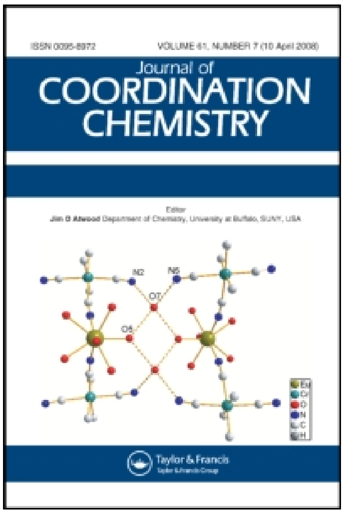

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Hydrothermal synthesis and characterization of a novel polyoxometallate-templated three-dimensional supramolecular network

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HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF A NOVEL POLYOXOMETALLATE-TEMPLATED THREE-DIMENSIONAL SUPRAMOLECULAR NETWORK

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The well-known polyoxomolybdate anion $[Mo_8O_{26}]^{4-}$ has been used as a noncoordinating anionic template for the construction of a novel three-dimensional (3D) supramolecular network, $[Co(phen)_3]_2[Mo_8O_{26}]\cdot 2.5H_2O$ (**1**) (phen = *o*-phenanthroline). Compound **1** has been characterized by elemental analyses, IR spectrum, X-ray photoelectron spectroscopy (XPS), TG analysis and single-crystal X-ray diffraction. Single-crystal X-ray diffraction analysis reveals that $[Co(phen)_3]^{2+}$ coordination complexes are packed together via aromatic π–π stacking and hydrogen-bonding interactions, and exhibit an interesting 3D supramolecular network with one-dimensional (1D) box-like channels in which the octamolybdate anions reside.

Keywords: Octamolybdate; Supramolecular network; Hydrothermal synthesis; Crystal structure

INTRODUCTION

Polyoxometallates (POMs) have attracted extensive interest in solid-state materials chemistry because of their potential applications in catalysis, photochemistry, electrochromism, magnetism and medicine, as well as the richness of their structures [1–4]. A new area of interest is the construction of supramolecular arrays based on POM building blocks and various organic ligands (such as *N*-containing ligands, amino acids, polypeptides, tetrathiafulvalenes, organometallics and cyclopentadienyl derivatives) [3,5–9]. These assemblies possess interesting one- (1D), two- (2D) and three-dimensional (3D) structures and have potential applications in catalysis, medicine, and electrically conductive and magnetic materials [10–12]. Several strategies have been developed to integrate POMs into hybrid solid-state materials [12], which are mainly based on simple materials, by hydrothermal methods. Most recently,

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POM-templated transition metal coordination polymers were synthesized [13]. The motivation for such studies lies not only in the combination of 'value-added properties' and introducing possible synergistic effects [3b,11b] but also in creating opportunities to use the redox properties of POMs to carry out chemical reactions within the intercrystalline voids, avoiding disruption of the framework topology and crystallinity [13].

In recent years, supramolecular assemblies constructed from organic and/or inorganic molecular building blocks have attracted interest because of their novel and diverse topologies and potential applications in host–guest chemistry, shape-selective catalysis, absorption, and electrically conductive, magnetic, and photosensitive materials [7a, 14–17]. The aromatic π–π stacking and hydrogen-bonding interactions play a crucial role in assembling complicated supramolecular architectures.

In the hope that the combination of transition metal complexes with POMs not only shows value-added properties and possible synergistic effects but also allows the creation of new networks with unique physical properties, here we report a novel POM-templated 3D supramolecular network $[Co(phen)_3]_2[Mo_8O_{26}] \cdot 2.5H_2O$ (phen = *o*-phenanthroline) **1**. Compound **1** exhibits an interesting 3D box-like 'host' network constructed from $[Co(phen)_3]^{2+}$ coordination complexes, by aromatic π–π stacking and hydrogen-bonding interactions, in which polyoxoanion 'guests' reside.

EXPERIMENTAL

General Procedures

All chemicals were prepared commercially and used as supplied. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Co and Mo were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG ESCALABMK II spectrometer with an Mg Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centauri FT-IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 at a heating rate of 10°C min^{-1}.

Preparation of 1

Compound **1** was prepared from a mixture of $CoCl_2 \cdot 6H_2O$ (0.25 mmol, Sigma, reagent grade), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.14 mmol, Sigma, reagent grade), SeO_2 (0.25 mmol, Sigma, reagent grade), phen (0.75 mmol, Sigma, reagent grade) and H_2O (9 mL). The starting pH value was adjusted to 5–6 by the addition of 2 M NaOH solution and the mixture was stirred for 30 min in air. The reagents were then sealed in an 18 mL Teflon-lined autoclave and heated at 200°C for 6 days. The autoclave was then cooled at 10°C h^{-1} to room temperature. The resulting brown block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: *ca* 60% based on molybdenum). The brown crystals were manually selected for structural determination and further characterization. The same product can also be obtained without SeO_2 in the reaction system. Elemental analysis of the brown crystals is consistent with the stoichiometry of **1**. Anal. Calcd. for $C_{72}H_{53}Co_2Mo_8N_{12}O_{28.5}$

1: C, 35.6; H, 2.2; Co, 4.9; Mo, 31.6; N, 6.9%. Found: C, 35.4; H, 2.3; Co, 4.8; Mo, 31.8; N, 7.0%. FT-IR data (cm^{-1}): 3065(m), 1625(m), 1581(m), 1518(s), 1493(m), 1426(s) 1343(w), 1317(w), 1223(m), 1145(m), 1104(m), 952(s), 917(s), 894(s), 869(s), 843(s), 804(w), 781(w), 766(w), 724(s), 665(s), 551(m), 499(m), 423(w).

X-ray Crystallography

The structure of Compound **1** was determined by single-crystal X-ray diffraction. A brown single crystal of **1** with dimensions 0.471 × 0.269 × 0.185 mm was mounted on a glass fiber. 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 $2.20 < \theta < 27.47°$. An empirical absorption correction (ψ scan) was applied. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXTL-97 [18]. All of the nonhydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were fixed at their ideal positions and those attached to oxygen atoms were not located accurately. A total of 13 344 (8175 unique, $R_{\text{int}} = 0.0794$) reflections were measured. Structure solution and refinement based on 8175 independent reflections with $I > 2\sigma(I)$ on 0 restraint and 559 parameters gave $R_1(wR_2) = 0.0542$ (0.1356) $\{R_1 = \sum \|F_0| - |F_C\| / \sum |F_0|;\ wR_2 = \sum[w(F_0^2 - F_C^2)^2] / \sum[w(F_C^2)^2]^{1/2}\}$.

A summary of the crystal data and structure refinement for Compound **1** is provided in Table I. Selected bond lengths and angles are listed in Table II and the atomic coordinates and equivalent isotropic displacement parameters for **1** are given in Table III.

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 217320. Copies of

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

Empirical formula	$C_{72}H_{53}Co_2Mo_8N_{12}O_{28.5}$
Formula weight	2427.64
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	11.479(2)
b (Å)	11.805(2)
c (Å)	15.070(3)
α (°)	83.00(3)
β (°)	71.17(3)
γ (°)	78.32(3)
Volume (Å^3)	1889.4(7)
Z	1
Dc (g cm^{-3})	2.134
Absorption coefficient (mm^{-1})	1.802
θ range for data collection (°)	2.20 to 27.47
Limiting indices	$-14 \le h \le 14$, $-14 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	13 344
Independent reflections	8175 [R(int) = 0.0794]
Completeness to $\theta = 27.48°$ (%)	94.4
Data/restraints/parameters	8175/0/559
Goodness-of-fit on F^2	0.974
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.1356$
R indices (all data)	$R_1 = 0.0672$, $wR_2 = 0.1435$

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

Mo(1)–O(12)	1.688(3)	Mo(1)–O(6)	1.941(3)
Mo(1)–O(9)	1.749(3)	Mo(1)–O(13)	2.136(3)
Mo(1)–O(5)	1.934(3)	Mo(1)–O(13)$^{\#1}$	2.393(3)
Mo(2)–O(2)	1.701(3)	Mo(2)–O(5)	1.988(3)
Mo(2)–O(11)	1.702(3)	Mo(2)–O(13)	2.345(3)
Mo(2)–O(4)	1.910(3)	Mo(2)–O(6)$^{\#1}$	2.365(3)
Mo(3)–O(10)	1.704(4)	Mo(3)–O(6)	1.999(3)
Mo(3)–O(1)	1.703(3)	Mo(3)–O(13)	2.307(3)
Mo(3)–O(3)	1.892(3)	Mo(3)–O(5)$^{\#1}$	2.357(3)
Mo(4)–O(8)	1.704(4)	Mo(4)–O(3)$^{\#1}$	1.919(4)
Mo(4)–O(7)	1.709(4)	Mo(4)–O(9)	2.273(3)
Mo(4)–O(4)$^{\#1}$	1.915(4)	Mo(4)–O(13)$^{\#1}$	2.475(3)
Co(5)–N(4)	2.117(4)	Co(5)–N(6)	2.134(4)
Co(5)–N(5)	2.125(4)	Co(5)–N(3)	2.144(4)
Co(5)–N(2)	2.131(5)	Co(5)–N(1)	2.220(5)
O(12)–Mo(1)–O(9)	104.15(17)	O(12)–Mo(1)–O(13)$^{\#1}$	175.64(14)
O(12)–Mo(1)–O(5)	102.41(15)	O(9)–Mo(1)–O(13)$^{\#1}$	80.14(13)
O(9)–Mo(1)–O(5)	96.49(14)	O(5)–Mo(1)–O(13)$^{\#1}$	77.67(12)
O(12)–Mo(1)–O(6)	100.20(15)	O(6)–Mo(1)–O(13)$^{\#1}$	78.27(12)
O(9)–Mo(1)–O(6)	97.28(14)	O(13)–Mo(1)–O(13)$^{\#1}$	75.88(13)
O(5)–Mo(1)–O(6)	149.68(13)	O(12)–Mo(1)–Mo(3)	90.55(12)
O(12)–Mo(1)–O(13)	99.83(15)	O(9)–Mo(1)–Mo(3)	133.08(11)
O(9)–Mo(1)–O(13)	156.02(14)	O(5)–Mo(1)–Mo(3)	123.87(10)
O(5)–Mo(1)–O(13)	78.16(12)	O(6)–Mo(1)–Mo(3)	35.84(9)
O(6)–Mo(1)–O(13)	78.29(12)	O(13)–Mo(1)–Mo(3)	45.73(8)
O(13)$^{\#1}$–Mo(1)–Mo(3)	85.85(7)	O(11)–Mo(2)–O(13)	97.09(14)
O(2)–Mo(2)–O(11)	104.00(17)	O(4)–Mo(2)–O(13)	77.47(12)
O(2)–Mo(2)–O(4)	100.47(17)	O(5)–Mo(2)–O(13)	72.28(12)
O(11)–Mo(2)–O(4)	102.23(16)	O(2)–Mo(2)–O(6)$^{\#1}$	87.03(14)
O(2)–Mo(2)–O(5)	101.84(16)	O(11)–Mo(2)–O(6)$^{\#1}$	165.93(14)
O(11)–Mo(2)–O(5)	97.29(16)	O(4)–Mo(2)–O(6)$^{\#1}$	83.95(13)
O(4)–Mo(2)–O(5)	145.67(13)	O(5)–Mo(2)–O(6)$^{\#1}$	71.55(12)
O(2)–Mo(2)–O(13)	158.72(14)	O(13)–Mo(2)–O(6)$^{\#1}$	71.69(11)
O(10)–Mo(3)–O(1)	104.5(2)	O(1)–Mo(3)–O(5)$^{\#1}$	87.16(16)
O(10)–Mo(3)–O(3)	101.67(18)	O(3)–Mo(3)–O(5)$^{\#1}$	84.74(13)
O(1)–Mo(3)–O(3)	100.11(18)	O(6)–Mo(3)–O(5)$^{\#1}$	71.54(12)
O(10)–Mo(3)–O(6)	97.09(17)	O(13)–Mo(3)–O(5)$^{\#1}$	71.85(11)
O(1)–Mo(3)–O(6)	100.62(17)	O(10)–Mo(3)–Mo(1)	86.97(14)
O(3)–Mo(3)–O(6)	147.45(13)	O(1)–Mo(3)–Mo(1)	135.28(14)
O(10)–Mo(3)–O(13)	96.24(17)	O(3)–Mo(3)–Mo(1)	120.02(10)
O(1)–Mo(3)–O(13)	159.00(16)	O(6)–Mo(3)–Mo(1)	34.66(8)
O(3)–Mo(3)–O(13)	78.48(13)	O(13)–Mo(3)–Mo(1)	41.55(8)
O(6)–Mo(3)–O(13)	73.20(11)	O(5)$^{\#1}$–Mo(3)–Mo(1)	78.37(8)
O(10)–Mo(3)–O(5)$^{\#1}$	165.27(16)	O(4)$^{\#1}$–Mo(4)–O(9)	78.10(13)
O(8)–Mo(4)–O(7)	105.0(2)	O(3)$^{\#1}$–Mo(4)–O(9)	77.33(13)
O(8)–Mo(4)–O(4)$^{\#1}$	101.38(18)	O(8)–Mo(4)–O(13)$^{\#1}$	161.23(16)
O(7)–Mo(4)–O(4)$^{\#1}$	98.17(19)	O(7)–Mo(4)–O(13)$^{\#1}$	93.68(17)
O(8)–Mo(4)–O(3)$^{\#1}$	104.23(18)	O(4)$^{\#1}$–Mo(4)–O(13)$^{\#1}$	74.15(12)
O(7)–Mo(4)–O(3)$^{\#1}$	98.09(19)	O(3)$^{\#1}$–Mo(4)–O(13)$^{\#1}$	73.80(12)
O(4)$^{\#1}$–Mo(4)–O(3)$^{\#1}$	144.77(14)	O(9)–Mo(4)–O(13)$^{\#1}$	69.50(11)
O(8)–Mo(4)–O(9)	91.78(16)	O(7)–Mo(4)–O(9)	163.17(17)
N(4)–Co(5)–N(5)	101.45(15)	N(5)–Co(5)–N(3)	96.63(16)
N(4)–Co(5)–N(2)	97.81(19)	N(2)–Co(5)–N(3)	95.20(17)
N(5)–Co(5)–N(2)	159.13(19)	N(6)–Co(5)–N(3)	170.73(16)
N(4)–Co(5)–N(6)	95.63(14)	N(4)–Co(5)–N(1)	171.36(18)
N(5)–Co(5)–N(6)	78.02(15)	N(5)–Co(5)–N(1)	84.66(19)
N(2)–Co(5)–N(6)	92.22(16)	N(2)–Co(5)–N(1)	77.1(2)
N(4)–Co(5)–N(3)	77.89(16)	N(6)–Co(5)–N(1)	91.60(17)
N(3)–Co(5)–N(1)	95.45(17)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x, -y+2, -z+1$.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U(eq)*
Mo(1)	1605(1)	9389(1)	4482(1)	25(1)
Mo(2)	964(1)	12 085(1)	4953(1)	32(1)
Mo(3)	288(1)	8630(1)	6643(1)	35(1)
Mo(4)	370(1)	8671(1)	2843(1)	38(1)
Co(5)	3957(1)	12 818(1)	7995(1)	33(1)
O(12)	2998(3)	9209(3)	4683(2)	38(1)
O(11)	2393(3)	11 902(3)	5113(3)	42(1)
O(10)	1721(4)	8473(4)	6797(3)	54(1)
O(6)	886(3)	8154(2)	5320(2)	30(1)
O(5)	1420(3)	10 970(3)	3958(2)	32(1)
O(4)	−137(3)	12 514(3)	6161(2)	40(1)
O(3)	−666(3)	9768(3)	7497(2)	41(1)
N(6)	2977(4)	13 864(3)	7114(3)	32(1)
N(5)	5342(4)	13 745(3)	7096(3)	37(1)
N(4)	4342(4)	11 285(3)	7279(3)	33(1)
O(2)	848(3)	13 380(3)	4328(3)	47(1)
O(1)	−296(4)	7438(3)	7224(3)	53(1)
N(3)	5158(4)	11 669(4)	8673(3)	41(1)
N(2)	2262(5)	12 514(5)	9033(3)	57(1)
N(1)	3534(5)	14 249(5)	8941(3)	62(1)
O(9)	1948(3)	8727(3)	3429(2)	35(1)
O(8)	1365(4)	7903(4)	1925(3)	56(1)
O(7)	−1066(4)	8854(4)	2683(3)	59(1)
C(36)	3592(4)	14 705(4)	6601(3)	32(1)
C(23)	5565(4)	10 613(4)	8314(3)	35(1)
C(24)	5111(4)	10 404(4)	7572(3)	33(1)
C(35)	4859(4)	14 648(4)	6596(3)	35(1)
C(28)	5540(5)	15 499(4)	6093(4)	43(1)
C(22)	3902(5)	11 105(5)	6604(3)	40(1)
C(29)	4950(6)	16 409(4)	5564(4)	50(1)
C(21)	4183(5)	10 038(5)	6209(4)	50(1)
C(16)	6378(5)	9743(5)	8645(4)	50(1)
C(33)	1280(5)	14 655(5)	6504(4)	46(1)
C(34)	1852(4)	13 844(4)	7049(3)	39(1)
C(31)	3059(5)	15 591(4)	6061(3)	40(1)
C(25)	6516(5)	13 663(5)	7074(4)	51(1)
C(19)	5440(5)	9319(4)	7205(4)	46(1)
O(13)	441(3)	10 307(2)	5683(2)	29(1)
C(32)	1877(5)	15 541(4)	6017(4)	45(1)
C(30)	3768(6)	16 449(4)	5556(4)	49(1)
C(13)	5554(6)	11 873(6)	9368(4)	58(2)
C(14)	6371(6)	11 050(7)	9731(4)	67(2)
C(12)	1801(6)	13 347(7)	9724(4)	71(2)
C(4)	2024(8)	15 117(8)	10 326(5)	83(2)
C(11)	2494(7)	14 240(6)	9646(4)	62(2)
C(27)	6765(6)	15 402(5)	6109(4)	57(2)
C(15)	6783(6)	10 003(6)	9357(4)	62(2)
C(10)	1657(7)	11 693(8)	9026(5)	84(3)
C(26)	7259(5)	14 494(6)	6589(5)	62(2)
C(20)	4957(6)	9155(5)	6504(4)	57(2)
C(18)	6276(6)	8440(5)	7564(5)	64(2)
C(1)	4172(8)	15 116(6)	8860(6)	79(2)
C(6)	265(8)	14 203(8)	11 118(4)	92(3)
C(17)	6713(6)	8633(6)	8240(5)	68(2)
C(3)	2763(10)	15 962(8)	10 184(6)	96(3)
C(7)	695(8)	13 329(8)	10 434(5)	92(3)
C(8)	64(9)	12 454(10)	10 449(8)	109(4)
C(9)	444(9)	11 636(9)	9775(7)	98(3)
C(2)	3782(10)	15 998(8)	9457(7)	103(3)
C(5)	941(11)	15 049(10)	11 033(6)	114(4)
OW2	7596(10)	11 129(10)	11 633(5)	177(5)
OW1	3100(20)	7350(30)	7938(17)	130(12)

this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis

Compound **1** was prepared in moderately good yield, starting from a slurry containing $CoCl_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, SeO_2 and phen. As the product can also be obtained without SeO_2 in the reaction system, SeO_2 is in fact unnecessary. The pH of the reaction has a crucial role in the synthesis. Indeed, Compound **1** only forms in the limited pH range of 5–6. Moreover, the influence of the conditions of synthesis is noteworthy. Increasing the ratio of phen to $CoCl_2 \cdot 6H_2O$ results in the formation of the tris-chelate cation $[Co(phen)_3]^{2+}$, which is found in the title compound. By contrast, reducing the ratio of phen to $CoCl_2 \cdot 6H_2O$ may prevent the formation of the tris-chelate, allowing the formation of the octamolybdate-supported cobalt phenanthroline complex $[Co(phen)_2]_2Mo_8O_{26}$ [19].

Structure Description

The single-crystal X-ray diffraction study reveals that Compound **1** consists of a centrosymmetric β-octamolybdate anion $[Mo_8O_{26}]^{4-}$ and two $[Co(phen)_3]^{2+}$ coordination cations. As shown in Fig. 1, the octamolybdate anion consists of an Mo_6O_6 ring capped on opposite faces by $\{MoO_6\}$ octahedra. The Mo_6O_6 ring contains six $\{MoO_6\}$ octahedra, in which every two adjacent $\{MoO_6\}$ octahedra are linked

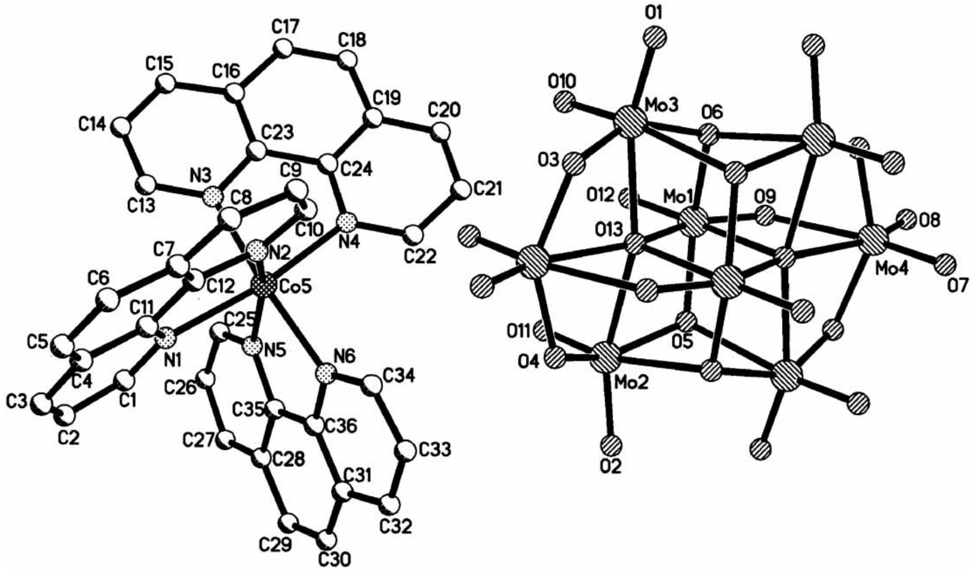

FIGURE 1 View of the structure of Compound **1** with atom-labeling scheme, showing the coordination environments of the molybdenum and cobalt atoms.

by edge-sharing. Two capping $\{MoO_6\}$ octahedra are also attached to each other by edge-sharing. The $\{MoO_6\}$ octahedra are all distorted, and the Mo–O bonds can be grouped into four categories: (i) 1.688(3)–1.709(4) Å for Mo–O(t); (ii) 1.749(3)–2.273(3) Å for Mo–O(μ_2); (iii) 1.934(3)–2.365(3) Å for Mo–O(μ_3); (iv) 2.136(3)–2.475(3) Å for Mo–O(μ_5). The cobalt site is distorted octahedral, coordinated with six nitrogen donors of the phen ligands. The Co–N bond lengths vary from 2.117(4) to 2.220(5) Å.

The most unusual structural feature of Compound **1** is that the $[Co(phen)_3]^{2+}$ coordination complexes are joined together by the aromatic π–π stacking and hydrogen-bonding interactions to form an interesting 3D supramolecular network with 1D box-like channels, as shown in Figs. 2 and 3. Of the three phen ligands on each Co center, one is used as a partition between the octamolybdate anions, and the other two are involved in π–π stacking interaction. The close contact distances between adjacent aromatic rings are *ca* 3.53 and 3.30 Å. The typical hydrogen bonds are listed in Table IV. The size of the box is *ca* 11.2 × 11.4 Å (see Fig. 3). The octamolybdate anion was encapsulated inside as a 'guest' cluster anion and well surrounded by these 'host' box-like units (Fig. 4). As shown in Fig. 2, each octamolybdate anion is surrounded by six $[Co(phen)_3]^{2+}$ coordination complexes, while each $[Co(phen)_3]^{2+}$

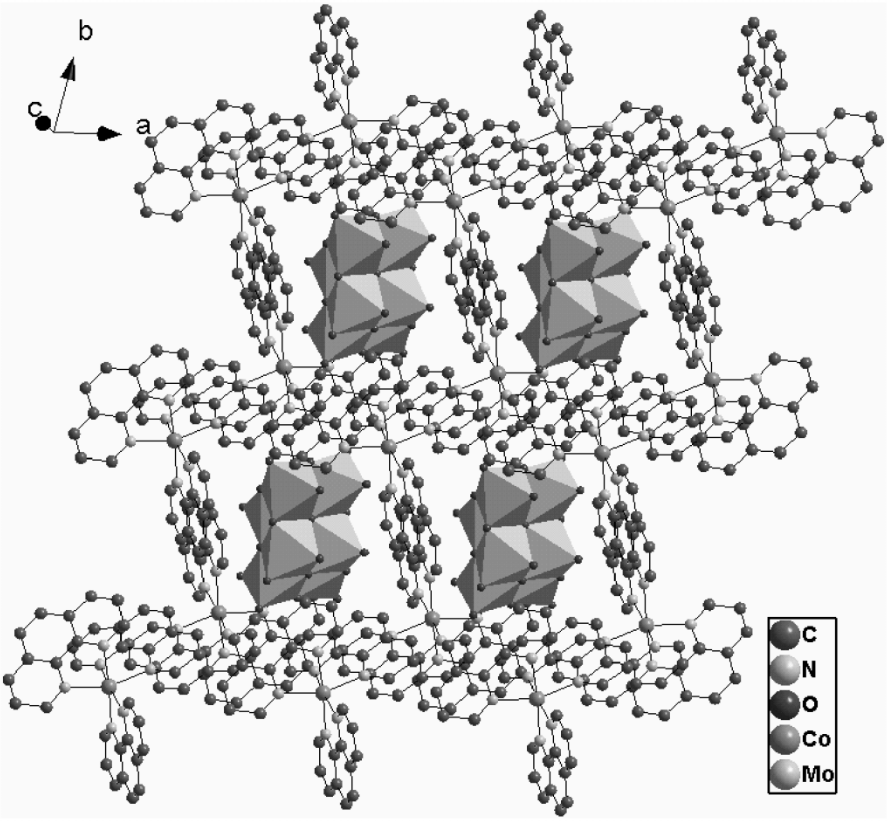

FIGURE 2 Ball-and-stick representation of the box-like cavities based on $[Co(phen)_3]^{2+}$ coordination complexes encircling octamolybdate anions shown in a polyhedral representation. The water molecules and all hydrogen atoms are omitted for clarity.

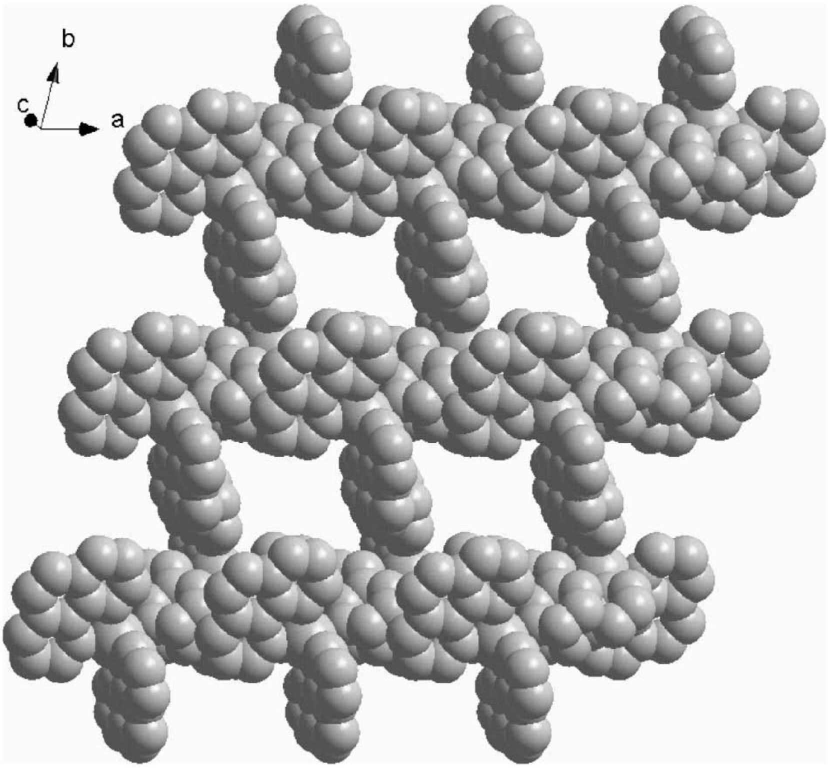

FIGURE 3 Space-filling diagram of the 3D ‘host’ network and the box-like cavities of the title compounds constructed from $[Co(phen)_3]^{2+}$ coordination complexes.

TABLE IV The typical hydrogen bonds in Compound **1**

A	*H*	*B*	*A–H* (Å)	*H* · · · *B* (Å)	*A* · · · *B* (Å)
C(3)	H(3)	O(8)	0.930	2.552	3.461
C(10)	H(10)	O(7)	0.930	2.430	3.037
C(21)	H(21)	O(12)	0.930	2.435	3.348
C(22)	H(22)	O(11)	0.930	2.500	3.205
C(25)	H(25)	O(8)	0.930	2.561	3.388
C(25)	H(25)	O(9)	0.930	2.465	3.048
C(27)	H(27)	O(2)	0.930	2.419	3.195
C(30)	H(30)	O(12)	0.930	2.573	3.416
C(32)	H(32)	O(6)	0.930	2.422	3.236

coordination complex is surrounded by three octamolybdate anions. By inspection of the structure of **1**, it seems that the formation of the unusual structure may be due to the 2 : 1 ratio of $[Co(phen)_3]^{2+}$ cations and $[Mo_8O_{26}]^{4-}$ anions.

Bond valence sum calculations [20] give the values of 5.99, 5.88, 5.92 and 5.97 for Mo(1), Mo(2), Mo(3) and Mo(4), respectively, showing that all Mo sites are in the +6 oxidation state. The calculation shows the value of 1.77 for Co, indicating that the Co site is occupied by the Co^{2+} ion. To confirm the calculated results, XPS

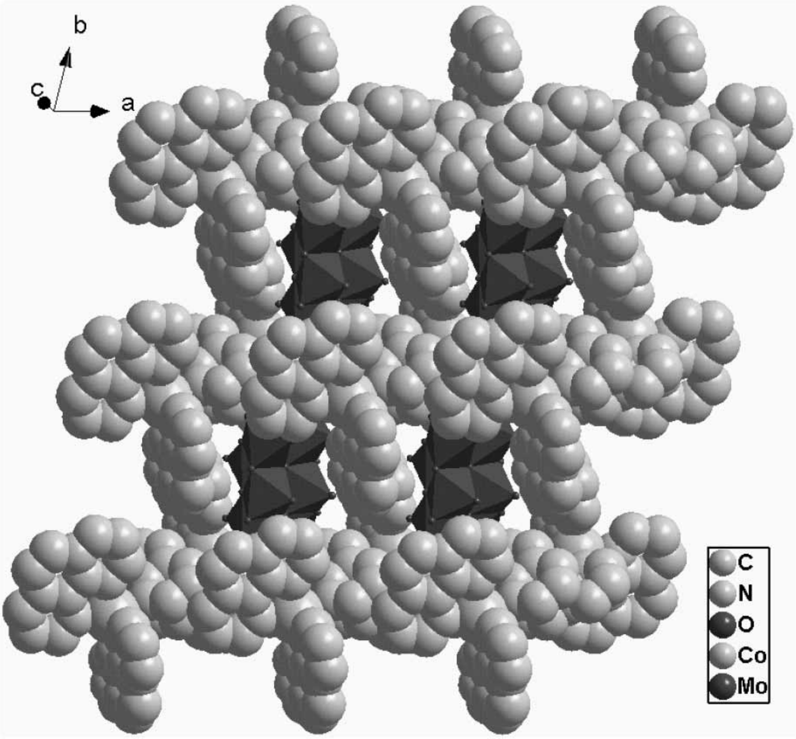

FIGURE 4 Space-filling diagram of the 3D 'host' network with 1D box-like channels and octamolybdate anions encapsulated inside as a 'guest' cluster anion.

of Compound **1** was also studied. The XPS measurements of Compound **1** in the energy regions of Mo_{3d} and Co_{2p} show peaks at 232.0 and 780.6 eV, attributable to Mo^{6+} [21] and Co^{2+} [22], respectively (see Fig. 5). These results further confirm the valences of the Mo and Co atoms.

FT-IR Spectroscopy

In the infrared spectrum of Compound **1** (as shown in Fig. 7), the strong bands at 952, 917, 894, 869, 843, 724 and 665 cm^{-1} could be due to ν(Mo=O) or ν(Mo–O–Mo) vibrations. Bands in the 1625–1145 cm^{-1} regions in the infrared spectrum of Compound **1** are attributed to characteristic peaks of the phen groups.

TG Analysis

The TG curve of Compound **1** (Fig. 6) exhibits four weight-loss steps. The first weight loss occurs in the range 80–13°C, corresponding to loss of H_2O. The observed weight loss (1.70%) is consistent with the calculated value (1.86%). The second weight loss is 2.13% from 330 to 400°C, the third is 15.05% from 400 to 465°C, and the fourth is 27.10% in the temperature range 465–610°C, all assigned to the loss of phen groups. The observed weight loss in the second, third and fourth steps (44.28%) is in

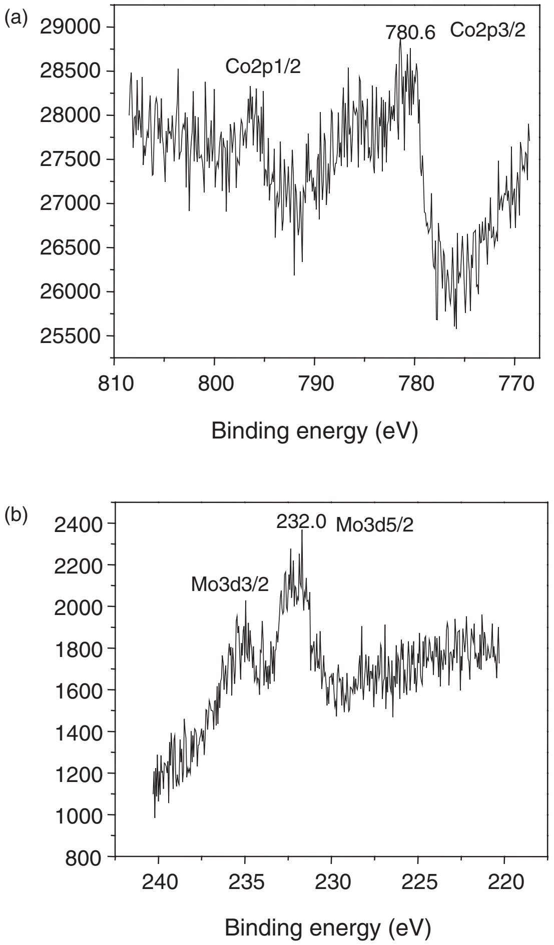

FIGURE 5 The X-ray photoelectron spectra of **1**.

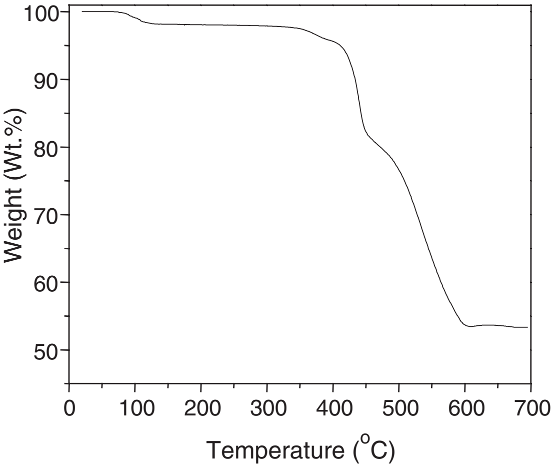

FIGURE 6 The TG curve of **1**.

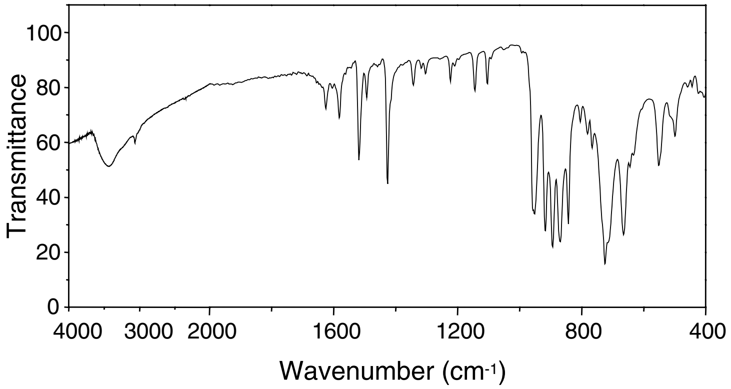

FIGURE 7 The IR spectrum of **1**.

agreement with the calculated value (44.54%). The sample does not lose weight at temperatures higher than 610°C.

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