Notes

Novel Three-Dimensional Cage Assembly of a μ_4-Carbonato-Bridged Cobalt(II) Compound $[Co_2(bpm)(H_2O)_2(CO_3)(OH)]NO_3 \cdot 4H_2O$

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Received November 16, 1998

Introduction

The reaction of cobalt(II) with 2,2′-bipyrimidine (hereafter noted as bpm) in aqueous solution has allowed the preparation of both mono-[1,2] and polynuclear[3,4] bpm-containing cobalt(II) complexes because of the chelating and bischelating coordination modes that this bis (α-diimine) type ligand can adopt. Bpm acts as a terminal bidentate ligand in the former complexes which are obtained when 1:3 and 1:2 metal to bpm molar ratios are used. Dinuclear,[3] chain,[3c] and two-dimensional[4] bpm-bridged cobalt(II) compounds are easily prepared for greater metal to bpm molar ratios. In these cases, the nuclearity of the resulting species is strongly dependent on the coordinating ability of the anionic coligand that balances the positive charge of the cobalt(II) ion.

In the framework of our current research work dealing with the preparation and magnetostructural characterization of polynuclear bpm-containing metal complexes,[5−8] we have obtained a new three-dimensional Co(II) complex of formula $[Co_2(bpm)(H_2O)_2(CO_3)(OH)]NO_3 \cdot 4H_2O$ (**1**) which contains μ_4-carbonato and single μ_2-hydroxo bridges together with bischelating bpm. The present contribution focuses on its preparation and its structural and magnetic characterization.

Table 1. Crystallographic Data for $[Co_2(bpm)(H_2O)_2(CO_3)(OH)]NO_3 \cdot 4H_2O$ (**1**)

formula	$C_9H_{19}Co_2N_5O_{13}$
fw	523.1
space group	*I*4/*m*
a, Å	16.444(3)
c, Å	14.178(5)
V, Å^3	3834(2)
Z	8
T, K	293
ρ_{calcd}, g cm^{-3}	1.813
λ, Å	0.710 73
μ(Mo Kα), cm^{-1}	18.00
R^a	0.095
$R_w{}^{b,c}$	0.105

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o) + 0.0070F_o{}^2]$.

Experimental Section

Materials. Cobalt(II) nitrate hexahydrate, 2,2′-bipyrimidine, and potassium bicarbonate were purchased from commercial sources andused as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Università degli Studi della Calabria. Cobalt content was determined by atomic absorption spectrometry.

Preparation of $[Co_2(bpm)(H_2O)_2(CO_3)(OH)]NO_3 \cdot 4H_2O$ (1). An aqueous solution containing 0.5 mmol of potassium bicarbonate was slowly added to an aqueous solution containing 0.2 mmol of cobalt(II) nitrate hexahydrate until a slight precipitate appeared (pH ca. 6.5). After the addition of 0.1 mmol of bpm, the small precipitate of cobalt(II) hydroxide was removed by filtration. Well-shaped orange polyhedral crystals of **1** separated from the mother liquor by slow evaporation at room temperature after 1 day. They were filtered off, washed with a small amount of cold water, and dried in air on filter paper. The yield is about 70%. Anal. Calcd for $C_9H_{19}Co_2N_5O_{13}$ (**1**): C, 20.67; H, 3.63; N, 13.39; Co, 22.54. Found: C, 20.65; H, 3.37; N, 13.33; Co, 22.10%.

The infrared spectrum of **1** reveals the occurrence of bischelating bpm (asymmetric doublet at 1578s and 1567w cm^{-1}),[9] hydroxo- (834w cm^{-1}),[10] and carbonato- (1485s and 1412s cm^{-1})[11] bridges. Uncoordinated nitrate (2426w and 1383s cm^{-1})[12] and coordinated and crystallization water molecules (3423s,br, 1637w, 834w, and 673w cm^{-1})[13] are also observed. All of these spectral suggestions have been confirmed by the X-ray structural determination of **1**.

Physical Techniques. The IR spectrum of **1** was obtained with a Perkin-Elmer 1750 FTIR spectrophotometer on a KBr pellet in the 4000−400 cm^{-1} region. Magnetic susceptibility measurements were performed on a polycrystalline sample of **1** with a Quantum Design SQUID susceptometer covering the 2.0−300 K temperature range and using an applied magnetic field of 0.1 T. The susceptometer was calibrated with $(NH_4)_2Mn(SO_4)_2 \cdot 12H_2O$. The experimental susceptibility data were corrected for the diamagnetism estimated from Pascal's constants[14] (-261×10^{-6} cm^3 mol^{-1} K).

X-ray Crystallographic Analysis. A crystal of **1** of dimensions 0.20 × 0.14 × 0.12 mm was mounted on a Siemens R3m/V automatic four-circle diffractometer and used for data collection. Diffraction data were collected at room temperature with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and using the $\omega-2\theta$ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range 15−30°. A summary of the crystallographic data and structure parameters are listed in Table 1. Examination of two standard reflections, monitored after every 48

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10.1021/ic981323n CCC: $18.00

Table 2. Selected Bond Lengths (Å) and Interbond Angles (deg)[a,b] for Compound **1**

Cobalt(II) Environment			
Co(1)−O(1)	2.040(9)	Co(1)−O(2)	2.087(10)
Co(1)−O(3)	2.104(8)	Co(1)−N(1)	2.202(10)
Co(1)−O(4c)	2.052(9)	Co(1)−N(2a)	2.164(10)
O(1)−Co(1)−O(2)	172.6(4)	O(1)−Co(1)−O(3)	80.2(4)
O(2)−Co(1)−O(3)	92.4(4)	O(1)−Co(1)−N(1)	92.6(5)
O(2)−Co(1)−N(1)	88.6(4)	O(3)−Co(1)−N(1)	97.3(4)
O(1)−Co(1)−O(4c)	93.0(5)	O(2)−Co(1)−O(4c)	87.2(4)
O(3)−Co(1)−O(4c)	94.3(4)	N(1)−Co(1)−O(4c)	167.8(4)
O(1)−Co(1)−N(2a)	97.1(4)	O(2)−Co(1)−N(2a)	90.2(4)
O(3)−Co(1)−N(2a)	173.0(4)	N(1)−Co(1)−N(2a)	76.3(4)
O(4c)−Co(1)−N(2a)	92.2(4)	Co(1)−O(1)−Co(1b)	96.5(6)
Carbonate Ligand			
C(5)−O(3)	1.31(2)	C(5)−O(4)	1.26(1)
Co(1)−O(3)−C(5)	131.6(4)	Co(1)−O(3)−Co(1b)	92.6(5)
O(3)−C(5)−O(4)	118.0(7)	O(3)−C(5)−O(4b)	118.0(7)
O(4)−C(5)−O(4b)	124.0(15)	C(5)−O(4)−Co(1f)	129.3(8)

Hydrogen−Bonding Contacts[c]

A	D	H	A···D	A···H	A···H−D
O(5)	O(1)	H(1o)	2.71(3)	1.87(3)	176(2)
O(4b)	O(2)	H(2w)	2.68(5)	1.85(1)	139(1)

[a] Estimated standard deviations are given in parentheses. [b] Symmetry code: (a) 1.5 − *x*, 1.5 − *y*, 1.5 − *z*; (b) *x*, *y*, 1 − *z*; (c) 1 − *y*, *x*, 1 − *z*, (f) *y*, 1 − *x*, 1 − *z*. [c] A = acceptor, D = donor.

reflections, showed no sign of crystal deterioration. Lorentz−polarization corrections were applied to the intensity data. The maximum and minimum transmission factors were 0.806 and 0.699, respectively. Of the 3214 measured reflections in the 2θ range 3−54° with index ranges $0 \leq h \leq 23$, $0 \leq k \leq 23$, and $0 \leq l \leq 19$, 2900 were unique. From these, 1209 were observed [$I > 3\sigma(I)$] and used for the refinement of the structure. The structure was solved by standard Patterson methods and subsequently completed and refined by Fourier recycling and least squares. From a ΔF map, the nitrate group was found to lie on the mirror plane. Its atoms have a very large thermal motion, because of the disorder above and below the plane. For this reason the atomic coordinates of the nitrate anion were refined with constraints, while the isotropic displacement parameter was fixed at a value of 0.160 Å^2. All attemps at refining the structure in a noncentrosymmetric space group failed to converge to a sensible structure. Two peaks corresponding to the crystallization water molecules were also found, one in general position and the other on the mirror plane. The atom on the mirror plane was refined with a 0.5 occupancy factor even though this does not account for all water molecules given by the chemical analysis. All non-hydrogen atoms, except those of the nitrate group and crystallization water molecules, were refined anisotropically. The hydrogen atoms of the coordinated water molecules and the hydroxide group were located on a ΔF map where those of bpm were set in calculated positions. All of the hydrogen atoms were refined as riding atoms, with a common fixed isotropic thermal parameter. The final Fourier-difference map showed maximum and minimum height peaks of 1.50 and −2.27 e Å^{-3}, respectively. The goodness of fit is 1.537. Solutions and refinements were performed with the SHELXTL PLUS system.[15] The final geometrical calculations were carried out with the PARST program.[16] Graphical manipulations were done using the XP utility of the SHELXTL PLUS system. Main interatomic bond distances and angles are listed in Table 2.

Results and Discussion

Description of the Structure of 1. The structure of **1** is made up of the cationic three-dimensional network $[Co_2(bpm)(H_2O)_2(CO_3)(OH)]^+$, uncoordinated nitrate, and crystallization water molecules. The cobalt(II) ions are bridged by a bischelating bpm molecule, a single μ_2-hydroxo group, and a μ_4-carbonate ligand. A fragment of this cationic motif with the atom numbering is shown in Figure 1. Electrostatic interactions as well as an extensive network of hydrogen bonds involving the nitrate counterion and the coordinated and crystallization water molecules (see end of Table 2) ensure the cohesion of the crystal lattice.

Each cobalt atom is in a distorted octahedral environment, being bonded to two bpm nitrogens [N(1) and N(2a)] and to four oxygen atoms of a hydroxo group [O(1)], a water molecule [O(2)], and two carbonate ligands [O(3) and O(4c)]. The Co−N and Co−O bond lengths and angles show no unexpected values. These values are similar to those reported in the literature for other bpm-[3,4] and hydroxo-bridged[17−19] cobalt(II) complexes. The cobalt to water bond length [2.087(10) Å] is somewhat longer than that of the hydroxo bond [2.040(9) Å], and this is in agreement with the smaller basicity of the water molecule. Particularly interesting is the μ_4-bridging mode of the carbonato

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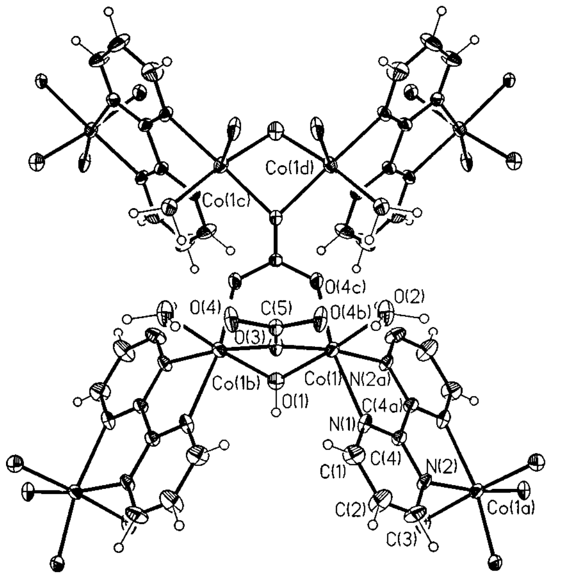

Figure 1. View of the structure of complex **1** showing the distribution of the hydroxo, carbonato, and bpm bridges and the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Crystallization water molecules and the uncoordinated nitrate are omitted for the sake of clarity.

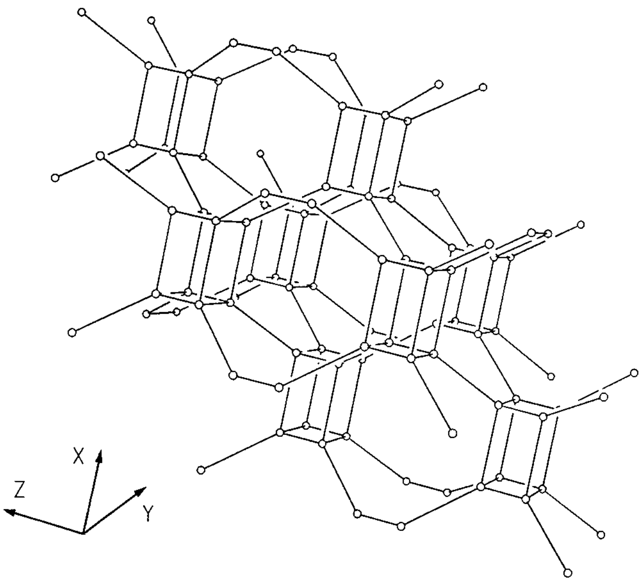

Figure 2. Schematic view of **1** (approximately along the *y* axis) showing the building of the polymer through the boxes where only the cobalt atoms are drawn for clarity.

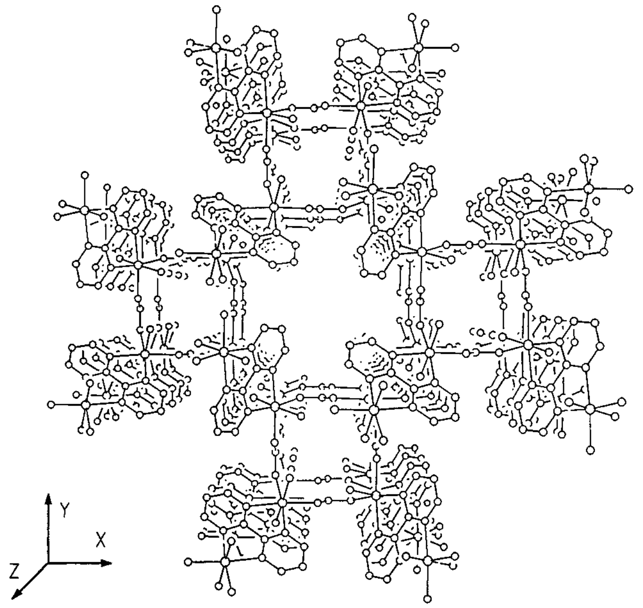

Figure 3. View of the polymer along the *z* axis.

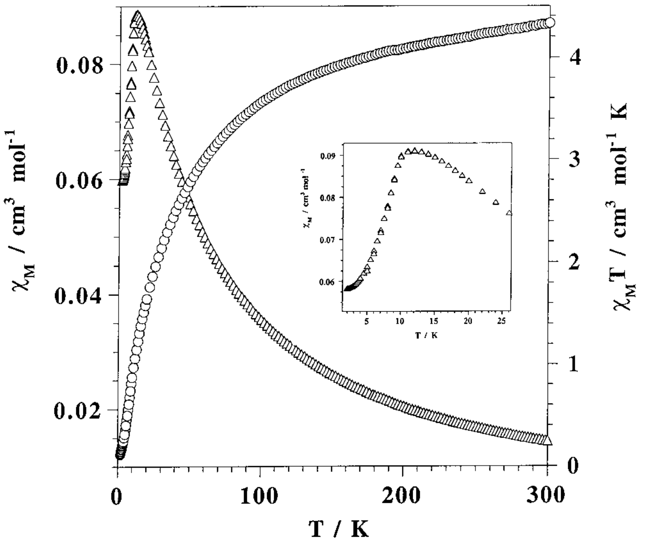

Figure 4. Thermal variation of χ_M (△) and $\chi_M T$ (○) for compound **1**. The inset shows the shape of the susceptibility curve in the lower temperature range.

which adopts the μ-1,1- and μ-2,3- (*syn-syn*) coordination modes. Eight cobalt atoms are linked together by means of four mutually perpendicular carbonate groups forming tetragonal prisms. A carbonate ligand that bridges four metal ions was found when looking at a rectangular face of this box. This μ_4-carbonato bridge was observed in three tetranuclear copper(II) complexes,[20,21] but the carbonate oxygen atoms were disordered. It deserves to be noted that the cobalt array and the carbonato bridging disposition in **1** most closely resemble those found in the copper-containing mineral azurite $[Cu_3(OH)_2)(CO_3)_2]$[22] [μ-1,1 and μ-2,3 (*syn-anti*) coordination modes]. The best equatorial plane around cobalt is defined by the N(1), N(2a), O(3), and O(4c) set of atoms [largest deviation from the mean plane is 0.073(10) Å at N(2a)], the cobalt atom being 0.014(2) Å out of this plane. The main distortion from the ideal octahedral geometry of the metal environment is due to the reduced bite angle of the bpm ligand [76.3(4)° for N(1)−Co(1)−N(2a)].

The bpm molecule is planar, and the carbon−carbon and carbon−nitrogen bonds within this ligand are as expected. The carbonate group has its expected trigonal geometry, and it is practically planar. The cobalt atom is displaced by 0.398(2) Å out of this plane. The carbon−oxygen bond distances and intra-anion bond angles average 1.28(1) Å and 120.0(10)°, respectively. The angle at the μ-1,1-carbonate oxygen atom is 92.6(5)° whereas that at the μ-2,3-carbonate oxygens is enlarged to 129.3(8)°. The angle at the hydroxo bridge is 96.5(6)°. The metal−metal separation through bridging bpm is 5.781(3) Å, a value which lies within the range observed for other bpm-bridged cobalt(II) compounds [5.942(2)−5.736(2) Å].[3,4] The metal−metal separations through the μ_4-carbonato bridge are 3.042(2) [Co(1)···Co(1b)], 5.321(2) [Co(1)···Co(1d)], and 6.129(2) Å [Co(1)···Co(1c)].

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The three-dimensional cobalt(II) polymer is formed by assembling the tetragonal prisms by means of bpm spacers, each box being linked to eight ones through its vertexes (see Figure 2). The prisms are placed one upon another at a distance of 14.178(3) Å along the z axis. In this way they define a pile. Four adjacent piles build a channel in the same direction, as shown in Figure 3. The uncoordinated nitrate and crystallization water molecules are placed in this cavity, and they are attached to the walls through hydrogen bonds with the hydroxo group and coordinated water molecule. However, they cannot fill the big cavity that they occupy, and they are disordered.

Magnetic Properties of 1. The magnetic behavior of compound **1** is shown in Figure 4 under the form of both χ_M [χ_M being the magnetic susceptibilty per two cobalt(II) ions] and $\chi_M T$ versus T plots. The susceptibility curve shows the presence of a maximum at 11.5 K whereas that of $\chi_M T$ exhibits a continuous decrease upon cooling, with $\chi_M T = 4.32$ cm^3 mol^{-1} K (μ_{eff} per Co$^{\mathrm{II}} = 4.17\ \mu_B$) at 300 K and an extrapolated value which vanishes when T approaches 0. The value of μ_{eff} per cobalt atom at room temperature is greater than that calculated for the spin-only case ($\mu_{\mathrm{eff}} = 3.87\ \mu_B$), revealing that a significant orbital contribution occurs. The occurrence of a maximum susceptibility is indicative of the existence of an antiferromagnetic coupling between the paramagnetic centers. In addition, the extrapolated value of χ_M at $T = 0$ is ca. 0.060 cm^3 mol^{-1} K (see inset of Figure 4), that is 2/3 its value at the temperature at which it is a maximum. This is the signature that we are dealing with a three-dimensional antiferromagnet.[23] This is not suprising because the three bridging ligands present in **1**, that is bischelating bpm,[3−9] single μ_2-hydroxo,[10b,24] and μ_4-carbonato,[21,22] are able to mediate relatively strong exchange interactions between paramagnetic centers bridged by them. In the case of bpm-bridged cobalt(II) dimers, the magnitude of the antiferromagnetic coupling through bpm varies in the range -7.0 to -4.7 cm^{-1} (the Hamiltonian being $\hat{H} = -J\hat{S}_A\cdot\hat{S}_B$). As far as we are aware, no magnetic data are available for single μ_2-hydroxo- and μ_4-carbonato-bridged cobalt(II) species. The lack of a theoretical expression to analyze the magnetic data of **1** precludes a detailed magnetostructural study of this unusual compound.

Acknowledgment. Financial support from the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica, the Spanish Dirección General de Investigación Científica y Técnica (DGICYT) (Project PB97-1397), and the Training and Mobility Research Program from the European Community (TMR Contract ERBFMRXCT-980181) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981323N

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