H_2O and metal atoms in formal oxidation states II, III, and III was reported [2c], $Ru_3O(O_2CCH_3)_6(PPh_3)_3$, with a non-equilateral trinuclear metal cluster. Vlachos *et al.* synthesized $[Cr_3O(O_2CPh)_6(MeOH)_3](NO_3) \cdot 2MeOH$ (**1** · 2MeOH), which is invaluable in synthesizing polynuclear chromium(III) carboxylate clusters with interesting physical and biological properties [2d].

These species serve as suitable models for studying electronic and magnetic metal–metal interactions in clusters, represent precursors for clusters of higher

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701583946

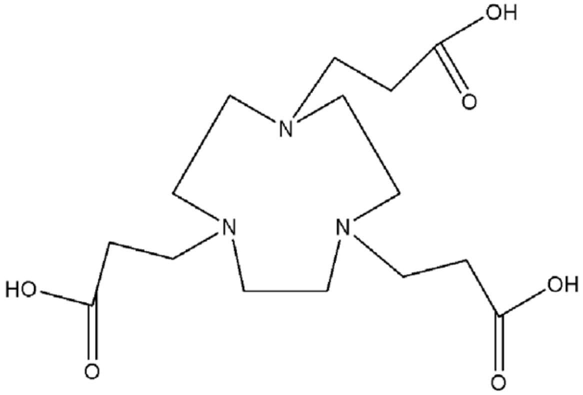

Figure 1. tacntp.

nuclearity whose unusual structural design and physical properties open new opportunities for experimental modeling of biocatalysis, and their structural variations allow a close examination of parameters affecting the stability of metal–ligand aggregates [2a–12].

Many complexes of TACN (TACN = 1,4,7-triazacyclononane) and its *N*-substituted derivatives are structural and functional models of various metallo-enzymes [13–19]. The synthesis of a manganese(III) complex containing tacntp was reported by Fukuda *et al.* [20]. Here we report a study of magnetic properties of the chromium(III) complex with tacntp and its synthesis and structure.

2. Experimental

2.1. *Materials and instrumentation*

TACN was prepared as previously [21, 22] and aqueous solutions containing the ligand tacntp (figure 1) were prepared as reported earlier [20, 23]. All starting materials and solvents were of analytical purity. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer instrument. IR spectra were measured using KBr disks in a Bruker Tensor 27 FTIR spectrophotometer in the 400–4000 cm^{-1} region.

2.2. *Preparation of the compound*

$[Cr_3(\mu_3\text{-}O)(HL)_2(H_2O)_3](ClO_4)_3$: A solution of $Cr(ClO_4)_3 \cdot 6H_2O$ (0.1406 g, 0.3 mmol) in acetonitrile (5 mL) was added to a solution of L (0.3 mmol) in water (10 mL). The reaction mixture was stirred under refluxing for 30 min giving a clear deep-green solution; then a solution of NaN_3 (0.0195 g, 0.3 mmol) in water (5 mL) was slowly added dropwise. The reaction mixture was stirred continuously for 2 h, filtered to remove insoluble particles and slowly evaporated to give dark-green crystals suitable for X-ray crystallographic analysis. Anal. Calcd for **1** (%): C 29.72, H 8.79, and N 6.94; Found: C 29.69, H 8.72, and N 6.90.

Table 1. Data collection and processing parameters for **1**.

Empirical formula	$C_{30}H_{56}Cl_3Cr_3N_6O_{28}$
Formula weight	1211.16
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pccn*
Unit cell dimensions (Å, °)	
a	18.245(3)
b	18.955(3)
c	27.806(4)
α	90
β	90
γ	90
V (Å^3)	9616(3)
Z	8
Dx (Mg m^{-3})	1.673
μ (mm^{-1})	0.93
F(000)	5000
Crystal size (mm^3)	0.20 × 0.16 × 0.14
θ range (°)	1.46–25.02
Reflections collected/unique	46,410/8448 [R(int) = 0.1339]
Max. (transmission)	1
Min.	0.632547
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8448/242/702
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\theta(I)$]	$R_1 = 0.0711$, $wR_2 = 0.1748$
R indices (all data)	$R_1 = 0.1838$, $wR_2 = 0.2843$

2.3. *X-ray crystallography*

Diffraction data for **1** was collected at 293 K with a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the $\omega - 2\theta$ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities [24]. The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares procedures on F^2 using SHELX-97 [25]. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Further details about crystal data and structure refinement are summarized in table 1. Bond lengths and angles for the complex are listed in table 2.

3. Results and discussion

The core of the complex consists of an isosceles triangle of Cr(III) centers with a central μ_3-oxo group (figure 2). Each Cr(III) ⋯ Cr(III) vector is further bridged by two COO$^-$ groups from two Htacntp ligands, while a terminal water molecule completes six coordination at each metal forming an octahedron. The Cr(III) atoms have almost identical distances to the central oxygen atom, Cr1–O are 1.89(15) Å and Cr2–O 1.9(3) Å. So the $Cr_3(\mu_3\text{-}O)$ unit presents a regular isosceles triangle (figure 3). The trigonal geometry at the μ_3–O bridge is reflected by Cr–μ_3–O–Cr angles close to 120°. All the distances between the Cr(III) atoms and the oxygen atoms of the COO-groups are 2.0(2) Å. The Cr–O bonds are 2.0(2) Å for water molecules. Cr–O bond lengths lie in

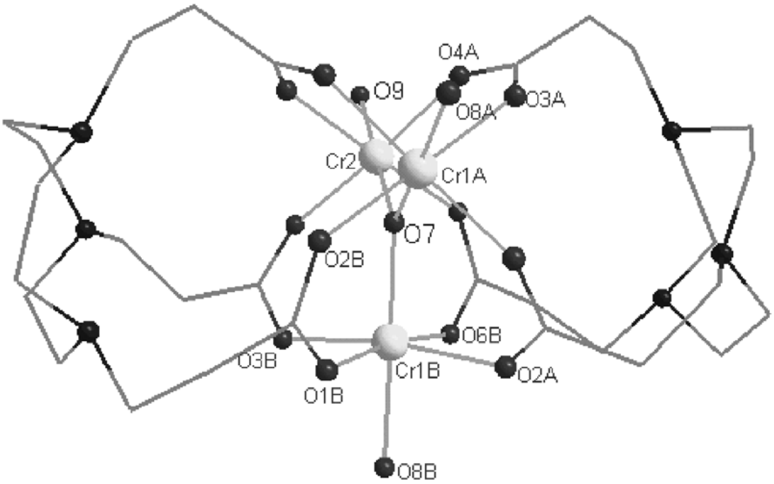

Figure 2. The diagram of **1** showing the coordination environment of Cr(III) ion, hydrogens are omitted for clarity.

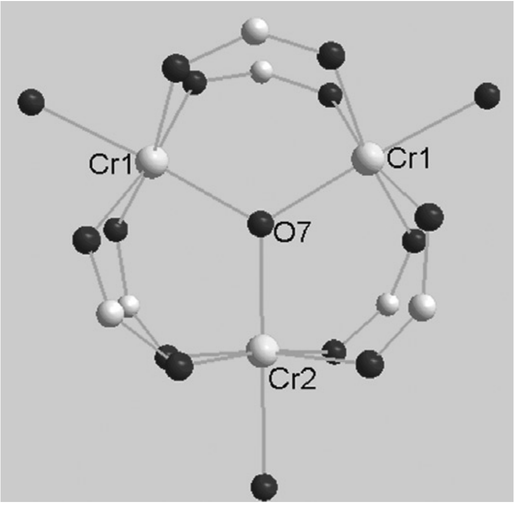

Figure 3. The diagram of the Cr_3 (μ_3-O) unit, hydrogens, nitrogens and part of carbons are omitted for clarity.

the expected range [26–29]. The complex joins a family of structurally characterized complexes containing the (μ_3-oxo)hexakis(μ-carboxylato)trichromium(III) structural unit [29].

3.1. *IR spectrum*

The IR spectrum exhibits strong bands at 1570 and 1397 cm^{-1}, assigned to the $\nu_{as(COO)}$ and $\nu_{s(COO)}$ modes, respectively [29–31]. The $\Delta\nu(\nu_{as(COO)}\text{-}\nu_{s(COO)})$ is 173 cm^{-1}, indicating

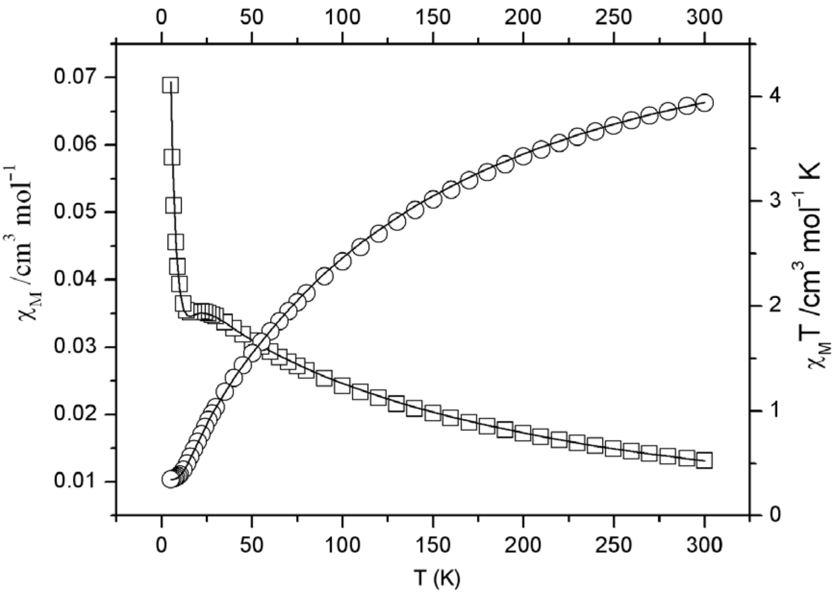

Figure 4. The χ_M and χ_{MT} *vs.* *T* plots.

monodentate carboxylate groups [32]. A strong band at 661 cm^{-1} is attributed to the $\nu_{as}(Cr_3O)$ vibration [33]. These IR results are consistent with the crystal structure.

3.2. *Magnetic susceptibility studies*

The magnetic susceptibility of the complex was measured in the temperature range 2–300 K on a SQUID MPMS XL-7 magnetometer. The χ_M and $\chi_M T$ *versus* *T* plots are shown in figure 4. The value of $\chi_M T$ at room temperature is 3.94 emu mol^{-1} K, smaller than expected for three uncoupled $S = 3/2$ spins (5.628 emu mol^{-1} K) indicative of antiferromagnetic coupling even at room temperature. Upon cooling, the $\chi_M T$ value decreases smoothly to a minimum at ca 2 K ($\chi_M T = 0.3080$ cm^3 mol^{-1} K). The shape of the curve is as expected for a triangular array of equivalent, antiferromagnetically coupled, Cr(III) ions [29, 34–36]. For this system, the magnetic susceptibility is given by

$$\chi_m = \frac{Ng^2\beta^2}{12KT} \left[\frac{445 + 512\exp(-gJ/KT) + 315\exp(-16J/KT) + 120\exp(-21J/KT) + 6\exp(-24J/KT)}{5 + 8\exp(-gJ/KT) + 9\exp(-16J/KT) + 8\exp(-21J/KT) + 2\exp(-24J/KT)}\right] + N_\alpha$$

where *J* is the exchange coupling constant. The experimental susceptibilities were fit to this expression employing *g* and *J* as variable parameters. Fitting the experimental data to the expression leads to $g_{Cr} = 1.92$, $J = -12.4$ cm^{-1}, the agreement factor *R* $[R = \sum(\chi_{obs} - \chi_{Cald})^2/\sum(\chi_{obs})^2] = 9.7186 \times 10^{-4}$. The value of *J* is in excellent agreement with the value of -10 cm^{-1} obtained by analysis of high temperature data for the related complex, $[Cr_3O(O_2CCH_3)_6(H_2O)_3]Cl \cdot 6H_2O$ [35, 36].

Table 2. Bond lengths (Å) and angles (°) for **1**.

Cr(1)–O(7)	1.89(15)
Cr(1)–O(1)	2.0(2)
Cr(1)–O(6)#1	2.0(2)
Cr(1)–O(3)	2.0(2)
Cr(1)–O(2)#1	2.0(2)
Cr(1)–O(8)	2.0(2)
Cr(2)–O(7)	1.9(3)
Cr(2)–O(4)	2.0(2)
Cr(2)–O(4)#1	2.0(2)
Cr(2)–O(5)#1	2.0(2)
Cr(2)–O(5)	2.0(2)
Cr(2)–O(9)	2.0(3)
O(7)–Cr(1)–O(1)	96(9)
O(7)–Cr(1)–O(6)#1	93(9)
O(1)–Cr(1)–O(6)#1	171(10)
O(7)–Cr(1)–O(3)	94(8)
O(1)–Cr(1)–O(3)	88(10)
O(6)#1–Cr(1)–O(3)	94(10)
O(7)–Cr(1)–O(2)#1	96(8)
O(1)–Cr(1)–O(2)#1	90(10)
O(6)#1–Cr(1)–O(2)#1	87(10)
O(3)–Cr(1)–O(2)#1	171(10)
O(7)–Cr(1)–O(8)	177(10)
O(1)–Cr(1)–O(8)	87(9)
O(6)#1–Cr(1)–O(8)	85(9)
O(3)–Cr(1)–O(8)	84(9)
O(2)#1–Cr(1)–O(8)	87(9)
O(7)–Cr(2)–O(4)#1	95(7)
O(4)–Cr(2)–O(4)#1	171(10)
O(7)–Cr(2)–O(5)#1	94(7)
O(4)–Cr(2)–O(5)	87(10)
O(4)#1–Cr(2)–O(5)	93(10)
O(5)#1–Cr(2)–O(5)	172(10)
O(7)–Cr(2)–O(9)	180(11)
O(4)–Cr(2)–O(9)	85(7)
O(5)–Cr(2)–O(9)	86(7)
Cr(1)–O(7)–Cr(1)#1	119(10)
Cr(1)–O(7)–Cr(2)	121(7)
Cr(1)#1–O(7)–Cr(2)	121(7)

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1/2$, $-y+1/2$, z; #2: $-x+3/2$, $-y+1/2$, z, c.

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 621955. Copies of the data can be obtained free of charge on application to CCDC, Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20331020).

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