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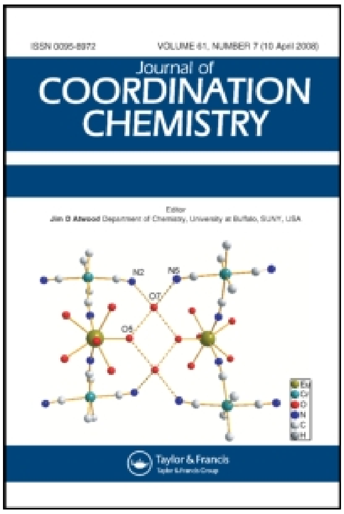

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The synthesis and crystal structure of two new isopolyoxoanion complexes: $[M_2(DMF)_{12}(Mo_6O_{19})_2]$ (M = Co, Ni, DMF = dimethylformamide)

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THE SYNTHESIS AND CRYSTAL STRUCTURE OF TWO NEW ISOPOLYOXOANION COMPLEXES: $[M_2(DMF)_{12}(Mo_6O_{19})_2]$ ($M = Co$, Ni, DMF = DIMETHYLFORMAMIDE)

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Two solid-state materials, $\{M_2(DMF)_{12}[Mo_6O_{19}]_2\}$ ($M = Co$, Ni, DMF = dimethylformamide), have been designed, synthesized under mild reaction conditions and characterized by elemental analyses, IR spectra and single-crystal X-ray diffraction. The structures exhibit extended 2D networks through hydrogen bonds among polyanions and $[M(DMF)_6]^{2+}$; hydrogen-bonding interactions are responsible for the stability of the crystal.

Keywords: Isopolyoxoanions; Transition metal; Crystal structure; Synthesis

INTRODUCTION

Polyoxometalates (POMs), in addition to their importance in catalysis, nanotechnology, biochemistry, medicine and material science [1], play an important role in the design of new materials with novel electronic, magnetic and topological properties [2]. In studies of these materials, an astonishing variety of novel phases arises from the combination of polyoxometalates and transition metal coordination polymers via various intermolecular interactions such as hydrogen bonding, π–π stacking and Coulombic interactions. Chen *et al.* and other groups have reported related work on monomeric metal complexes that extended into 3D network via supramolecular interactions [3]. Zubieta has prepared several organodiamine–molybdenum oxide composite materials, organodianium–molybdenum oxide phases, and molybdenum oxide phases containing organodiamine-ligated heterometals [4]. Recently, several structures based on metal coordination polymers and POMs have been realized, including the incorporation of a POM ion as a non-coordinating anion into a 3D copper(II)

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4,4′-bipyridine network [5], incorporation of POMs into porous Co phosphates and a copper(II)–organoamine network [6,7]. Our group has reported three novel supramolecular assemblies from polyoxometalate and crown ether building blocks [8].

A part of our work is to incorporate $Mo_6O_{19}^{2-}$ into transition metal coordination compounds under mild reaction conditions. However, reactions of polymolybdate and transition metals usually results in precipitation; relatively few synthetic routes to clusters containing transition metals have been established. We find an organic system containing amide can slow precipitation, affording stable crystals, and anticipate that the combination of transition ions and POMs could lead to interesting magnetic and catalytic properties in future investigations of this family of materials. In this article, we report the syntheses and single crystal structure analysis of two complexes: $\{Co_2(DMF)_{12}[Mo_6O_{19}]_2\}$ (**1**), $\{Ni_2(DMF)_{12}[Mo_6O_{19}]_2\}$ (**2**). Their structures exhibit extended 2D networks through hydrogen-bonding interactions. Use of an organic system containing amide offers the possibility for design of isopolyanion materials under suitable reaction conditions, based on molecular building blocks yielding a solid-state magnetic material of given composition and properties.

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EXPERIMENTAL

All chemicals purchased were reagent grade and used without further purification. $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$ was synthesized by the improved methods of the literature [9] and characterized by IR spectra and TG analyses. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN instrument. Mo, Co and Ni were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer with pressed KBr pellets.

Preparation

Synthesis of $\{Co_2(DMF)_{12}[Mo_6O_{19}]_2\}$ (*1*)

4 cm^3 DMF solution of $[Bu_4N]_2Mo_6O_{19}$ (0.1 mmol, 0.110 g) and 10 cm^3 ethanol (EtOH) solution of *p*-phthalic acid (0.5 mmol, 0.083 g) were added dropwise to a stirred 10 cm^3 ethanol (EtOH) solution of $CoCl_2 \cdot 6H_2O$ (0.5 mmol, 0.1189 g) in succession. The light-blue solution was stirred at 60°C for 2 h. The resulting solution was filtered and then allowed to evaporate in air at room temperature. Slow evaporation afforded light-red crystals of **1**. Yield, 60 mg (21.8% based on Mo). *p*-Phthalic acid is necessary for this reaction although it is not incorporated into the structure of the compounds. Anal. Calcd. for $C_{36}H_{84}N_{12}O_{50}Co_2Mo_{12}$ (%): C, 15.70; H, 3.07; N, 6.10; Mo, 41.80; Co, 4.28. Found: C, 15.78; H, 3.03; N, 5.97; Mo, 41.65; Co, 4.28.

Synthesis of $\{Ni_2(DMF)_{12}[Mo_6O_{19}]_2\}$ (*2*)

The preparation of **2** was similar to that of **1** except that $NiCl_2 \cdot 6H_2O$ was used. Yield, 75 mg (27.2% based on Mo). Anal. Calcd. for $C_{36}H_{84}N_{12}O_{50}Ni_2Mo_{12}$ (%): C, 15.70; H, 3.07; N, 6.10; Mo, 41.80; Ni, 4.26. Found: C, 15.73; H, 3.04; N, 6.21; Mo, 41.67; Ni, 4.23.

TABLE I Crystal data and structural refinement for **1**

	1	**2**
Formula	$\{Co_2(DMF)_{12}[Mo_6O_{19}]_2\}$	$\{Ni_2(DMF)_{12}[Mo_6O_{19}]_2\}$
Formula weight	2754.29	2753.81
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
a (Å)	15.208(3)	15.239(3)
b (Å)	17.294(4)	17.251(4)
c (Å)	15.867(3)	15.770(3)
β (°)	91.53(3)	91.40(3)
V (Å^{-3})	4171.6(14)	4144.5(14)
Z	2	2
$F(000)$	2684	2688
μ (mm^{-1})	2.222	2.291
Reflections collected	17222	16680
Independent reflections	9317($R_{\text{int}} = 0.0877$)	9301($R_{\text{int}} = 0.0432$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.802	0.897
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.0543$	$R_1 = 0.0393$, $wR_2 = 0.0873$
R indices (all data)	$R_1 = 0.1573$, $wR_2 = 0.0659$	$R_1 = 0.0948$, $wR_2 = 0.1214$

$R_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.

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Crystal Structure Determination

A red single crystal of **1** with dimensions of $0.266 \times 0.171 \times 0.143\,\text{mm}^3$ was mounted on the tip of a glass fiber in air. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $2.18 < \theta < 27.48°$. An empirical absorption correction was applied (2.222 mm^{-1}) [10]. A total of 17 222 (9317 unique, $R_{\text{int}} = 0.0877$) reflections were measured ($-19 \leq h \leq 19$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$).

A green single crystal of **2** with dimensions $0.327 \times 0.224 \times 0.171\,\text{mm}^3$ was mounted on the tip of a glass fiber in air. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $1.75 < \theta < 27.45°$. An empirical absorption correction was applied (2.291 mm^{-1}) [10]. A total of 16 680 (9301 unique, $R_{\text{int}} = 0.0423$) reflections were measured ($-19 \leq h \leq 19$, $-20 \leq k \leq 22$, $-20 \leq l \leq 20$).

All structures were solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXL-97 software [11]. All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located in the Fourier difference maps. A summary of the crystallographic data and structural determination for **1** and **2** is provided in Table I.

Results and Discussion

The isolation of the title compounds depends on solvent system and temperature. When the reaction temperature was higher than 75°C, only colorless crystals of $[(n\text{-}C_4H_9)_4N]_4[\beta\text{-}Mo_8O_{26}]$ could be obtained. When the reaction was performed in EtOH–$C_5H_8O_2$ (acetylacetone)–HAc mixed solvent system, we could not obtain the title compounds. If p-phthalic acid was replaced by a mixture of succinic anhydride $[(CH_2CO)_2O]$ and phthalimide $(C_6H_4(CO)_2NH)$, the expected single crystal was unstable.

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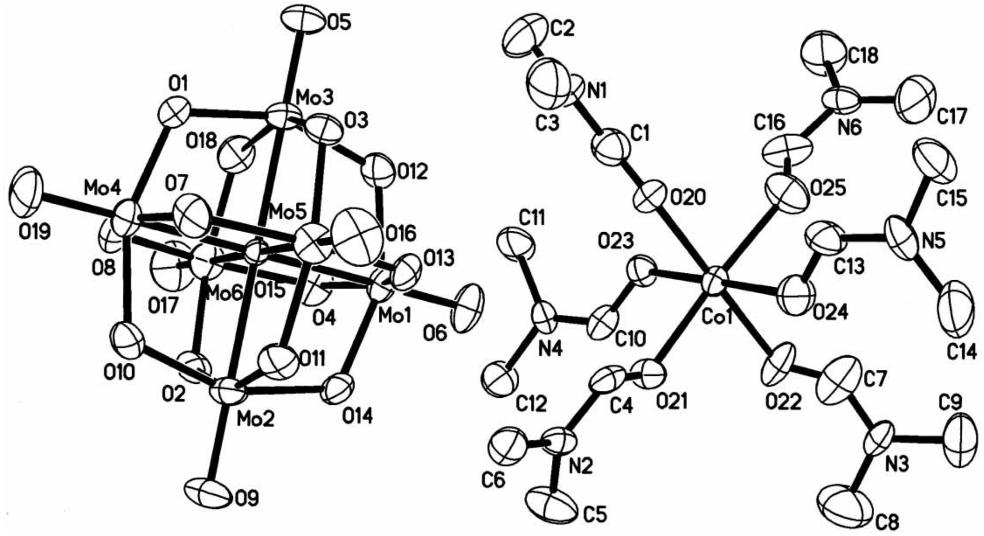

FIGURE 1 View of the structure of $[Co(DMF)_6Mo_6O_{19}]$ compound with atom labeling scheme. The hydrogen atoms are omitted for clarity.

TABLE II Selected bond distances (Å) and angles (°) for Compound **1**

Mo(1)–O(6)	1.675(4)	Mo(1)–O(15)	2.327(4)
Mo(1)–O(4)	1.903(5)	Mo(2)–O(9)	1.672(4)
Mo(2)–O(11)	1.922(5)	Mo(2)–O(15)	2.317(4)
Mo(3)–O(5)	1.674(4)	Mo(3)–O(12)	1.922(4)
Mo(3)–O(15)	2.309(3)	Mo(4)–O(19)	1.683(5)
Mo(4)–O(8)	1.925(5)	Mo(4)–O(15)	2.297(4)
Co(1)–O(20)	2.074(4)	Co(1)–O(22)	2.079(5)
Co(1)–O(23)	2.093(5)	Co(1)–O(25)	2.067(5)
O(6)–Mo(1)–O(4)	103.7(2)	O(4)–Mo(1)–O(13)	153.14(18)
O(4)–Mo(1)–O(12)	86.7(2)	O(6)–Mo(1)–O(15)	179.2(2)
O(4)–Mo(1)–O(15)	76.52(17)	O(21)–Co(1)–O(20)	92.58(18)
O(21)–Co(1)–O(22)	86.6(2)	O(20)–Co(1)–O(22)	178.2(2)
O(21)–Co(1)–O(24)	90.1(2)	Mo(3)–O(1)–Mo(4)	116.1(2)
Mo(4)–O(15)–Mo(3)	90.04(12)	Mo(3)–O(15)–Mo(2)	179.4(2)
C(10)–O(23)–Co(1)	122.0(4)	C(16)–O(25)–Co(1)	138.0(7)

A single-crystal X-ray analysis reveals that Complex **1** consists of one $[Co(DMF)_6]^{2+}$ cation and one isopolyanion $Mo_6O_{19}^{2-}$ (Fig. 1, selected bond lengths and angles in Table II). The cobalt atom adopts distorted octahedral geometry, and is bound with six oxygen atoms from six DMF molecules with Co–O distances in the range 2.046(4)–2.109(5) Å and bond angles 86.1(2)–178.80(19)°. The $Mo_6O_{19}^{2-}$ isopolyanion is the well-known Lindquist structure [1a], constructed by six MoO_6 octahedra that are connected with each other via edge-sharing oxygen atoms and thus exhibits an approximate O_h symmetry. Three kinds of oxygen atoms exist in the cluster, that is, the terminal oxygen O_a, double-bridging oxygen O_b, and central oxygen O_c. Thus, the Mo–O bond lengths can be grouped into three sets: Mo–O_a 1.672(4)–1.683(5) Å, Mo–O_b 1.901(4)–1.940(4) Å, and Mo–O_c 2.297(4)–2.327(4) Å.

It is striking that the structure of the compound exhibits hydrogen-bonding interactions between the oxygen atoms from the polyoxoanions and hydrogen atoms

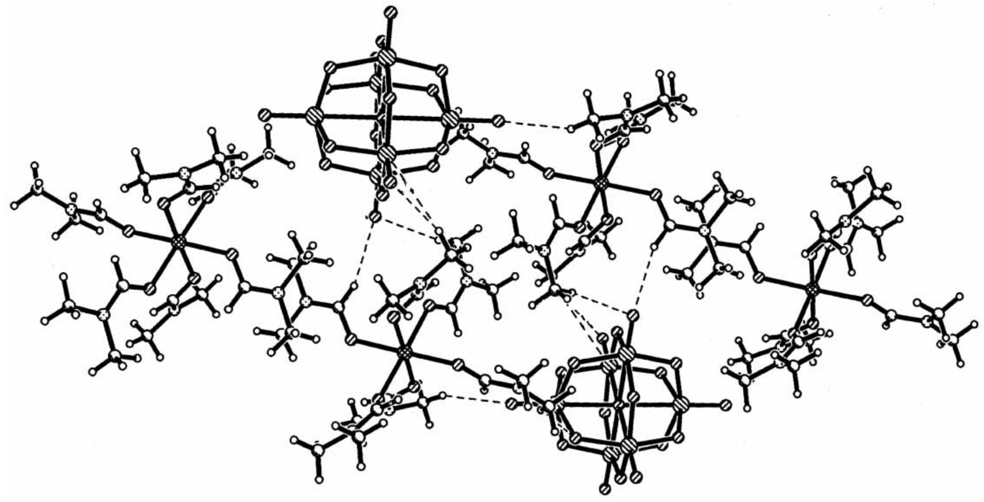

FIGURE 2 Hydrogen-bonding interactions between monomeric metal cations and polyoxoanions.

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TABLE III Interatomic distances (Å) involving hydrogen-bonded atoms in Compound **1**

C	*H*	*O*	*C–H* *Distance* (Å)	*H···O* *Distance* (Å)	*C···O* *Distance* (Å)
C(3B)	H(3AB)	O(17B)	0.960 (0.960)	2.548	3.424
C(4B)	H(4AB)	O(17B)	0.960 (0.960)	2.533	3.418
C(11A)	H(11A)	O(9B)	0.960 (0.960)	2.533	3.333

from the methyl group of DMF molecules (Fig. 2). Thus the polyoxoanions and cations are both stabilized by the extensive hydrogen bonds. Representative hydrogen bonds are O(17B)···H(3AB), O(17B)···H(4AB) and O(9B)···H(11A), whose lengths are 2.548, 2.533 and 2.533 Å, respectively (see Table III). Hydrogen-bonding interactions further link the molecules into an interesting two-dimensional supramolecular network along the *b* axis. In this 2D architecture, the polyoxoanion $Mo_6O_{19}^{2-}$ acts as the joint to connect four $[Co(DMF)_6]^{2+}$ building blocks through hydrogen-bonding interactions. The polyoxoanions are encapsulated inside the network (Fig. 3). The structure of Compound **2** is similar to that of **1**.

In the complex $[NH_4][La(DMF)_7(\beta\text{-}Mo_8O_{26})]$ [12], the lanthanum center adopts a nine-coordinate geometry. The La atom is bound to seven oxygen atoms of seven DMF ligands and two terminal oxygen atoms from a $\beta\text{-}[Mo_8O_{26}]^{4-}$ cage. In our title compounds, M (Co, Ni) is coordinated with six oxygen atoms from six DMF molecules; to our knowledge, this coordination pattern has not previously been reported. In addition, there are significant hydrogen-bonding interactions between the terminal oxygen atoms of $[Mo_6O_{19}]^{2-}$ and the hydrogen atoms of DMF.

The DMF molecules, as coordination ligands, effectively protect the transition metal cation from further reaction, preventing formation of an insoluble solid under mild reaction conditions. The title compounds containing transition metals may possess new and unique properties in contrast to discrete ligands and POMs. The successful

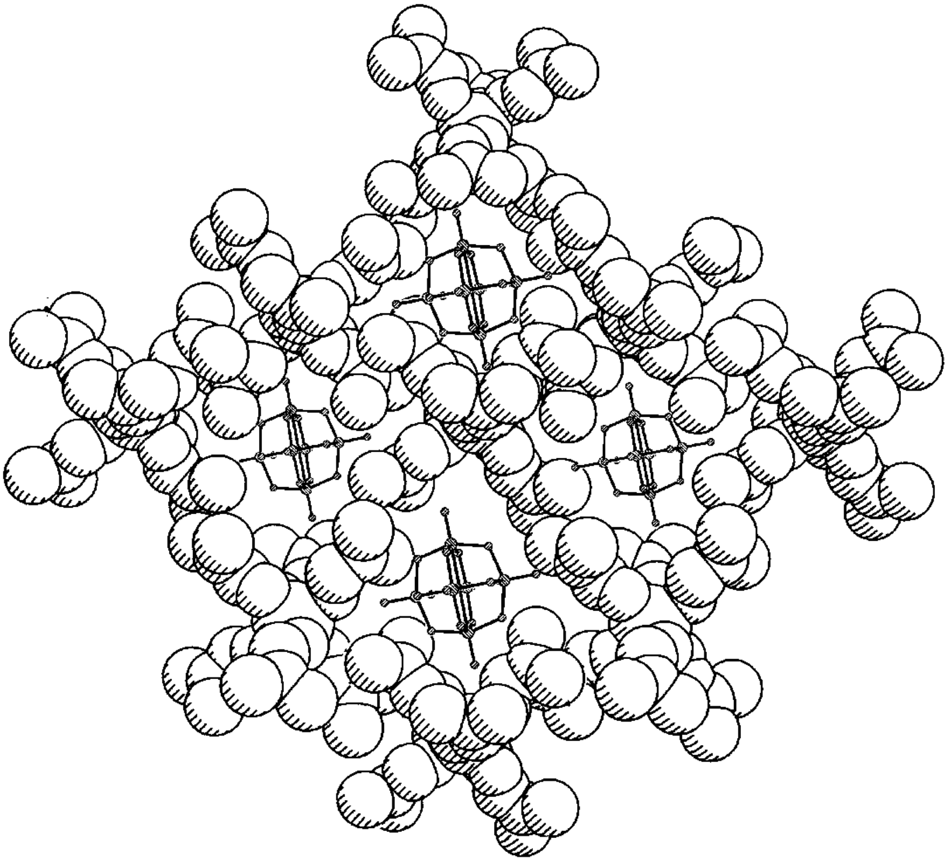

FIGURE 3 Space-filling diagram showing the 2D supramolecular assembly of **1** along the *b* axis.

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preparation of these two new DMF-coordinated transition metal POMs might provide information for the development of novel transition metal-based heterometallic complexes.

FT-IR Spectroscopy

In the IR spectrum of **1**, the bands at 799 and 962 cm^{-1} are due to the ν(Mo–O–Mo) and ν(Mo=O) of the $Mo_6O_{19}^{2-}$ polyanions, respectively. The feature band at 1652 cm^{-1} can be ascribed to ν(C=O) of DMF. Bands in the range 1498–1060 cm^{-1} are characteristic of DMF. The IR spectrum of **2** is very similar to that of **1**.

Acknowledgments

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