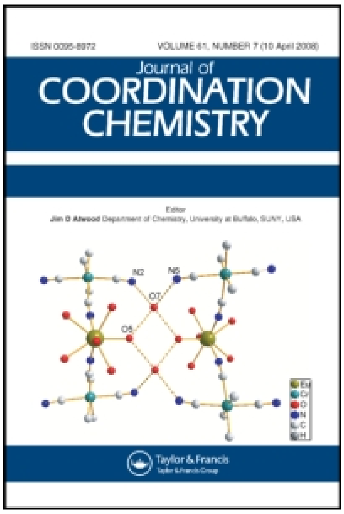

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Synthesis, crystal structure and magnetic property of an octacyanometalate-bridged complex

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Synthesis, crystal structure and magnetic property of an octacyanometalate-bridged complex

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An octacyanometalate-bridged complex, $[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3]\cdot 2H_2O$, has been prepared and characterized and the magnetic properties studied. The complex was characterized using IR, elemental analysis and UV-Vis. The magnetic susceptibility measured over the range 1.8–300 K shows antiferromagnetic interaction.

Keywords: Crystal structure; Octacyanometalate; Antiferromagnetic

1. Introduction

Cyanide anions possess the ability to link various central atoms and also to mediate magnetic interaction between paramagnetic ions. Over the past decade, Prussian blue analogues involving hexacyanometalate $[M(CN)_6]^{n-}$ with 3d metals and polyhexacyanometalates containing organic ligands have occupied a special position in the design and synthesis of new molecular based magnets due to their high critical temperatures and properties such as photo-induced magnetism [1–3]. Recently octacyanometalate and 3d transition metal molecular precursors for design and construction of new crystalline materials with potentially adjustable magnetic properties have developed into an area of intense research [4]. Octacyanometalates $[M(CN)_8]^{n-}$ $(M = Mo, W)$ are versatile building blocks that can adopt three different spatial configurations (e.g., square antiprism (D_{4h}), dodecahedron (D_{2d}), bicapped trigonal prism (C_{2V})), depending on their chemical environment, such as the surrounding ligands and the choice of metal ion [5]. A variety of coordination geometries are found in the crystal structure of their complexes. The magnetic properties of these materials can be modulated by these flexible molecular structures. In this paper we report the synthesis, structure of a new complex $[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3]\cdot 2H_2O$ which shows antiferromagnetic interaction.

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2. Experimental

All of the starting materials were of reagent grade and were used without further purification. IR spectra were obtained using a Shimadzu IR-408 Infrared Spectrometer in the 4000–600 cm^{-1} regions. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C analyzer. The ultraviolet and visible spectra were measured on a Shimadzu UV-570 spectrophotometer. Magnetic properties were measured on a SQUID MPMS XL-7 Magnetometer. Cyanide salts are toxic and should be handled with caution!

3. Synthesis

3.1. *The single crystal synthesis of* $[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3] \cdot 2H_2O$

A 10 ml aqueous solution of $K_4[W(CN)_8] \cdot 2H_2O$ (58.4 mg, 0.1 mmol) was added to a 10 ml DMF/H_2O (1 : 1) solution of $[Ni(en)_2(H_2O)_2](ClO_4)_2$ (37.8 mg, 0.1 mmol). After stirring for three hours at room temperature, the solution was filtered. Yellow crystals were obtained from the filtrate in about two weeks. Yield (based on $K_4[W(CN)_8] \cdot 2H_2O$): 48%. Anal. Calcd. for $C_{18}H_{46}N_{18}Ni_2O_3W$ (%): C, 25.00; H, 5.32; N, 29.17. Found: C, 25.46; H, 5.69; N, 29.63.

3.2. *Crystallographic data collection and refinement*

Details for the crystal data and refinement are given in table 1. Selected bond lengths and angles are presented in table 2. Data collection was performed on a Bruker Smart 1000 area detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 294(2) K. Intensity data were measured at 294(2) K by the $\omega/2\theta$ technique. Semiempirical absorption analysis was performed using the SADABS program. The structure was solved by direct-method successive Fourier difference analysis (SHELXS-97) and refined by the full-matrix least-squares on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXS-97). Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters.

4. Results and discussion

4.1. *Crystal structure of* $[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3] \cdot 2H_2O$

The title complex has been structurally characterized by single crystal X-ray crystallography. A perspective view is shown in figure 1. The complex, crystallized as $[Ni(en)_3] \cdot 2H_2O[Ni(en)_2(H_2O)W(CN)_8]$, belongs to the orthorhombic system. There is a $[Ni(en)_3]^{2+}$ cation, a bimetallic $[W(CN)_8Ni(en)_2(H_2O)]^{2-}$ anion and two uncoordinated water molecules in the unit. In the $[Ni(en)_3]^{2+}$ cation, Ni(2) is coordinated with six N atoms from three en molecules in a distorted octahedral

Table 1. Crystal data and structure refinement for complex.

Formula	$C_{18}H_{46}N_{18}Ni_2O_3W$
Formula weight	864.00
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system (mm^3)	Orthorhombic
Space group	$P2(1)2(1)2(1)$
Unit cell dimensions (Å, °)	
a	11.6069(10)
b	15.0074(13)
c	18.9102(16)
α	90
β	90
γ	90
V (Å^3)	3294.0(5)
Z	4
Absorption coefficient	4.666
$F(000)$	1736
Calculated density	1.742
Crystal size (mm^3)	$0.18 \times 0.16 \times 0.1$
θ range for data collection (°)	1.73–26.37
Limiting indices	$-14 \le h \le 13$, $-7 \le k \le 18$, $-23 \le l \le 23$
Reflections collected	8741
Reflections collected/unique	18773/6733 [$R_{(int)} = 0.0344$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.571 and 0.436
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6733/9/379
Goodness-of-fit on F^2	0.991
Absolute structure parameter	−0.016(7)
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0256$, $wR_2 = 0.0468$
R indices (all data)	$R_1 = 0.0345$, $wR_2 = 0.0493$
Largest diff. peak and hole (eÅ^{-3})	0.811 and −1.553
Primary method of solution	Direct

coordination environment. In $[W(CN)_8Ni(en)_2(H_2O)]^{2-}$, Ni(1) is six-coordinate with a distorted octahedral geometry by means of four nitrogen atoms of two en ligands and a nitrile nitrogen atom from a $[W(CN)_8]^{4-}$ anion and an oxygen atom of H_2O. The distances between two oxygen atoms are $O1 \cdots O2 = 7.0$ Å, $O1 \cdots O3 = 8.4$ Å, $O2 \cdots O3 = 2.7$ Å. Through a combination of hydrogen bonds, $[Ni(en)_3]^{2+}$, $[W(CN)_8Ni(en)_2(H_2O)]^{2-}$ and water molecules are interconnected into a 3D network.

4.2. *IR and UV-visible spectra*

IR spectra of the solid phase show ν_{CN} bands at 2163 cm^{-1} and 2146 cm^{-1}. The band at 2146 cm^{-1} is due to the terminal and the band at 2163 cm^{-1} is due to bridging CN groups of $[W(CN)_8]^{4-}$. The UV spectrum of the aqueous solution of the complex displays a weak peak at 1174 nm, attributed to the d–d transition of Ni(II) ion.

4.3. *Magnetic properties*

The magnetic susceptibility of complex was studied in the temperature range of 1.8–300 K. Figure 2 shows the experimental data plotted as χ_M *versus* T, μ_{eff} *versus* T

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

W(1)–C(1)	2.156(5)	Ni(1)–N(9)	2.107(4)
W(1)–C(3)	2.156(5)	Ni(1)–N(12)	2.111(4)
W(1)–C(5)	2.169(4)	Ni(1)–N(10)	2.114(4)
W(1)–C(6)	2.170(5)	Ni(1)–O(1)	2.137(3)
W(1)–C(7)	2.172(5)	Ni(2)–N(14)	2.113(4)
W(1)–C(8)	2.173(5)	Ni(2)–N(15)	2.127(4)
W(1)–C(2)	2.177(4)	Ni(2)–N(18)	2.128(4)
W(1)–C(4)	2.189(5)	Ni(2)–N(16)	2.129(4)
Ni(1)–N(1)	2.084(4)	Ni(2)–N(17)	2.138(4)
Ni(1)–N(11)	2.104(4)	Ni(2)–N(13)	2.152(4)
C(8)–W(1)–C(2)	75.33(19)	C(1)–W(1)–C(3)	85.02(17)
C(1)–W(1)–C(4)	141.90(16)	C(1)–W(1)–C(5)	143.11(17)
C(6)–W(1)–C(4)	74.10(17)	C(3)–W(1)–C(5)	104.32(17)
C(2)–W(1)–C(4)	123.15(18)	C(1)–W(1)–C(6)	71.77(17)
N(9)–Ni(1)–N(10)	81.35(15)	C(3)–W(1)–C(6)	79.30(17)
N(1)–Ni(1)–O(1)	91.71(14)	C(5)–W(1)–C(6)	144.62(18)
N(9)–Ni(1)–O(1)	93.76(15)	C(1)–W(1)–C(7)	109.61(18)
N(10)–Ni(1)–O(1)	87.82(13)	C(5)–W(1)–C(7)	83.49(18)
N(14)–Ni(2)–N(18)	94.80(17)	C(1)–W(1)–C(8)	73.67(17)
N(14)–Ni(2)–N(16)	169.99(17)	C(3)–W(1)–C(8)	144.62(19)
N(15)–Ni(2)–N(16)	81.48(16)	C(6)–W(1)–C(8)	118.40(17)
N(14)–Ni(2)–N(17)	93.99(15)	C(7)–W(1)–C(8)	70.53(18)
N(18–Ni(2)–N(17)	81.41(16)	C(1)–W(1)–C(2)	75.42(16)
N(11)–Ni(1)–O(1)	86.67(14)	C(5)–W(1)–C(2)	3.90(17)
N(12)–Ni(1)–O(1)	169.35(13)	C(6)–W(1)–C(2)	137.83(18)
N(15)–Ni(2)–N(18)	174.74(16)	N(1)–Ni(1)–N(11)	91.49(15)
N(14)–Ni(2)–N(13)	81.92(15)	N(11)–Ni(1)–N(9)	176.32(17)
N(18)–Ni(2)–N(13)	90.24(16)	N(1)–Ni(1)–N(12)	82.70(15)
N(16)–Ni(2)–N(13)	93.81(16)	N(9)–Ni(1)–N(12)	96.89(16)
N(17)–Ni(2)–N(13)	170.40(16)	N(12)–Ni(1)–N(10)	93.76(16)

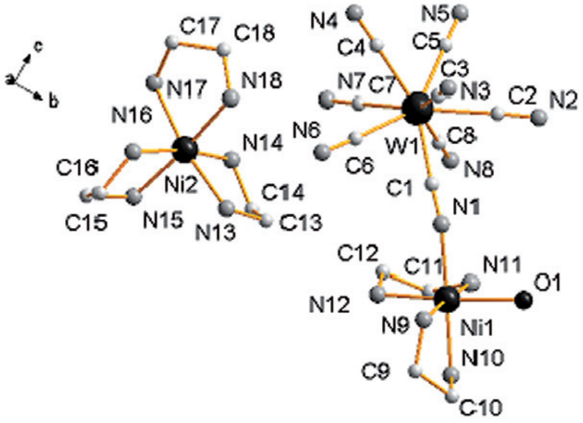

Figure 1. The molecular structure of $[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3] \cdot 2H_2O$ (H and H_2O not shown for clarity).

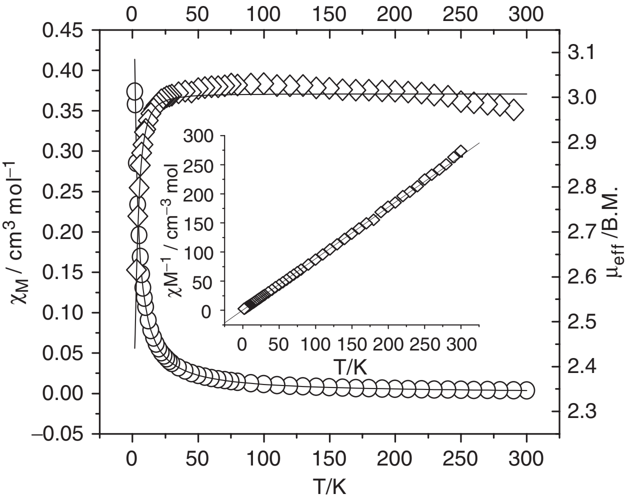

Figure 2. χ_M(○) *vs.* T and μ_{eff}(◇) *vs.* T plots for complex. The inset is the $1/\chi_M$(□) *vs.* T for complex.

and $1/\chi_M$ *versus* T. At 300 K, the μ_{eff} is 2.96 B.M., slightly larger than the spin-only value of 2.83 B.M. for the magnetically isolated spin system $(S_{Ni}) = (1)$, suggesting the presence of some magnetic interaction. When the temperature is lowered, the μ_{eff} remains constant until 12 K. Then μ_{eff} decreases abruptly on further lowering the temperature due to zero-field splitting, suggesting the presence of an antiferromagnetic interaction for the complex.

Considering the zero-field splitting, the temperature dependence of the magnetic susceptibility can be expressed as:

$$\chi_{\parallel} = \frac{2Ng^2\beta^2}{kT}\frac{\exp(-D/kT)}{1+2\exp(-D/kT)} \tag{1}$$

$$\chi_{\perp} = \frac{2Ng^2\beta^2}{D}\frac{1-\exp(-D/kT)}{1+2\exp(-D/kT)} \tag{2}$$

$$\chi = \frac{2x_{\perp} + x_{\parallel}}{3} \tag{3}$$

Best fitting for the experimental data leads to $D = -7.854\,\text{cm}^{-1}$, $g = 2.127$ with the agreement factor $R = 3.89 \times 10^{-3}$.

From 1.8–300 K, the data can be roughly fitted to a Curie–Weiss law with $C = 1.13\,\text{emu K mol}^{-1}$ and $\theta = -0.48\,\text{K}$. The Weiss constant is negative which also indicates that the dominant magnetic interaction is antiferromagnetic.

5. Conclusions

$[Ni(en)_2(H_2O)W(CN)_8][Ni(en)_3] \cdot 2H_2O$ has been synthesized from $[W(CN)_8]^{4-}$ and structurally characterized. The magnetic susceptibility measured over the range 1.8–300 K shows antiferromagnetic interaction due to the zero-field splitting.

Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 294118. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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