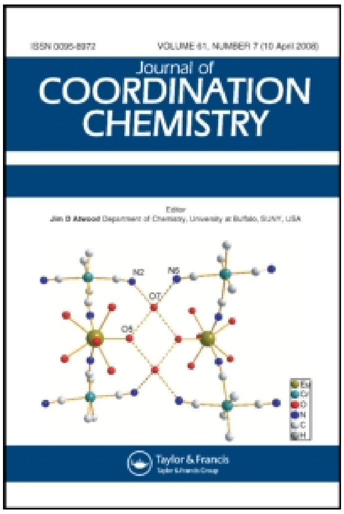

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A linear trinuclear cobalt(II) complex with 4-(2-pyridine)-1,2,4-triazole: synthesis, structure and characterization

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The linear trinuclear cobalt(II) complex $[Co_3(pytrz)_6(H_2O)_6](NO_3)_6$ (**1**) with pytrz = 4-(2-pyridine)-1,2,4-triazole has been prepared and characterized. It crystallizes in the rhombohedral R-3 space group with $Z = 3$, $a = 13.955(2)$, $b = 13.955(2)$, $c = 28.942(9)$ Å, $\gamma = 120°$, $V = 4881.2(18)$ Å^3. The structure of **1** comprises the cation $[Co_3(pytrz)_6(H_2O)_6]^{6+}$, in which linear trinuclear Co(II) units are bridged by six L ligands and have six aqua molecules as terminal ligands. The six free nitrates link the terminal aqua ligands through N–H $\cdots$ O hydrogen bonds with C_3 symmetry. **1** was characterized by FT-IR, electronic spectra and magnetic measurements. The variable-temperature magnetic measurements reveal weak anti-ferromagnetic interactions in **1**.

Keywords: 4-(2-Pyridine)-1,2,4-triazole; Cobalt(II); Electronic spectra; Anti-ferromagnetic

1. Introduction

Multinuclear transition metal complexes are of interest in coordination chemistry due to the special chemical and physical properties that result from the mutual interaction of two or more metal centers. In particular, trinuclear transition metal complexes have developed due to the discovery of the fundamental role played by these metal systems in several catalytic biological systems [1, 2].

1,2,4-Triazole and its derivatives are interesting ligands combining coordination geometries of both pyrazoles and imidazoles in the arrangement of their three heteroatoms. Transition metal complexes of 1,2,4-triazole derivatives are intriguing from both theoretical and practical viewpoints and the subject of several magnetism studies [3–8]. Of special interest are the 4-R-1,2,4-triazoles which are coordinated to the metal ions via the nitrogen atoms in the N_1 and N_2 positions to give polynuclear linear compounds with a triple bridge. The 4-(2-pyridine)-1,2,4-triazole (pytrz) as a 4-R-1,2,4-triazole can demonstrate diverse coordination modes. A previous

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article deals with two copper(II)-pytrz coordination complexes, in which the coordination octahedron of the central copper ions are compressed and elongated [9].

We have also explored metal triazole systems [10]. To further investigate the structures and properties of triazole-based metal complexes, in this contribution, 4-(2-pyridine)-1,2,4-triazole (pytrz) was used to synthesize a linear trinuclear cobalt(II) complex $[Co_3(pytrz)_6(H_2O)_6](NO_3)_6$ (**1**). **1** was characterized by FT-IR, electronic spectra and magnetic measurements. The variable-temperature (2–250 K) magnetic measurements reveal the existence of weak anti-ferromagnetic interactions in **1**.

2. Experimental

2.1. *General*

The triazole ligand pytrz was synthesized according to the literature method [11]. All other reagents were commercially available and used without further purification. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bio-Rad FTS 135 spectrometer and electronic spectra on a Shimadzu UV-2001 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.

2.2. *Preparation of $[Co_3(pytrz)_6(H_2O)_6](NO_3)_6$ (1)*

To a solution of pytrz (0.0877 g, 0.6 mmol) in boiling water (15 mL) was added an aqueous solution (3 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.0732 g, 0.2 mmol) with stirring. Red crystals of **1** suitable for X-ray diffraction were obtained by evaporation of the solution. Yield: 44%. $C_{42}H_{48}Co_3N_{30}O_{24}$ (%): Calcd C, 32.88; H, 3.15; N, 29.39. Found: C, 32.78; H, 3.20; N, 29.45. IR (KBr pellets, cm^{-1}): $\nu = 3368.5$ br and 3084.5 s ν(OH), 1598.3 s and 1532.2 s $\nu(N_{pyridine})$, 636.6 s $\nu(N_{triazole})$, 1474.7 m, 1440.2 m, 1385.9 s, 1328.1 s, 1258.7 m, 1057.7 m, 959.9 w, 783.5 s, 706.3 m, 519.5 m, 470.4 m.

2.3. *X-ray crystallography*

Diffraction intensities for **1** were collected on a computer controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares using the SHELXS-97 and SHELXL-97 programs [12]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths are listed in tables 1 and 2, respectively. CCDC reference number 258245 for **1**. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Description of crystal structures*

Complex **1** has a linear trinuclear structure, as shown in figure 1. The fundamental unit of **1** contains $[Co_3(pytrz)_6(H_2O)_6]^{6+}$ and six nitrate anions. The central Co(II) and two terminal Co(II) ions are bridged by three pytrz ligands. Each terminal Co(II) ion completes its octahedral geometry with three aqua ligands. A C_3 axis exits along the metal-metal chain. The six nitrates link the six terminal aqua ligands through $N–H \cdots O$ hydrogen bonds with C_3 symmetry. The central Co(II) ion has six identical Co–N bond

Table 1. Crystallographic data and structural refinement for **1**.

Empirical formula	$C_{42}H_{48}Co_3N_{30}O_{24}$
Formula mass	1533.89
Crystal size (mm^3)	0.20 × 0.18 × 0.16
Crystal system	Rhombohedral
Space group	*R*-3
Unit cell dimension (Å, °)	
a	13.955 (2)
b	13.955 (2)
c	28.942 (9)
α	
β	
γ	120.00
V (Å^3)	4881.2 (18)
Z	3
D_{calcd} ($g\,m^{-3}$)	1.565
$F(000)$	2349
θ range for data collection (°)	1.83–26.46
Reflections collected	9678
Independent reflections	2245
Data/restraints/parameters	2245/338/203
Goodness of fit on F^2	1.050
$R_1{}^a$ $[I=2\sigma(I)]$	0.0643
$wR_2{}^a$ (all data)	0.2025

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

Co(1)–N(1)	2.131(3)	Co(2)–O(4)	2.096(4)
Co(2)–N(2)	2.111(3)	N(1)#1–Co(1)–N(1)#2	89.42(11)
N(1)#1–Co(1)–N(1)	179.999(1)	N(1)#2–Co(1)–N(1)	90.58(11)
O(4)#3–Co(2)–O(4)	90.09(18)	O(4)–Co(2)–N(2)	87.75(15)

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

lengths (2.131(3) Å) and the corresponding bond angles around the central Co(II) ions are 90.1(8)°, indicating that the central Co(II) ion is in a nearly ideal octahedral geometry. The terminal Co(II)–N bond length is 2.111(3) Å, slightly shorter than the central Co(II)–N bond length. Complex **1** has a similar structure as the previous copper(II) complex, but the coordination environment about the metal ions is quite different [9]. The dihedral angle formed by the triazole ring and the pyridine ring in **1** is 16.2(5)°.

3.2. *FT-IR characterizations*

FT-IR spectroscopy can be used as a diagnostic tool for identifying the coordination modes of the triazole ligand, which can be monodentate, bidentate or tridentate [13]. The free ligand shows one strong band at 1594 cm^{-1}, attributable to the pyridine ring vibration [14]. The triazole out of plane ring absorption is observed at 639 cm^{-1} [15]. For **1**, the medium band at 1025 cm^{-1} and the strong band at 1385 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibration modes of the non-coordinated nitrate, respectively [16]. Broad bands from 3000 to 3400 cm^{-1} indicate that the existence of coordinated water and broad bands at 3214 and 3302 cm^{-1} are attributed to N–H stretching bands. The FT-IR results are in agreement with the X-ray results.

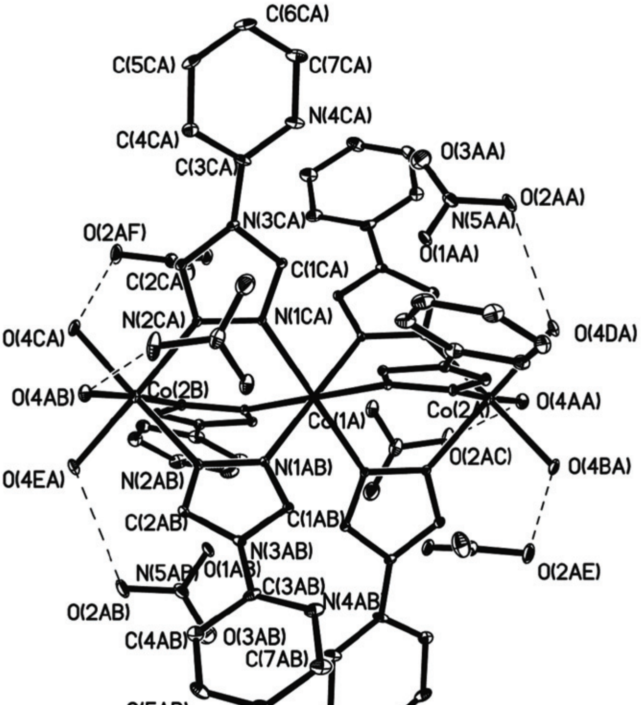

Figure 1. ORTEP view of the linear trinuclear cobalt(II) unit in **1** showing six nitrate anions hydrogen-bonded to terminal oxygen with C_3 symmetry.

3.3. *Electronic spectra*

The electronic spectra of the ligand and **1** in acetonitrile are shown in figure 2 which contains two regions, 200–350 and 350–600 nm. The free ligand in acetonitrile consists of two major bands: one centered at 226 nm and the other at 267 nm, similar to that of *N*-[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine [17]. Comparison of the spectra obtained for **1** with the free ligand in the region of 200–350 nm show only small shifts. In the region of 350–600 nm the spectra show a broad band centered at 448 nm. Molar extinction coefficients ($\varepsilon_{\max} = 1.4 \times 10^3\,\mathrm{M^{-1}cm^{-1}}$) for the band at 448 nm were obtained from Beer's law plots of standard solutions of the Co(II) complex. The broad bands can be assigned to the metal-to-ligand charge-transfer bands (MLCT) from the metal(II) centers to the π^*-orbitals originating from L.

3.4. *Magnetic properties of 1*

The trinuclear **1** was studied by magnetic susceptibility measurements in the 2–250 K regions. The magnetic behavior of **1** is shown in figure 3 in the form of a $\chi_M T$ *versus* T plot. The $\chi_M T$ value is $5.52\,\mathrm{cm^3\,mol^{-1}\,K}$ at 250 K, about the value expected for three uncoupled Co(II) (S = 3/2) ions. As the temperature is reduced, $\chi_M T$ smoothly decreases indicating that overall anti-ferromagnetic interactions between Co(II) ions dominate the magnetic properties of **1**. The magnetic exchange interactions in centrosymmetric trimers are usually described by the isotropic Hamiltonian $H = -2J[(S_1 \cdot S_2) + (S_2 \cdot S_3)] - 2J_{13}(S_1 \cdot S_3)$, where J and J_{13} represent the exchange constants between neighboring and terminal metal ions, respectively. In the absence of a clearly defined exchange pathway between the terminal Co(II) ions, J_{13} was taken as zero. The best fitting for the experimental data gives $J = -17.8\,\mathrm{cm^{-1}}$ and $g = 2.06$. The agreement factor $R = \sum(\chi_{\text{obsd}} - \chi'_{\text{cacld}})^2 / \sum(\chi_{\text{obsd}})^2$

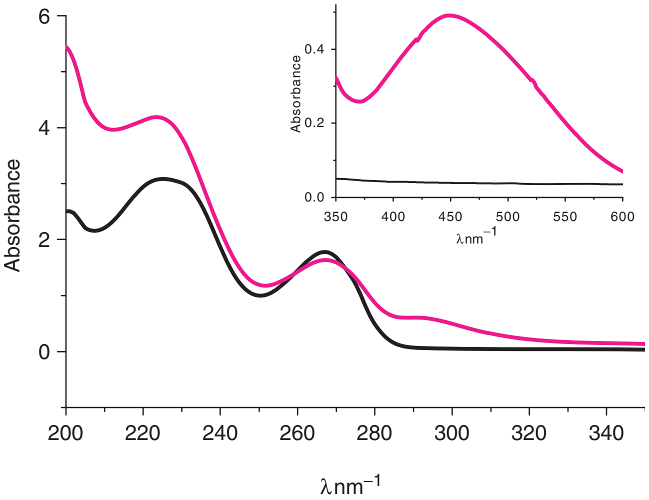

Figure 2. UV–Vis electronic spectra for pytrz (black lines) and **1** (pink lines; color online only) in acetonitrile solution in the region of 200–350 nm and 350–600 nm (inset).

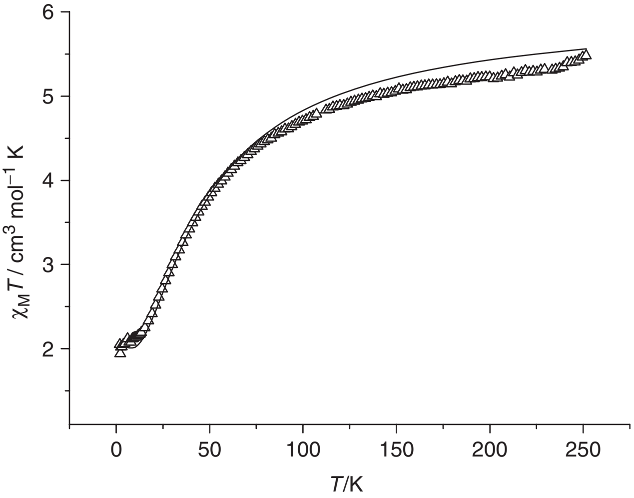

Figure 3. $\chi_M T$ (Δ) *vs.* T plot for **1**; the solid line represents the best fit.

is 1.4×10^{-3}. The solid curve is the theoretical prediction of χT, also shown in figure 3. The model was also fitted with the Ising model with $S = 3/2$ and anisotropic g value. The *Van Vleck* formula for **1** is expressed as,

$$\mathrm{H} = -J(S_{A1} \cdot S_B + S_{A2} \cdot S_B)$$

where $S_A = S_B = 3/2$. The best fit for temperatures greater than 20 K gives $g_A = 2.13$, $g_B = 2.02$, $J = -21.08\,\mathrm{cm}^{-1}$ with $R = 9.1 \times 10^{-3}$. The resulting fit is not as good as that fitted by the isotropic Hamiltonian method. However, both results reveal the weak anti-ferromagnetic interactions between neighboring Co(II) ions. The antiferromagnetic exchange interactions can be compared with $[Co_3(NCS)_6(admtrz)_6]\cdot CH_3OH \cdot H_2O$ and $[Co_3(t\text{-Butrz})_8(NCS)_4](NCS)_2(H_2O)$ with $J = -2.8\,\mathrm{cm}^{-1}$ and $J = -9.0\,\mathrm{cm}^{-1}$, respectively [18]. Comparison of the calculated values with the data for **1** indicates that different groups in the triazole ligands do not noticeably affect the efficiency of the anti-ferromagnetic exchange interactions between Co(II) ions.

4. Conclusion

Using a 4-substituted triazole ligand, 4-(pyridine-2)-1,2,4-triazole, a linear trinuclear cobalt(II) complex $[Co_3(pytrz)_6(H_2O)_6](NO_3)_6$ has been prepared and characterized by single X-ray diffraction, FT-IR spectra and electronic spectra. The central cobalt(II) ion has nearly ideal octahedral geometry, quite different from that of the copper(II) ion in a previous report. Variable-temperature (2–250 K) magnetic measurements reveal the existence of weak anti-ferromagnetic interactions in **1**.

Supplementary material

Additional materials, consisting of atomic coordinates and equivalent isotropic displacement parameters, are available from CCDC. Deposit number is 258245. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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