Cyano-bridged Heterotrinuclear Molybdenum(IV)-Nickel(II) Complexes: Synthesis, Crystal Structure and Magnetic Properties

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CYANO-BRIDGED HETEROTRINUCLEAR MOLYBDENUM(IV)–NICKEL(II) COMPLEXES: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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Two novel cyano-bridged heterotrinuclear molybdenum(IV)–nickel(II) complexes ([Ni(en)$_2$(H$_2$O)]$_2$-[Mo(CN)$_8$] · 2H$_2$O, **1**, and [NiL(H$_2$O)]$_2$[Mo(CN)$_8$] · 4H$_2$O, **2**), where en = 1,2-diaminoethane and L = 1,3,6,9,11,14-hexaazacyclo[12,2,1,1^{6,9}]octodecanne were synthesized and characterized. The crystal structure of **1** was determined. The structure consists of trinuclear units, space group $C2/c$, with unit cell dimensions $a = 17.178(9)$, $b = 11.032(5)$, $c = 17.629(8)$ Å, $\beta = 108.484(8)°$. The temperature dependence of the magnetic susceptibilities for **1** and **2** was analyzed by means of a Hamiltonian expression leading to $J = -0.87\,\text{cm}^{-1}$, $ZJ' = 0.65\,\text{cm}^{-1}$, $D = 0.02\,\text{cm}^{-1}$, $g_{\text{Ni}} = 2.45$ for complex **1**, and $J = -0.87\,\text{cm}^{-1}$, $ZJ' = 0.56\,\text{cm}^{-1}$, $D = 0.02\,\text{cm}^{-1}$, $g_{\text{Ni}} = 2.45$ for complex **2**.

Keywords: Molybdenum; Nickel; Cyanide; X-ray structure; Magnetic properties

INTRODUCTION

The design, synthesis, and characterization of molecular-magnetic materials represents one of the main challenges in the field of molecular science [1]. Prussian blue analogues [M(CN)$_n$] have 4, 6 or 8 terminal cyanides which can give 4, 6 or 8 exchange paths, and, having high symmetry, allow efficient control of the nature and amplitude of the exchange interaction between M and M′ [2–4]. With this fact in mind, and in continuation of our interest in cyano-bridging complexes [5–11], by using [Mo(CN)$_8$]$^{4-}$ as a precursor, two heterotrinuclear complexes [Ni(en)$_2$(H$_2$O)]$_2$[Mo(CN)$_8$] · 2H$_2$O, **1**, and [NiL(H$_2$O)]$_2$[Mo(CN)$_8$] · 4H$_2$O, **2**, were synthesized and characterized. The crystal structure of **1** and magnetic properties of **1** and **2** were investigated.

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EXPERIMENTAL

General

All chemicals were of A. R. grade and used as received, The mononuclear precursors $K_4[Mo(CN)_8]$ [12], $[Ni(en)_2]Cl_2 \cdot 6H_2O$ (en = 1,2-diminoethande) [13], and $[NiL]-(ClO_4)_2 \cdot 3H_2O$ (L = 1,3,6,9,11,14-hexaazacyclo[12,2,1,1^{6,9}]octodecanne) [14], were prepared as described in the literature [11]. IR spectra: Shimadzu IR-408 spectrometer; KBr pellets; only main bands are given in cm^{-1}. Variable-temperature magnetic susceptibilities: Quantum Design MPMS-7 SQUID magnetometer; diamagnetic corrections made with Pascal's constants for all constituent atoms [15]. Elemental analyses (C, H, N): Perkin-Elmer 240 analyzer.

$[Ni(en)_2(H_2O)]_2[Mo(CN)_8] \cdot 2H_2O$ (1)

Yellow, single crystals were obtained by slow diffusion in water in an H-shaped tube sealed by agar of two 10 mL aqueous solutions containing $K_4[Mo(CN)_8]$ (0.5 mmol, 230 mg) and $[Ni(en)_2]Cl_2 \cdot 6H_2O$ (1 mmol, 289 mg). IR (KBr): 3418(s), 3280(s), 2131 (vs), 2114 (vs). *Anal*. Calc. for $C_{16}H_{36}MoN_{16}Ni_2O_4$ (%): C, 26.32; H, 4.97; N, 30.71. Found: C, 26.34; H, 5.01; N, 30.48%.

$[NiL(H_2O)]_2[Mo(CN)_8] \cdot 4H_2O$ (2)

This was synthesized as described for **1**, with $[NiL](ClO_4)_2 \cdot 3H_2O$ instead of $[Ni(en)_2]Cl_2 \cdot 6H_2O$, to give yellow microcrystals. IR (KBr): 3418s(br.), 3273m, 2127vs, 2116m. *Anal*. Calc. for $C_{16}H_{46}Cl_2CuN_8NiO_{14}$ (%): C, 37.01; H, 6.21; N, 26.98. Found: C, 37.19; H, 6.26; N, 26.84.

X-ray Crystallography

Determination of the unit cell and data collection were performed at room temperature on a BRUKER SMART 1000 diffractometer, using graphite-monochromated MoKα radiation ($\lambda = 0.71073\,\text{Å}$). The structure was solved by direct methods using SHELXS-97 and refined by least-squares procedures on F_o^2 with SHELXL-97 by minimizing the function $Rw(F_o^2 - F_c^2)$, where F_o and F_c are the observed and calculated structure factors, respectively [16]. Crystal data and structure refinement details for **1** are summarized in Table I. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-186565. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; e-mail; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Description of the Structure of $[Ni(en)_2(H_2O)]_2[Mo(CN)_8] \cdot 2H_2O$ (1)

The structure of complex **1** consists of a neutral trinuclear unit $[Ni(en)_2(H_2O)]_2$-$[Mo(CN)_8] \cdot 2H_2O$ and two waters. A perspective view of the trinuclear moiety is depicted in Fig. 1, and selected bondlengths and angles are listed in Table II.

TABLE I Summary of crystal data for complex **1**

Empirical formula	$C_{16}H_{36}MoN_{16}Ni_2O_4$
Formula weight	729.93
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 17.178(9)$ Å $b = 11.032(5)$ Å
	$c = 17.629(8)$ Å $\beta = 108.484(8)°$
Volume, Z	3168(3) Å^3, 4
Density (calculated)	1.496 Mg/m^3
$F(000)$	1432
Crystal size	$0.30 \times 0.20 \times 0.15$ mm
θ range for data collection	2.23 to 25.02°
Reflections collected	6495
Independent reflections	2800 [$R(\text{int}) = 0.0698$]
Data/restraints/parameters	2800/0/186
Goodness-of-fit on F^2	0.990
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0501$, $wR2 = 0.1231$
R indices (all data)	$R1 = 0.0818$, $wR2 = 0.1337$
Largest diff. peak and hole	0.684 and -0.912 eA^{-3}
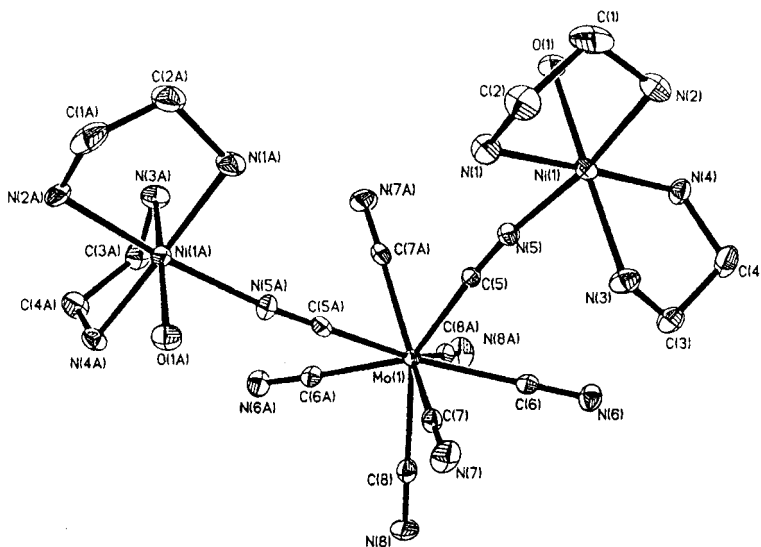
FIGURE 1 An ORTEP drawing of **1** showing thermal ellipsoids drawn at the 30% probability level.

TABLE II Selected bondlengths (Å) and angles (°) for **1**

Mo(1)–C(5)	2.157(6)	Mo(1)–C(6)	2.155(7)
C(5)–N(5)	1.159(8)	C(6)–N(6)	1.163(8)
Ni(1)–N(5)	2.083(5)	Ni(1)–N(1)	2.102(5)
Ni(1)–N(2)	2.107(5)	Ni(1)–O(1)	2.194(5)
Mo(1)–C(8)	2.178(7)	N(3)–C(11)	1.142(8)
C(5)–Mo(1)–C(5)#	79.9(3)	C(6)–Mo(1)–C(5)	72.3(2)
N(5)–C(5)–Mo(1)	175.4(6)	C(5)–N(5)–Ni(1)	170.1(5)
N(5)–Ni(1)–O(1)	88.24(19)	N(5)–Ni(1)–Ni(2)	171.5(2)
N(5)–Ni(1)–N(1)	88.7(2)	N(1)–Ni(1)–N(2)	83.7(2)
O(2)$\cdots$O(3)	2.767	O(2)$\cdots$N(6)	2.843
O(3)$\cdots$O(1)	2.663	O(3)$\cdots$N(8)	2.836

The molybdenum(IV) atom lies in a distorted dodecahedron coordination environ-ment. Two cyanides link two [Ni(en)$_2$(H$_2$O)] units Mo–C–N– with C–N = 1.159(8) Å, but terminal C–N bonds are in the range 2.168(7) to 2.178(7) Å. Similar to other Prussian blue analogues, the linkage has a certain degree of twist with $\angle$Mo–C–N = 175.4(6), $\angle$C–N–Ni = 170.1(5)° [17]. Each nickel(II) atom is in an octahedron coordina-tion environment; four nitrogen atoms from two en ligands coordinate from one side and the other two sites are occupied by a bridging cyanide and a water molecule. The Ni $\cdots$ Ni distance in the trinuclear unit is 7.178 Å, and the nearest distance between neighbouring Ni atoms is 5.348 Å. The two lattice waters, coordinated water and terminal cyanides construct a two dimensional network in the *ac* plane through hydrogen bonds.

Magnetic Properties

In these two complexes, [Mo(CN)$_8$]$^{4-}$ is diamagnetic, so that only Ni^{2+} ions contribute to the magnetism. The magnetic behaviour of **1** and **2** is shown in Fig. 2 in the form of χ_M *vs* T and μ_{eff} *vs* T plots, respectively. The experimental curves are similar.
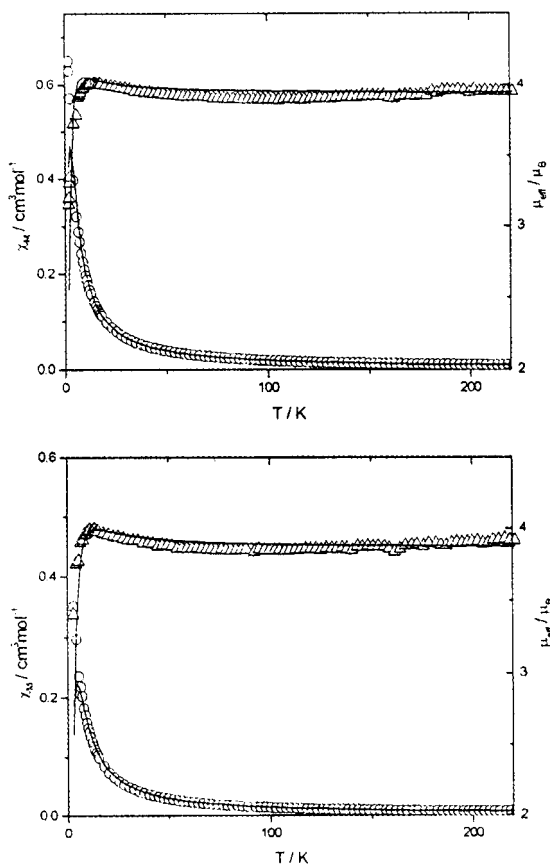

FIGURE 2   Temperature dependence of χ_M and μ_{eff} for **1** (upper) and **2** (lower). The solid line represents theoretical values.

As temperature is lowered, the magnetic moment gradually decreases, with a minimum of about $3.0\,\mu_B$; there are saddle points around $15\,K$. These features are similar to those previously reported by Ginsberg *et al.* [17] for binuclear nickel(II) and can be attributed to intramolecular exchange (J), zero-field splitting (D) and intermolecular exchange (zJ′). To analyze the magnetic data of the present complexes we used the magnetic susceptibility expression published by Ginsberg *et al.* [17,18] for binuclear nickel(II) compounds, as follows.

$$\hat{H} = -2J\hat{s}_1\hat{s}_2 - D(\hat{s}_{1z}^2 + \hat{s}_{2z}^2) - 2zJ'\hat{S}_z\langle\hat{S}_z\rangle - g\beta H\hat{S}_z$$

Least-squares fitting to the experimental data led to $J = -1.03\,cm^{-1}$, $ZJ' = 0.65\,cm^{-1}$, $D = 0.02\,cm^{-1}$, $g_{Ni} = 2.45$ ($R = \sum(\chi_{obsd} - \chi_{cacld})^2 / \sum\chi_{obsd}^2 = 4.2 \times 10^{-3}$) for complex **1** and $J = -1.04\,cm^{-1}$, $ZJ' = 0.56\,cm^{-1}$, $D = 0.02\,cm^{-1}$, $g_{Ni} = 2.45$ ($R = \sum(\chi_{obsd} - \chi_{cacld})^2 / \sum\chi_{obsd}^2 = 1.4 \times 10^{-3}$) for complex **2**. The very weak intramolecular exchange interaction ($-1.03\,cm^{-1}$ for **1** and -1.04 for **2**) could be ascribed to the longer distances between the Ni ions separated by the diamagnetic ion $[Mo(CN)_8]^{4-}$ in the trinuclear unit, and the shorter distance between Ni ions results in a higher inter-molecular exchange interaction.

Acknowledgments

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