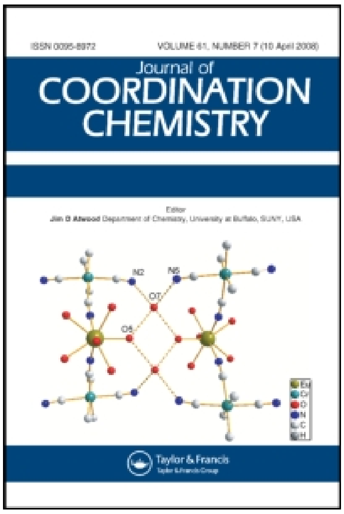

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Hydrothermal Synthesis, Crystal Structures and Magnetic Properties of two Bimetallic Cage Cluster Vanadate Complexes $[Co(phen)_2]_2V_4O_{12}$ and $[Co(2,2'\text{-}bipy)_2]_2V_4O_{12}$

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HYDROTHERMAL SYNTHESIS, CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF TWO BIMETALLIC CAGE CLUSTER VANADATE COMPLEXES $[Co(phen)_2]_2V_4O_{12}$ AND $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$

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Two new bimetallic cluster complexes, $[Co(phen)_2]_2V_4O_{12}$ **1** (phen = phenanthroline) and $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$ **2** (2,2′-bipy = 2,2′-bipyridine), have been synthesized hydrothermally. X-ray crystallography reveals that both **1** and **2** possess a similar metal cage cluster core, $Co_2V_4O_{12}$. Magnetic studies of **1** and **2** indicate that both the complexes exhibit antiferromagnetic interactions between the cobalt(II) ions.

Keywords: Hydrothermal synthesis; Cobalt; Cluster; Crystal structure; Polyoxovanadium; Magnetic properties

INTRODUCTION

Research on organic–inorganic hybrid vanadium oxides and polyvanadate clusters has received much attention because of their intriguing structural diversity and potential applications in molecular adsorption, ion exchange, magnetic chemistry, photochemistry and heterogeneous catalysis [1–3]. They may also find application in secondary lithium batteries and electrochromic devices [4,5]. Hydrothermal synthesis has been proved to be a powerful method to obtain such complexes. Usually, the organic component acts as a structure-directing, charge-compensating and space-filling constituent. Furthermore, recent developments in this area indicate that some organic components can function as ligands and resulting transition metal complexes or fragments are then covalently linked to the metal framework or polyanion clusters [6]. Many infinite chain and layer structures of vanadium oxide complexes are known [7–9], but only a few discrete polyoxovanadate clusters have been reported.

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These are limited to $V_4O_{12}^{4-}$ [11], $V_{10}O_{29}^{8-}$ [12], and $V_8O_{23}^{6-}$ [13]. In this article, we report the hydrothermal synthesis and crystal structures of two new bimetallic cluster complexes, $[Co(phen)_2]_2V_4O_{12}$, **1** (phen = phenanthroline) and $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$, **2** (2,2′-bipy = 2,2′-bipyridine). Both complexes **1** and **2** are based upon the same vanadium oxide cluster $V_4O_{12}^{4-}$ [11].

EXPERIMENTAL

All reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Heraeus Chn-Rapid instrument. Infrared spectra were recorded on a Perkin-Elmer 2000 spectrophotometer using pressed KBr pellets. Variable temperature magnetic susceptibility data were collected for crystalline samples (87.22 mg for complex **1** and 151.95 mg for complex **2**) from 5 to 300 K in a magnetic field of 10 kG after zero-field cooling using a SQUID magnetometer. Diamagnetic corrections were estimated from Pascal constants.

All hydrothermal reactions were performed in 25 mL polytetrafluoroethylene-lined stainless steel Parr bombs under autogenous pressure. The reactants were stirred briefly before heating.

$[Co(phen)_2]_2V_4O_{12}$ (1)

A mixture of NH_4VO_3 (117 mg), $H_2C_2O_4 \cdot 2H_2O$ (252 mg), $Co(NO_3)_2 \cdot 6H_2O$ (291 mg), 1,10-phenanthroline (396 mg) and H_2O (16 mL) was heated at 170°C for six days, yielding dark red rods of **1** in *ca.* 60% yield based on Co, together with minor yellow plates of an unknown material. *Anal.* Calc. for $C_{48}H_{32}N_8O_{12}Co_2V_4$ (%): C, 46.71; H, 2.61; N, 9.07. Found: C, 46.63; H, 2.75; N, 8.97. IR (cm^{-1}): 1624(w), 1583(w), 1515(w), 1425(m), 1344(w), 1145(w), 1103(w), 938(vs), 906(s), 954(vs), 775(m), 748(m), 728(s), 841(m), 557(w), 424(w).

$[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$ (2)

A procedure similar to that used for the synthesis of **1** was adopted. A mixture of NH_4VO_3 (117 mg), $H_2C_2O_4 \cdot 2H_2O$ (252 mg), $Co(NO_3)_2 \cdot 6H_2O$ (291 mg), 2,2′-bipyridine (312 mg) and H_2O (16 mL) was heated at 170°C for six days, yielding red rods of **2** in *ca.* 80% yield based on Co. *Anal.* Calc. For $C_{40}H_{32}N_8O_{12}Co_2V_4$ (%): C, 42.20; H, 2.83; N, 9.84. Found: C, 42.03; H, 2.94; N, 9.71. IR (cm^{-1}): 1598(m), 1572(w), 1472(w), 1441(s), 1313(w), 1250(w), 1171(w), 1104(w), 1058(w), 1021(w), 943(vs). 901(vs), 950(vs), 762(s), 651(m), 528(w), 420(w).

Crystal Structure Determination

Crystal data collection for complexes **1** and **2** as performed on a Bruker SMART APEX CCD with Mo*Kα* radiation (λ = 0.71073 Å). The data were corrected for Lorentz-polarization effects, and absorption corrections were applied. All nonhydrogen atoms were refined anisotropically and all of the hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms. The structure **1** was solved by Patterson methods and the structure of **2** by direct methods. Both structures

TABLE I Crystal data and structure refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_{48}H_{32}N_8O_{12}Co_2V_4$	$C_{40}H_{32}N_8O_{12}Co_2V_4$
Formula weight	1234.44	1138.36
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Rhombohedral	Rhombohedral
Space group	*Pbcn*	*P4₂/n*
a (Å)	19.160(4)	12.0208(17)
b (Å)	15.198(3)	12.0208(17)
c (Å)	16.316(3)	14.977(3)
Volume (Å^3)	4751.1(16)	2164.2(6)
Z	4	2
ρ_{calc} (g cm^{-3})	1.726	1.747
μ (mm^{-1})	1.510	1.649
F (000)	2472	1140
θ range (deg)	2.12–33.55	2.17–33.53
Index ranges	$-29 \le h \le 28$, $-17 \le k \le 23$, $-25 \le l \le 24$	$-18 \le h \le 18$, $-10 \le k \le 18$, $-22 \le l \le 20$
Independent reflections	8935($R_{int} = 0.1440$)	4108 ($R_{int} = 0.0674$)
Observed reflections ($I > 2\sigma(I)$)	2702	2156
Goodness of fit on F^2	0.804	0.987
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0577$, $wR_2 = 0.0798$	$R_1 = 0.0403$, $wR_2 = 0.0622$
R indices (all data)	$R_1 = 0.1973$, $wR_2 = 0.0937$	$R_1 = 0.0865$, $wR_2 = 0.0664$
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.936/− 0.491	0.754/− 0.357

were refined by using SHELXL 97 [14]. Crystal data and collection and refinement parameters for are given in Table I. Atomic coordinates and equivalent isotropic displacement parameters as well as selected bondlengths and angles for the complexes are given in Tables II–V.

RESULTS AND DISCUSSION

Synthesis

Novel inorganic–organic material have been synthesized by hydrothermal methods and difficulties due to differential solubilities of organic and inorganic precursors can be overcome by using the method [15]. Many factors, including stoichiometry, temperature, pressure, acidity, and time of reaction can influence the outcome of reaction even with the same basic metal–ligand system. For example, reaction of NH_4VO_3, H_3BO_3, $Co(NO_3)_2 \cdot 6H_2O$, and 1,10-phenanthroline in the mol ratio 1 : 1.5 : 1 : 2 in water at 165°C for five days yielded dark brown crystals of Co(2,2′-biphen)$V_3O_{8.5}$ [10], where 2,2′-biphenanthroline was formed by dehydrogenous coupling of phenanthroline, and the structure of Co(2,2′-biphen)$V_3O_{8.5}$ consists of a 2D neutral framework in which (2,2′-biphen)Co units are covalently linked to vanadium oxide V_6O_{17} chains. However reaction of NH_4VO_3, $H_2C_2O_4$, $Co(NO_3)_2 \cdot 6H_2O$ and 1,10-phenanthroline in the mol ratio 1 : 2 : 1 : 2 in water at 170°C for six days produced red crystals of $[Co(phen)_2]_2V_4O_{12}$, **1**. Reaction of NH_4VO_3, H_3BO_3, $Co(NO_3)_2 \cdot 6H_2O$ and 2,2′-bipyridine in H_2O in the mol ratio 1 : 1.5 : 1 : 2 at 165°C for five days yielded brown crystals of Co(bipy)(H_2O)V_2O_6 [16], which show two-dimensional layers formed *via* corner-sharing tetrahedral $(VO_3)_n^{2n-}$ chains linked through Ni(bipy)$(H_2O)^{2+}$ fragments.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq[a]
Co(1)	0.5000	−0.46778(5)	0.2500	0.0435(2)
Co(2)	0.5000	0.02518(4)	0.2500	0.0336(2)
V(1)	0.44489(4)	−0.27593(4)	0.35625(4)	0.03585(18)
V(2)	0.41292(4)	−0.16622(4)	0.17443(4)	0.03648(19)
O(1)	0.46935(15)	−0.37672(17)	0.33531(17)	0.0617(9)
O(2)	0.39086(15)	−0.2777(2)	0.43157(17)	0.0664(9)
O(3)	0.52004(13)	−0.21433(17)	0.38688(15)	0.0493(8)
O(4)	0.40562(14)	−0.22591(17)	0.26905(15)	0.0545(8)
O(5)	0.33989(13)	−0.17128(17)	0.12739(16)	0.0514(8)
O(6)	0.43261(13)	−0.06078(16)	0.19281(15)	0.0459(8)
C(1)	0.4865(3)	−0.6107(3)	0.3902(3)	0.0592(14)
C(2)	0.4469(3)	−0.6640(3)	0.4432(3)	0.0643(15)
C(3)	0.3777(3)	−0.6697(3)	0.4376(3)	0.0609(15)
C(4)	0.3425(3)	−0.6211(3)	0.3765(3)	0.0461(12)
C(5)	0.2698(3)	−0.6220(3)	0.3652(3)	0.0522(13)
C(6)	0.2405(3)	−0.5805(3)	0.3002(3)	0.0567(14)
C(7)	0.2817(2)	−0.5323(3)	0.2430(3)	0.0436(11)
C(8)	0.2534(2)	−0.4909(3)	0.1735(3)	0.0509(12)
C(9)	0.2963(3)	−0.4428(3)	0.1255(3)	0.0551(14)
C(10)	0.3668(3)	−0.4370(3)	0.1449(3)	0.0544(13)
C(11)	0.3526(2)	−0.5256(2)	0.2556(3)	0.0373(10)
C(12)	0.3846(2)	−0.5715(2)	0.3228(3)	0.0373(11)
C(13)	0.4344(2)	−0.0118(3)	0.4214(3)	0.0439(11)
C(14)	0.3843(2)	−0.0039(3)	0.4828(3)	0.0510(13)
C(15)	0.3281(2)	0.0470(3)	0.4708(3)	0.0504(13)
C(16)	0.3207(2)	0.0932(3)	0.3971(3)	0.0372(11)
C(17)	0.2607(2)	0.1436(3)	0.3767(3)	0.0480(12)
C(18)	0.2572(2)	0.1877(2)	0.3047(3)	0.0500(13)
C(19)	0.3145(2)	0.1875(2)	0.2481(3)	0.0378(10)
C(20)	0.3138(2)	0.2334(3)	0.1732(3)	0.0527(13)
C(21)	0.3702(3)	0.2260(3)	0.1225(3)	0.0546(13)
C(22)	0.4261(2)	0.1729(3)	0.1439(3)	0.0444(11)
C(23)	0.3732(2)	0.1356(2)	0.2654(2)	0.0322(10)
C(24)	0.3764(2)	0.0858(2)	0.3407(2)	0.0332(10)
N(1)	0.4546(2)	−0.5664(2)	0.3299(2)	0.0455(10)
N(2)	0.39589(18)	−0.4765(2)	0.2083(2)	0.0439(10)
N(3)	0.43229(16)	0.03284(19)	0.35266(19)	0.0327(8)
N(4)	0.42813(17)	0.12807(19)	0.2136(2)	0.0363(9)

[a] Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Reaction of NH_4VO_3, $H_2C_2O_4$, $Co(NO_3)_2 \cdot 6H_2O$ and 2,2′-bipyridine in H_2O in the mol ratio 1 : 2 : 1 : 2 at 170°C for six days gave red rods of $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$, **2**. These examples illustrate that small changes of reactants (H_3BO_3 was replaced by $H_2C_2O_4$), pH and reaction temperature, pressure and time can result in entirely new structures.

Crystal Structures

The structure of **1** is composed of isolated, neutral, hexanuclear cage clusters, $[Co(phen)_2]_2V_4O_{12}$ (Fig. 1). There are two crystallographically independent vanadium atoms; V1 shares oxygen atoms with the $Co(1)N_4O_2$ octahedron and two neighboring VO_4 tetrahedra while V2 atom shares oxygen atoms with the $Co(2)N_4O_2$ octahedron and two adjacent VO_4 tetrahedra. Four VO_4 tetrahedra connect to form a $[V_4O_{12}]^{4-}$

TABLE III Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **2**

Atom	*x/a*	*y/b*	*z/c*	*U*eq^b
Co(1)	0.7500	−0.2500	−0.00100(3)	0.03469(11)
V(1)	0.72398(3)	−0.08090(3)	−0.19518(2)	0.03331(10)
N(1)	0.91554(14)	−0.20447(15)	0.01209(11)	0.0372(4)
N(2)	0.74527(14)	−0.11992(15)	0.09778(10)	0.0391(4)
O(1)	0.61360(13)	−0.14259(13)	−0.25824(10)	0.0552(4)
O(2)	0.71920(12)	−0.12669(14)	−0.09195(9)	0.0534(4)
O(3)	0.70869(13)	0.05174(12)	−0.19596(11)	0.0587(5)
C(1)	0.99788(19)	−0.2521(2)	−0.03397(15)	0.0471(6)
C(2)	1.10714(19)	−0.2235(2)	−0.02200(16)	0.0601(8)
C(3)	1.1323(2)	−0.1432(2)	0.03868(18)	0.0642(8)
C(4)	1.04925(19)	−0.0930(2)	0.08593(15)	0.0520(7)
C(5)	0.94040(17)	−0.12452(19)	0.07169(13)	0.0372(5)
C(6)	0.84447(18)	−0.07420(18)	0.11702(13)	0.0370(5)
C(7)	0.8531(2)	0.01677(19)	0.17385(14)	0.0503(6)
C(8)	0.7579(2)	0.0636(2)	0.20815(16)	0.0600(7)
C(9)	0.6560(2)	0.0197(2)	0.18603(16)	0.0569(7)
C(10)	0.6537(2)	−0.0729(2)	0.13204(15)	0.0526(6)

^{b}Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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

Co(2)–O(6)	2.060(2)	Co(2)–O(6)$^{\#1}$	2.060(2)
Co(2)–N(3)	2.122(3)	Co(2)–N(3)$^{\#1}$	2.122(3)
Co(2)–N(4)$^{\#1}$	2.167(3)	Co(2)–N(4)	2.167(3)
Co(1)–O(1)	2.049(3)	Co(1)–O(1)$^{\#1}$	2.049(3)
Co(1)–N(2)	2.112(3)	Co(1)–N(2)$^{\#1}$	2.112(3)
Co(1)–N(1)$^{\#1}$	2.168(3)	Co(1)–N(1)	2.168(3)
V(1)–O(2)	1.607(2)	V(1)–O(1)	1.638(3)
V(1)–O(4)	1.780(2)	V(1)–O(3)	1.789(3)
V(2)–O(5)	1.598(2)	V(2)–O(6)	1.673(2)
V(2)–O(3)$^{\#1}$	1.785(3)	V(2)–O(4)	1.796(3)
O(6)–Co(2)–O(6)$^{\#1}$	101.29(15)	O(6)–Co(2)–N(3)	90.53(11)
O(6)–Co(2)–N(3)$^{\#1}$	93.46(11)	O(6)$^{\#1}$–Co(2)–N(3)	93.46(11)
O(6)$^{\#1}$–Co(2)–N(3)$^{\#1}$	90.53(10)	N(3)—Co(2)–N(3)$^{\#1}$	173.71(16)
O(6)–Co(2)–N(4)$^{\#1}$	168.57(11)	O(6)$^{\#1}$–Co(2)–N(4)$^{\#1}$	86.28(11)
N(3)–Co(2)–N(4)$^{\#1}$	97.61(12)	N(3)$^{\#1}$–Co(2)–N(4)$^{\#1}$	77.78(12)
O(6)–Co(2)–N(4)	86.28(11)	O(6)$^{\#1}$–Co(2)–N(4)	168.57(11)
N(3)–Co(2)–N(4)	77.73(12)	N(3)$^{\#1}$–Co(2)–N(4)	97.61(12)
N(4)$^{\#1}$–Co(2)–N(4)	87.61(16)	O(1)$^{\#1}$–Co(1)–O(1)	95.02(16)
O(1)–Co(1)–N(2)	89.46(12)	O(1)–Co(1)–N(2)$^{\#1}$	95.43(13)
O(1)$^{\#1}$–Co(1)–N(2)	95.51(13)	O(1)$^{\#1}$–Co(1)–N(2)$^{\#1}$	89.46(12)
N(2)$^{\#1}$–Co(1)–N(2)	172.77(18)	O(1)$^{\#1}$–Co(1)–N(1)	172.68(18)
O(1)$^{\#1}$–Co(1)–N(1)$^{\#1}$	86.74(12)	N(2)–Co(1)–N(1)$^{\#1}$	98.14(13)
N(2)$^{\#1}$–Co(1)–N(1)$^{\#1}$	76.78(14)	O(1)–Co(1)–N(1)	86.74(12)
O(1)$^{\#1}$–Co(1)–N(1)	172.04(12)	N(2)–Co(1)–N(1)	76.78(14)
N(2)$^{\#1}$–Co(1)–N(1)	98.14(13)	N(1)$^{\#1}$–Co(1)–N(1)	92.59(17)
O(2)–V(1)–O(1)	109.15(15)	O(2)–V(1)–O(4)	110.25(14)
O(1)–V(1)–O(4)	110.71(14)	O(2)–V(1)–O(3)	108.28(13)
O(1)–V(1)–O(3)	108.51(13)	O(4)–V(1)–O(3)	109.88(12)
O(5)–V(2)–O(6)	109.24(13)	O(5)–V(2)–O(3)$^{\#1}$	109.97(14)
O(6)–V(2)–O(3)$^{\#1}$	109.30(12)	O(5)–V(2)–O(4)	108.68(13)
O(6)–V(2)–O(4)	110.32(13)	O(3)$^{\#1}$–V(2)–O(4)	109.32(12)
V(1)–O(1)–Co(1)	148.81(17)	V(2)$^{\#1}$–O(3)–V(1)	129.58(15)
V(1)–O(4)–V(2)	150.44(17)	V(2)–O(6)–Co(2)	146.07(16)

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

TABLE V Selected bond distances (Å) and angles (°) for **2**

Co(1)–O(2)$^{\#2}$	2.0469(15)	Co(1)–O(2)	2.0469(15)
Co(1)–N(1)	2.0731(17)	Co(1)–N(1)$^{\#2}$	2.0731(17)
Co(1)–N(2)	2.1534(17)	Co(1)–N(2)$^{\#2}$	2.1534(17)
V(1)–O(3)	1.6051(15)	V(1)–O(2)	1.6421(14)
V(1)–O(1)	1.7895(15)	V(1)–O(1)$^{\#3}$	1.7927(15)
O(2)$^{\#2}$–Co(1)–O(2)	96.56(9)	O(2)$^{\#2}$–Co(1)–N(1)	94.62(6)
O(2)–Co(1)–N(1)	92.60(6)	O(2)$^{\#2}$–Co(1)–N(1)$^{\#2}$	92.60(6)
O(2)$^{\#2}$–Co(1)–N(1)	94.62(6)	N(1)–Co(1)–N(1)$^{\#2}$	169.15(9)
O(2)$^{\#2}$–Co(1)–N(2)	171.05(6)	O(2)–Co(1)–N(2)	85.79(7)
N(1)–Co(1)–N(2)	76.63(7)	N(1)$^{\#2}$-Co(1)–N(2)	95.82(7)
O(2)$^{\#2}$–Co(1)–N(2)$^{\#2}$	85.79(7)	O(2)–Co(1)–N(2)$^{\#2}$	171.05(6)
N(1)–Co(1)–N(2)$^{\#2}$	95.82(7)	N(1)$^{\#2}$–Co(1)–N(2)$^{\#2}$	76.63(7)
N(2)$^{\#2}$–Co(1)–N(2)	93.21(9)	O(3)–V(1)–O(2)	109.62(8)
O(3)–V(1)–O(1)	108.83(8)	O(2)–V(1)–O(1)	109.39(8)
O(3)–V(1)–O(1)$^{\#3}$	108.50(8)	O(2)–V(1)–O(1)$^{\#3}$	108.92(8)
O(1)$^{\#2}$–V(1)–O(1)	111.54(8)		

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

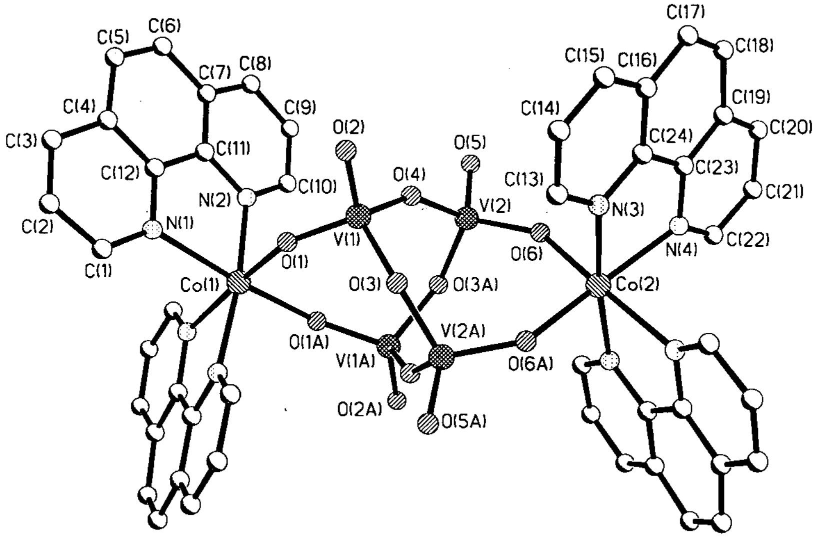

FIGURE 1 View of the structure of $[Co(phen)_2]_2V_4O_{12}$ **1**, showing the numbering scheme.

ring. Two $[Co(phen)_2]^{2+}$ fragments bond to this $[V_4O_{12}]^{4-}$ ring and a cage bimetallic core, $[Co_2V_4O_{12}]$ with a Co–Co distance of 7.492 Å is thus formed. Each $[Co(phen)_2]^{2+}$ moiety bonds to two oxygen atoms from 1,3-vanadium oxo tetrahedra or 2,4-vanadium oxo tetrahedra of the $[V_4O_{12}]^{4-}$ ring, which exhibits distinct curvature and a boat-like configuration. A similar $[V_4O_{12}]^{4-}$ ring also has been found in $[Zn(2,2'\text{-}bipy)_2]_2V_4O_{12}$ [11]. However, this bonding mode is quite different from that of $[Zn(phen)_2]_2V_4O_{12}\cdot H_2O$, where two $[Zn(phen)_2]^{2+}$ moieties covalently bond to the terminal oxo groups of adjacent vanadium sites (i.e., 1,2-positions and 3,4-positions), making the $[V_4O_{12}]^{4-}$ ring exhibit a distinctly chair-like configuration [11].

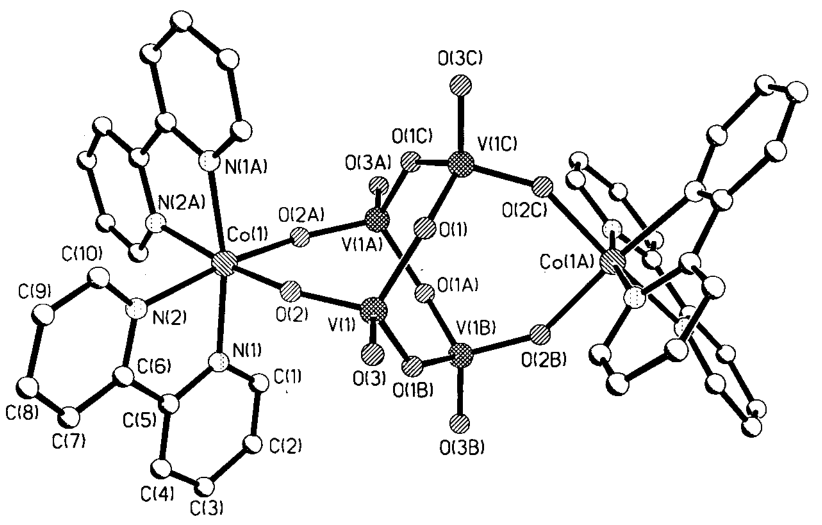

FIGURE 2 View of the structure of $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$ **2**, showing the numbering scheme.

There are two crystallographically independent cobalt atoms in **1**. Each Co(II) coordination geometry is defined by four nitrogen donors from two 1,10-phenanthroline ligands and two *cis*-oxygen donors from vanadium oxides Co(1)–N and Co(1)–O bond distances [average 2.140(3) and 2.049(3) Å, respectively] are slightly smaller than those of Co(2)–N and Co(2)–O [average 2.145(3) and 2.060(2) Å, respectively], but all Co–N and Co–O bondlengths are within normal ranges [16]. The O1–Co(1)–O1$^{\#1}$ ($^{\#1}$ $-x$, y, $-z+1/2$) bond angle (95.02(16)° is smaller than that of O6–Co(2)–O6$^{\#1}$ ($^{\#1}$ $-x$, y, $-z+1/2$) (101.29 (15)°).

Complex **2** and the already reported complex $[Zn(2,2'\text{-bipy})_2]_2V_4O_{12}$ [11] are isomorphous. As shown in Fig. 2, the structure of **2** consists of isolated neutral cage hexanuclear clusters, $[Co(2,2'\text{-bipy})_2]_2V_4O_{12}$. The cobalt atom has a distorted octahedral environment. It is coordinated to four N atoms from two 2,2′-pyridine ligands and two oxygen atoms from the vanadium oxygen cluster, which adopt a *cis*-orientation. Co–N and Co–O bondlengths [average 2.1133 (17) and 2.0469(15) Å, respectively] are comparable with those of $Co(bipy)(H_2O)V_2O_6$ [average 2.113(2) Å for Co–N and 2.078(2) Å for Co–O] [16]. The Co–Co distance (7.459 Å) of the cage bimetallic core $[Co_2V_4O_{12}]$ is a little shorter than that of complex **1** (7.492 Å).

Magnetic Properties

Magnetic studies of complex **1** showed that the variable temperature magnetic susceptibility data in the range 5–300 K can be fitted well to a Curie–Weiss law plot with $\theta = -6.29$ K, and $C = 6.29$ emu K mol^{-1} (Fig. 3). The effective magnetic moment (μ_{eff}) per cobalt ion at 300 K, 3.417 BM, is typical for octahedral Co(II) compounds [17]. The product $\chi_M T$ continuously decreases with decreasing temperature. This behavior is characteristic of a system with antiferromagnetic interactions, and the negative Weiss constant ($\theta = -6.29$ K) also indicates the presence of antiferromagnetic interactions between Co(II) ions.

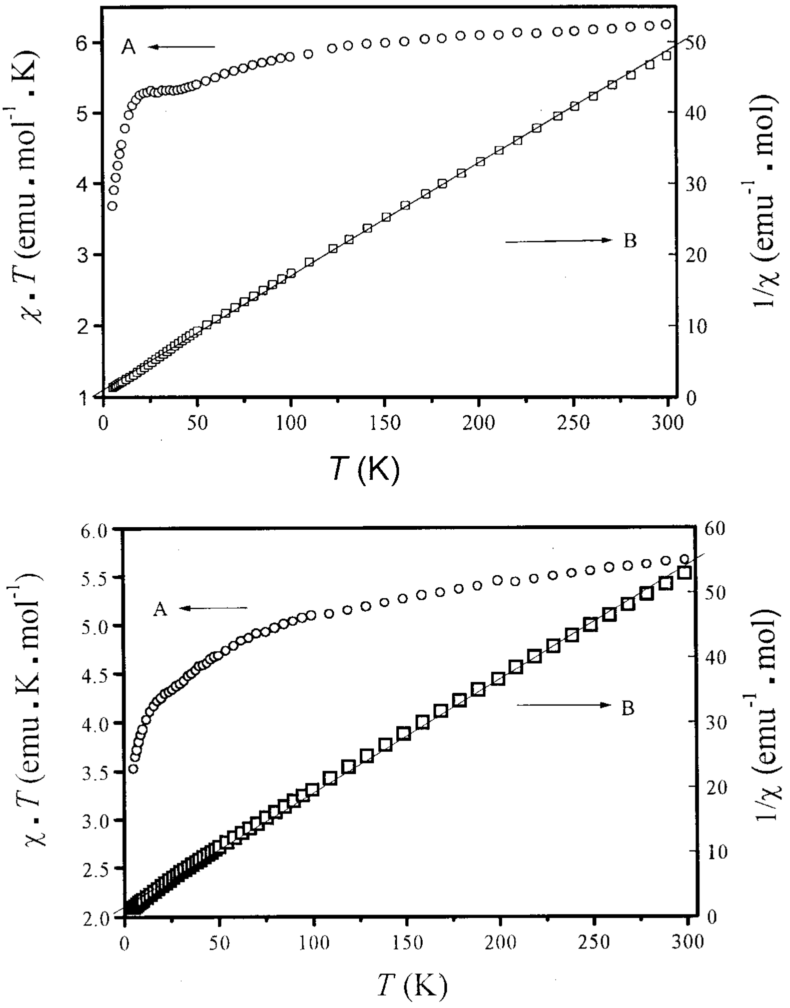

FIGURE 3 Plots of the dependence of $\chi_M T$(o) and χ^{-1}(□) on temperature for complexes **1** (upper) and **2** (lower).

Magnetic susceptibility data for complex **2** over the temperature range 5–300 K are shown in Figure 3. They also fit well to a Curie–Weiss law plot but with $\theta = -8.93$ K, and $C = 5.71$ emu K mol^{-1}. The effective magnetic moment (μ_{eff}) per cobalt ion at 300 K is 3.585 BM, a little larger than that of complex **1**, is still within the normal range for octahedral Co(II) compounds [17]. The Weiss constant ($\theta = -8.93$ K) is more negative than that in complex **1**, suggesting complex **2** possesses stronger aniferromagnetic interactions. This is in agreement with the structural characteristics of two complexes; the Co–Co distance in complex **2** is a little shorter than that in complex **1**.

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