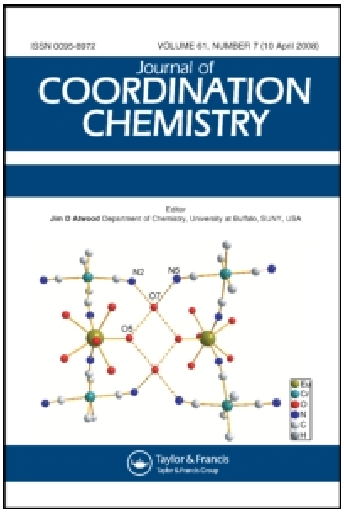

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A Macrocyclic Chromium(III) complex with mixed Hydroxo and Carbonato bridges: Crystal structure and Magnetic properties of $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}CO_3)Cr(tacn)](ClO_4)_2\cdot 3H_2O$ (tacn=1,4,7-Triazacyclononane)

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A MACROCYCLIC CHROMIUM(III) COMPLEX WITH MIXED HYDROXO AND CARBONATO BRIDGES: CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $[(tacn)Cr(\mu\text{-}OH)_2\ (\mu\text{-}CO_3)Cr(tacn)](ClO_4)_2\cdot 3H_2O$ (tacn=1,4,7-TRIAZACYCLONONANE)

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A novel homodinuclear complex $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}CO_3)Cr(tacn)](ClO_4)_2\cdot 3H_2O$ (tacn = 1,4,7-triazacyclononane) has been synthesized and characterized by single-crystal X-ray diffraction analysis. The complex crystallizes in space group *Pnma*, with $a = 14.323(2)$, $b = 21.958(3)$, $c = 9.0092(14)$ Å, $Z = 4$, $R_1 = 0.0552$, $wR_2 = 0.1222$. The structure consists of the binuclear cation $[(tacn)Cr(\mu\text{-}OH)_2(\mu\text{-}CO_3)Cr(tacn)]^{2+}$, uncoordinated perchlorate anions and lattice water molecules. Metal centres are linked together by two hydroxo bridges and one carbonato bridge and there are intramolecular Cr–Cr interactions. The geometry around each chromium(III) ion is distorted octahedral. Hydrogen atoms of two neighbouring 1,4,7-triazacyclononane ligands connect with the uncoordinated oxygen atom of the carbonato group through hydrogen bonds to form a 1-D chain. Measurements of variable-temperature (2–300 K) magnetic susceptibilities show an antiferromagnetic interaction between Cr(III) ions.

Keywords: Chromium(III) complex; 1,4,7-Triazacyclononane; Crystal structure; Magnetic properties

INTRODUCTION

Both homo- and heterodinuclear transition metal complexes occupy an important position in modern inorganic chemistry. Impetus for the study of these complexes derives from interests in connection with magnetic exchange interactions and electron transfer between metal ions and from their significance as models for biological systems [1–6]. Electronic and magnetic properties of dinuclear hydroxo-bridged complexes have received the attention of biochemists, inorganic chemists, and physicists. Over the

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past few years several new mixed-bridged metal complexes have been synthesized and structurally characterized [7–11]. The first dinuclear chromium complex containing mixed amido and hydroxo bridges was reported by Andersen and co-workers [12]. In addition, since the early work of Pedersen, Cram and Lehn [13], macrocyclic chemistry has attracted much attention from scientists in different areas, ranging from chemistry to solid-state physics and biology, because of its potential impact on materials science, catalysis and metallo-biochemistry [14]. The ligand 1,4,7-triazacyclononane has long been used in our group as a tridentate capping ligand [15,16]. In this article the mixed-bridged complex $[(\mathrm{tacn})\mathrm{Cr}(\mu\text{-OH})_2(\mu\text{-CO}_3)\mathrm{Cr}(\mathrm{tacn})](\mathrm{ClO}_4)_2 \cdot 3\mathrm{H}_2\mathrm{O}$ is reported together with its structural characterization. Its spectroscopic and magnetic properties are also presented.

EXPERIMENTAL

Synthesis

Anhydrous $CrCl_3$ (0.079 g, 0.5 mmol) dissolved in a minimum amount of water was slowly added to an aqueous solution of 1,4,7-triazacyclononane (0.129 g, 1.0 mmol). Several drops of triethylamine were added until the pH was equal to 8. The mixture was refluxed and stirred until it gave a clear red solution. After addition of $NaClO_4$ (1 g), the mixture was filtered and then left to stand. Several days later, well-shaped, red, single crystals suitable for X-ray structure analysis were obtained. Yield: 52%. Anal. Calcd. for $C_{13}H_{44}Cl_2Cr_2N_6O_{16}$ (%): C, 20.15; H, 6.20; N, 11.75. Found: C, 20.73; H, 5.85; N, 11.81.

Physical Measurements

Analyses for C, H and N were carried out on a Perkin-Elmer instrument at the Institute of Elemento-Organic Chemistry, Nankai University. Infrared spectra, using KBr pellets, were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 cm^{-1} and electronic spectra (aqueous solution) on a Jasco-570 spectrophotometer. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Crystal Structure Determination

A red single crystal having approximate dimensions $0.30 \times 0.25 \times 0.20$ mm was mounted on a glass fibre. Determination of the unit cell and data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from least-squares refinement of the setting angles of 25 well-centred reflections in the range 2.44–25.02° (θ) at 293 K. Intensities of the $\pm hkl$ reflections were measured up to $\theta_{\max} = 25.02°$; the ω–2θ scan technique was employed. The index range is $-5 \le h \le 17$, $-26 \le k \le 16$ and $-10 \le l \le 8$. The structure was solved by direct methods using the program SHELXS-97 [18] and subsequent Fourier difference techniques, and refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [19].

TABLE I Crystal data and structure refinement details for the complex

Empirical formula	$C_{13}H_{44}Cl_2Cr_2N_6O_{16}$
Formula weight	715.44
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions (Å)	$a = 14.323(2)$ $b = 21.958(3)$ $c = 9.0092(14)$
Volume (Å^3)	2833.3(8)
Z	4
Calculated density (Mg m^{-3})	1.658
Absorption coefficient (mm^{-1})	1.034
$F(000)$	1472
Reflections collected/unique	5535/2416 [$R(\text{int}) = 0.0634$]
Completeness to $\theta = 25.02$	93.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8199 and 0.7467
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2416/10/190
Goodness-of-fit on F^2	0.961
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0552$, $wR2 = 0.1222$
R indices (all data)	$R1 = 0.1254$, $wR2 = 0.1447$
Largest diff. peak and hole (e Å^{-3})	0.728 and −0.380

TABLE II Selected bond lengths (Å) and angles (°) for the complex

Cr(1)–O(1)	1.946(4)	Cr(1)–Cr(1)$^{\#1}$	2.8909(17)
Cr(1)–O(3)	1.956(4)	O(1)–Cr(1)$^{\#1}$	1.946(4)
Cr(1)–O(2)	1.981(4)	O(2)–Cr(1)$^{\#1}$	1.981(4)
Cr(1)–N(3)	2.070(4)	Cr(1)–N(1)	2.095(5)
Cr(1)–N(2)	2.087(5)		
O(1)–Cr(1)–O(3)	93.89(19)	O(2)–Cr(1)–N(3)	95.17(19)
O(1)–Cr(1)–O(2)	81.10(17)	O(1)–Cr(1)–N(2)	173.0(2)
O(3)–Cr(1)–O(2)	93.30(19)	O(3)–Cr(1)–N(2)	92.94(18)
O(1)–Cr(1)–N(3)	91.6(2)	O(2)–Cr(1)–N(2)	97.23(18)
N(2)–Cu(1)–N(1)	83.97(15)	N(3)–Cr(1)–N(2)	81.76(19)
O(3)–Cr(1)–N(3)	170.51(17)	O(1)–Cr(1)–N(1)	98.11(18)
O(3)–Cr(1)–N(1)	89.21(19)	O(2)–Cr(1)–N(1)	177.4(2)
N(3)–Cr(1)–N(1)	82.37(19)	N(2)–Cr(1)–N(1)	83.3(2)

$^{\#1}x, -y + 3/2, z$.

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystal parameters and structure refinement details are summarized in Table I. Selected bond lengths and angles are listed in Table II.

RESULTS AND DISCUSSION

Description of Structure

The X-ray crystallographic study reveals that a mixed-bridged Cr(III)–Cr(III) complex has been formed in such a way that a confacial bioctahedral geometry containing two chromium(III) ions is present in the lattice (Fig. 1). Besides the cation there are two

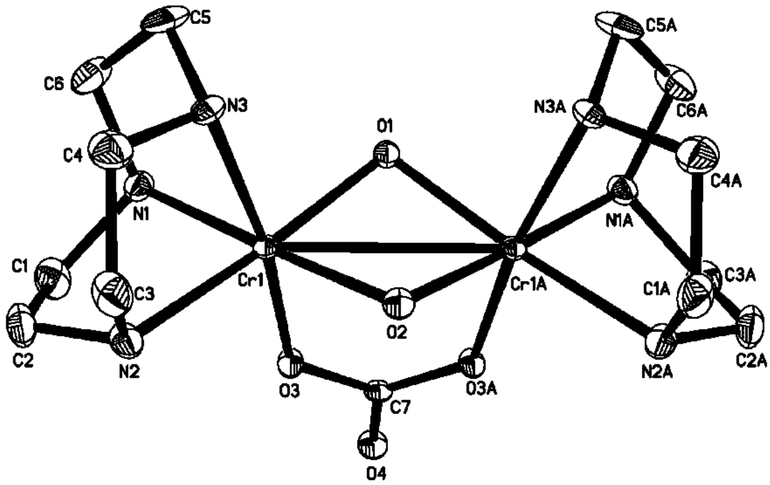

FIGURE 1 Crystal structure of [(tacn)Cr(μ-OH)$_2$(μ-CO$_3$)Cr(tacn)]$^{2+}$. Hydrogen atoms have been omitted for clarity.

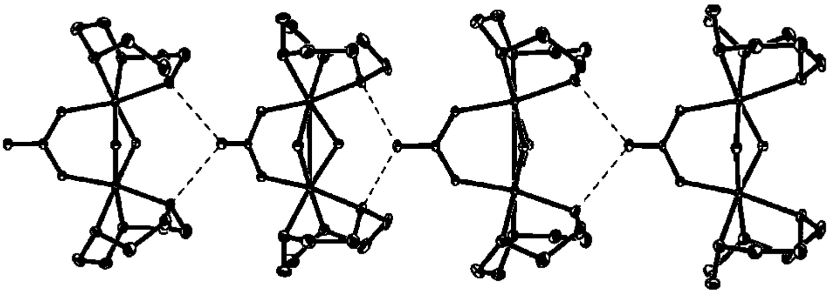

FIGURE 2 1-D structure of [(tacn)Cr(μ-OH)$_2$(μ-CO$_3$)Cr(tacn)](ClO$_4$)$_2 \cdot$ 3H$_2$O. Hydrogen atoms and water molecules have been omitted for clarity.

well-separated perchlorate anions and three water molecules. The two metal ions are bridged by two hydroxo groups and one carbonato group, which certainly comes from carbon dioxide in the air absorbed by the alkaline reaction solution. Two facially coordinated tridentate amine ligands complete the distorted octahedral coordination sphere of the metal centres. In the compound there are Cr–Cr interactions with a distance of 2.8909(17) Å, which is in the range of published Cr–Cr bond lengths (2.6–3.1 Å) [20], indicating the presence of an intramolecular metal–metal interaction. Cr–O distances in the range 1.946(4)–1.981(4) Å are identical to the distances in an analogous trihydroxo-bridged ions. Deviation from idealized orthogonal geometry is found for tacn; the N–Cr–N angles range between 81.76(19) and 83.3(2)°, whereas O–Cr–O angles fall between 81.10(17) and 93.89(19)°, somewhat larger than other results in the literature [21] and due to the carbonato bridge.

Two oxygen atoms of the carbonato group coordinate as the bridging ligand. The uncoordinated oxygen atom forms hydrogen bonds with hydrogen atoms of two 1,4,7-triazacyclononane ligands of neighbouring molecules, leading to the one-dimensional structure shown in Fig. 2. The average N–H$\cdots$O bond distance is 2.782(5) Å.

IR and Electronic Spectroscopy

Besides ligand modes, the IR spectrum exhibits a sharp, strong band at 3520–3560 cm^{-1} due to ν(O–H) stretching. One characteristic of the infrared spectrum is a very strong carbonyl stretching vibration at 1570–1600 cm^{-1}. The broad strong band at approximately 1100 cm^{-1} is characteristic of the perchlorate ion.

The electronic spectrum of the complex was measured in aqueous solution at room temperature. Besides a strong CT band at 226 nm, the spectrum shows a maximum at 512 nm and a shoulder at 373 nm, similar to the spectrum of the tris(μ-hydroxo)-bridged dimer $[Cr_2(Me_3[9]aneN_3)_2(OH)_3]^{3+}$ ($Me_3[9]aneN_3 = $ 1,4,7-trimethyl-1,4,7-triazacyclononane) [22]. The band at 512 nm can be assigned to the first spin-allowed transition $^4A_{2g}(t_{2g}^3) \rightarrow {}^4T_{2g}(t_{2g}^2e_{2g}^1)$, and the second spin-allowed transition $^4A_{2g} \rightarrow {}^4T_{1g}$ occurs at 373 nm. A remarkable feature is the presence of very weak absorptions in the 750 to 630 nm region. These absorptions are due to the spin-forbidden $^4A_{2g} \rightarrow {}^2E_g$ transitions with intensity gained from exchange coupling [23].

Magnetic Properties

The variable-temperature (2–298 K) magnetic susceptibilities of the complex were measured on a crystalline sample under an applied magnetic field of 10 KOe. Plots of $\chi_M T$ *versus* T are shown in Fig. 3, where χ_M is the magnetic susceptibility per binuclear unit. The $\chi_M T$ value at 298 K is *ca.* 3.55 emu K mol^{-1} (the spin-only value is 3.75 emu K mol^{-1}, expected for two non-coupled spins of $S_{Cr} = 3/2$), which decreases smoothly with decreasing temperature. The $\chi_M T$ value reaches a minimum value near zero at 2 K, showing antiferromagnetic coupling between Cr(III) ions resulting in a non-magnetic $S = 0$ ground state. We may anticipate that in Cr(III), however, the unpaired spins are in t_{2g} orbitals (for octahedral coordination), and these orbitals are not directed toward the bridging oxygen atoms; the coupling is thus fairly weak. For the Cr(III)–Cr(III) complex, we used a different Hamiltonian containing

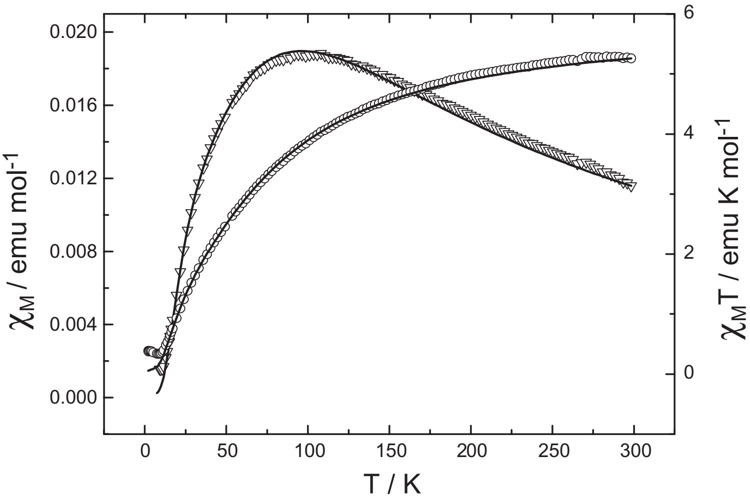

FIGURE 3 Temperature dependence of χ_M (▽) and $\chi_M T$ (○) measured at 10 KOe. The solid line represents the theoretical curve with the best-fit parameters.

a biquadratic term to obtain a good fit of the data to the theoretical susceptibility equation [24]. The Hamiltonian describing the exchange coupling in the bimetallic chromium(III) is

$$\hat{\mathrm{H}} = -2J\hat{\mathrm{S}}_1 \cdot \hat{\mathrm{S}}_2 - j(\hat{\mathrm{S}}_1 \cdot \hat{\mathrm{S}}_2)^2$$

where j is the biquadratic coupling constant. The temperature dependence of magnetic susceptibilities was calculated using the following equation derived from the above Hamiltonian operator

$$x = \frac{J}{kT}, \qquad x' = \frac{j}{kT}$$

and a temperature independent susceptibility term (N_α) was also included and set as $2.0 \times 10^{-4}\,\mathrm{cm^3\,mol^{-1}}$.

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{kT}\frac{2\exp(2x - 6.5x') + 10\exp(6x - 13.5x') + 28\exp(12x - 9x')}{1 + 3\exp(2x - 6.5x') + 5\exp(6x - 13.5x') + 7\exp(12x - 9x')} + Na.$$

The least-squares fit (solid line in Fig. 3) yielded the values: $J = -14.1\,\mathrm{cm^{-1}}$, $j = 2.47\,\mathrm{cm^{-1}}$ and $g = 2.02$.

Hodgson [24] has systematically studied the magnetic properties of first-row transition-metal dimers containing hydroxo bridges. For di-μ-hydroxochromium(III) complexes, exchange-coupling constant values range from -6.5 to $-14\,\mathrm{cm^{-1}}$ [24]. In contrast to these compounds, the antiferromagnetic coupling of our complex is correspondingly larger.

In conclusion we have successfully synthesized the first carbonato-bridged chromium(III) macrocyclic complex. A study of magnetic properties indicates that the metal centres are antiferromagnetically coupled.

Acknowledgments

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Supplementary Material

Additional material, consisting of atomic coordinates and equivalent isotropic displacement parameters, is available from CCDC, deposit number 188069. Copies of the data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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