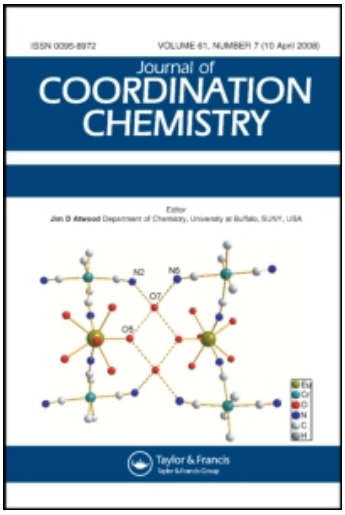

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HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW α-KEGGIN UNIT-SUPPORTED COBALT BIPYRIDYL COMPLEX: $[Co(2,2'\text{-BIPY})_3]_{1.5}[SiW_{12}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$

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A new α-Keggin unit-supported transition metal complex $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW_{12}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$ has been hydrothermally synthesized and characterized by X-ray crystallography, showing that $[Co(2,2'\text{-bipy})_2(H_2O)]^{2+}$ units are covalently bonded to the α-Keggin cluster $[SiW^{V}W^{VI}_{11}O_{50}]^{5-}$. Intermolecular hydrogen bonding interactions and short O···O contacts force the structure into an interesting one-dimensional supramolecular array. Crystals are monoclinic space group $C2/c$, with $a = 46.676(9)$, $b = 14.348(3)$, $c = 26.010(5)$ Å, $\beta = 90.33(3)^\circ$, $V = 17419(6)$ Å^3, $Z = 8$.

Keywords: Hydrothermal synthesis; Cobalt(II); Cluster complex; Crystal structure; Polyoxoanion complex; Keggin ion

INTRODUCITON

Increasing attention has been paid to polyoxometalates owing to their potential applications in many areas such as catalysis, electric conductivity, nanotechnology, magnetism, nonlinear optical materials and medicine [1]. Recently, their use as ligands to produce polyoxoanion-supported transition metal complexes has been an important advance in the design of new organic–inorganic hybrid materials [2–3]. We are interested in the exploitation of such materials in which organic amines function as ligands rather than structural directors to compensate charges and fill spaces [3]. Herein we report the hydrothermal synthesis and crystal structure of a new α-Keggin unit-supported cobalt bipyridyl complex $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW_{12}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$, **1**, which exhibits an interesting extended one-dimensional supramolecular structure.

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EXPERIMENTAL

All reagents were obtained from commercial sources and were used as supplied. Elemental analyses were performed on a Heraeus CHN-Rapid instrument. IR spectra were recorded on a Perkin-Elmer 2000 spectrophotometer using pressed KBr pellets.

Synthesis

A mixture of H_2MoO_4 (3.0 mmol), $SiO_2{\cdot}12WO_3{\cdot}24H_2O$ (0.5 mmol), $Co(en)_3Cl_3$ (1.0 mmol), 2,2′-bipyridine (1.0 mmol) and H_2O (16 cm^3) was stirred for 20 mins and then transferred into a 25 cm^3 Teflon-lined steel autoclave. The mixture was heated at 170°C for 6 days, when dark blocky crystals of **1** had separated from the resulting blue solution. Yield: 30% based on $Co(en)_3Cl_3$. Elemental analysis (%) calcd for $W_{12}Co_{2.5}SiO_{41.5}N_{13}C_{65}H_{55}$: C 19.21, H 1.36, N 4.48; found: C 19.15, H 1.42, N 4.40. IR (cm^{-1}): 3385(bs), 1599(m), 1472(w), 1441(s), 1315(w), 959(s), 914(vs), 789(vs).

X-ray Analysis

Data were collected on a BRUKER SMART APEX CCD WITH Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 36195 reflections was collected, of which 19760 were unique and 11452 had $I > 2\sigma(I)$. These were used in the structure solution and refinement. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques based on F^2 using the SHELXL-97 program [4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for those in water molecules, were placed at calculated positions, but their parameters were not refined. Crystal data and collection and refinement parameters for Complex **1** are given in Table I. Atomic coordinates, equivalent isotropic displacement parameters and selected bond lengths and angles are listed in Tables II and III.

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

Empirical formula	$W_{12}Co_{2.5}SiO_{41.5}N_{13}C_{65}H_{55}$
Formula weight	4063.83
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	46.676(9)
b (Å)	14.348(3)
c (Å)	26.010(5)
β(°)	90.33(3)
Volume (Å^3)	17419(6)
Z	8
ρ_{calc} (g cm^{-3})	3.099
μ (mm^{-1})	16.347
F (000)	14700
θ range (deg)	0.87–27.48
Index ranges	$-59 \le h \le 60$, $-18 \le k \le 18$, $-33 \le l \le 33$,
Independent reflections	19760
Observed reflections [$I \ge 2\sigma(I)$]	16694
Goodness of fit on F^2	1.092
Final *R* indices [$I \ge 2\sigma(I)$]	$R_1 = 0.0599$, $wR_2 = 0.1588$
R indices (all data)	$R_1 = 0.0723$, $wR_2 = 0.1710$

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

Atom	*x/a*	*y/b*	*z/c*	*Ueq*[a]
Si1	0.11868(6)	0.78057(19)	0.04673(10)	0.0095(5)
Co1	0.24175(4)	0.20257(12)	0.20551(6)	0.0223(3)
Co2	0.07115(4)	0.35690(11)	−0.07024(6)	0.0197(3)
Co3	0.0000	0.81771(17)	−0.2500	0.0270(5)
W1	0.054370(9)	0.69930(3)	0.100756(18)	0.01860(12)
W2	0.147546(10)	0.79869(3)	0.171851(18)	0.01850(12)
W3	0.114972(10)	0.58002(3)	0.125474(18)	0.01879(12)
W4	0.085463(10)	0.57230(3)	0.008410(18)	0.01861(12)
W5	0.087558(10)	0.91835(3)	0.144484(18)	0.01840(12)
W6	0.149789(10)	0.98645(3)	0.094605(18)	0.01819(11)
W7	0.183571(10)	0.66180(3)	0.070804(19)	0.02056(12)
W8	0.154233(11)	0.64854(4)	−0.046279(19)	0.02157(12)
W9	0.088158(11)	0.77904(4)	−0.077750(18)	0.02194(12)
W10	0.118516(11)	0.97628(3)	−0.036085(19)	0.02286(12)
W11	0.184925(10)	0.84787(4)	−0.006661(19)	0.02165(12)
W12	0.056516(11)	0.90305(4)	0.01367(2)	0.02452(13)
O1	0.21161(19)	0.6024(6)	0.0966(4)	0.0269(19)
O1W	0.0273(2)	0.3913(8)	−0.0804(4)	0.035(2)
O2	0.1642(2)	0.7834(7)	0.2300(3)	0.028(2)
O2W	0.0000	0.5000	0.0000	0.110(11)
O3	0.15110(18)	0.5890(6)	0.0941(3)	0.0207(17)
O4	0.17967(19)	0.5988(6)	0.0053(3)	0.0237(18)
O5	0.07910(18)	0.9967(6)	−0.0186(4)	0.0239(19)
O6	0.09969(15)	0.6907(6)	0.0635(3)	0.0139(15)
O7	0.18100(19)	0.7477(6)	−0.0561(3)	0.0239(18)
O8	0.07544(17)	0.6105(6)	0.1407(3)	0.0208(17)
O9	0.1208(2)	0.4901(6)	0.1672(4)	0.029(2)
O10	0.10082(18)	0.5115(6)	0.0678(3)	0.0221(18)
O11	0.07248(19)	0.4773(6)	−0.0252(3)	0.0231(18)
O12	0.11528(17)	1.0141(5)	0.1317(3)	0.0166(15)
O13	0.0236(2)	0.9532(8)	0.0125(4)	0.037(2)
O14	0.12605(17)	0.6869(5)	0.1647(3)	0.0178(16)
O15	0.20371(18)	0.7593(6)	0.0371(3)	0.0219(17)
O16	0.12931(18)	1.0092(6)	0.0321(3)	0.0197(17)
O17	0.07735(19)	0.6694(6)	−0.0373(3)	0.0235(18)
O18	0.05253(17)	0.6019(6)‘	0.0480(3)	0.0234(18)
O19	0.07059(17)	0.9419(5)	0.0789(3)	0.0171(16)
O20	0.14950(16)	0.7458(5)	0.0239(3)	0.0122(14)
O21	0.12531(18)	0.7241(6)	−0.0764(3)	0.0229(18)
O22	0.16333(16)	0.9197(6)	0.1533(3)	0.0169(16)
O23	0.17419(17)	0.7434(6)	0.1257(3)	0.0193(16)
O24	0.12378(19)	0.5806(6)	−0.0159(3)	0.0229(18)
O25	0.06923(17)	0.7970(6)	0.1398(3)	0.0187(16)
O26	0.11384(17)	0.8648(6)	0.1939(3)	0.0183(16)
O27	0.10172(16)	0.8384(5)	0.0022(3)	0.0159(15)
O28	0.0206(2)	0.6849(7)	0.1255(4)	0.030(2)
O29	0.05474(19)	0.8396(6)	−0.0519(3)	0.0238(18)
O30	0.2138(2)	0.9059(7)	−0.0319(4)	0.031(2)
O31	0.04792(18)	0.7862(6)	0.0473(3)	0.0235(18)
O32	0.15434(19)	0.9119(6)	−0.0394(3)	0.0240(18)
O33	0.12385(15)	0.8466(5)	0.0961(3)	0.0120(14)
O34	0.16642(19)	1.0918(6)	0.1031(4)	0.027(2)
O35	0.0761(2)	0.7486(7)	−0.1372(3)	0.034(2)
O36	0.06494(19)	0.9751(6)	0.1845(4)	0.0251(19)
O37	0.1264(2)	1.0743(6)	−0.0701(4)	0.029(2)
O38	0.1622(2)	0.5781(7)	−0.0971(4)	0.033(2)
O39	0.17656(17)	0.9211(6)	0.0529(3)	0.0211(17)
O40	0.10460(19)	0.8975(6)	−0.0912(3)	0.0243(18)

(*continued*)

TABLE II Continued

Atom	*x*/a	*y*/*b*	*z*/*c*	*Ueq*[a]
N1	0.2698(2)	0.2944(8)	0.1641(4)	0.027(2)
N2	0.2128(3)	0.2945(8)	0.1676(5)	0.031(2)
N3	0.2748(2)	0.1063(8)	0.2271(4)	0.024(2)
N4	0.2448(2)	0.1139(8)	0.1398(4)	0.022(2)
N5	0.2094(2)	0.1335(8)	0.2480(4)	0.024(2)
N6	0.2436(2)	0.2720(7)	0.2770(4)	0.024(2)
N7	0.0817(3)	0.4262(8)	−0.1383(4)	0.031(3)
N8	0.0716(3)	0.2472(9)	−0.1245(4)	0.030(2)
N9	0.0633(3)	0.2702(8)	−0.0071(5)	0.036(3)
N10	0.1128(3)	0.3253(8)	−0.0439(5)	0.036(3)
N11	−0.0059(3)	0.7139(11)	−0.1921(8)	0.070(6)
N12	−0.0459(2)	0.8068(8)	−0.2429(5)	0.031(3)
N13	−0.0040(2)	0.9317(8)	−0.3006(4)	0.025(2)
C1	0.2985(3)	0.2954(11)	0.1665(6)	0.037(3)
C2	0.3150(4)	0.3525(14)	0.1362(7)	0.050(4)
C3	0.3009(4)	0.4160(13)	0.1045(7)	0.050(4)
C4	0.2716(4)	0.4181(12)	0.1029(7)	0.045(4)
C5	0.2563(3)	0.3554(10)	0.1328(5)	0.031(3)
C6	0.2250(3)	0.3498(9)	0.1315(5)	0.030(3)
C7	0.2083(4)	0.3989(11)	0.0963(7)	0.047(4)
C8	0.1797(4)	0.3931(11)	0.0975(8)	0.048(4)
C9	0.1664(4)	0.3366(12)	0.1352(9)	0.053(5)
C10	0.1840(3)	0.2883(11)	0.1696(7)	0.043(4)
C11	0.2875(3)	0.1026(11)	0.2725(5)	0.034(3)
C12	0.3106(4)	0.0450(13)	0.2825(6)	0.046(4)
C13	0.3202(4)	−0.0127(15)	0.2428(6)	0.055(5)
C14	0.3064(4)	−0.0104(15)	0.1973(6)	0.053(5)
C15	0.2840(3)	0.0507(10)	0.1895(5)	0.025(3)
C16	0.2682(3)	0.0601(9)	0.1394(5)	0.022(2)
C17	0.2765(3)	0.0117(12)	0.0957(5)	0.037(3)
C18	0.2596(4)	0.0192(12)	0.0510(6)	0.042(4)
C19	0.2357(3)	0.0722(12)	0.0520(6)	0.038(3)
C20	0.2288(3)	0.1208(12)	0.0958(6)	0.037(3)
C21	0.1905(3)	0.0692(10)	0.2307(5)	0.030(3)
C22	0.1682(3)	0.0354(11)	0.2605(6)	0.037(3)
C23	0.1646(3)	0.0711(12)	0.3080(6)	0.040(4)
C24	0.1837(3)	0.1362(12)	0.3276(6)	0.036(3)
C25	0.2058(3)	0.1643(10)	0.2966(5)	0.026(3)
C26	0.2280(3)	0.2337(9)	0.3140(5)	0.025(3)
C27	0.2320(3)	0.2532(12)	0.3658(5)	0.036(3)
C28	0.2529(3)	0.3153(12)	0.3800(6)	0.037(3)
C29	0.2695(3)	0.3553(11)	0.3414(6)	0.036(3)
C30	0.2639(3)	0.3327(10)	0.2918(6)	0.033(3)
C31	0.0862(4)	0.5167(11)	−0.1435(7)	0.045(4)
C32	0.0902(6)	0.5590(14)	−0.1898(8)	0.085(9)
C33	0.0892(9)	0.5087(15)	−0.2314(9)	0.133(17)
C34	0.0828(9)	0.4135(15)	−0.2295(8)	0.115(14)
C35	0.0802(4)	0.3734(12)	−0.1815(6)	0.047(4)
C36	0.0770(4)	0.2731(10)	−0.1727(5)	0.036(3)
C37	0.0802(5)	0.2090(12)	−0.2123(7)	0.058(6)
C38	0.0790(5)	0.1149(11)	−0.1995(6)	0.050(5)
C39	0.0743(3)	0.0878(11)	−0.1498(6)	0.035(3)
C40	0.0706(3)	0.1562(9)	−0.1139(5)	0.028(3)
C41	0.0362(6)	0.2424(13)	0.0065(7)	0.061(6)
C42	0.0326(7)	0.1824(18)	0.0483(9)	0.079(8)
C43	0.0556(8)	0.1563(16)	0.0740(9)	0.087(10)
C44	0.0827(6)	0.1789(13)	0.0610(7)	0.072(8)
C45	0.0861(4)	0.2399(9)	0.0176(5)	0.041(4)

(*continued*)

TABLE II Continued

Atom	*x*/a	*y*/*b*	*z*/*c*	*Ueq*[a]
C46	0.1136(5)	0.2674(10)	−0.0025(7)	0.057(6)
C47	0.1400(5)	0.2385(13)	0.0160(9)	0.061(6)
C48	0.1633(6)	0.2664(18)	−0.0039(11)	0.085(9)
C49	0.1637(5)	0.328(2)	−0.0466(13)	0.092(10)
C50	0.1370(4)	0.3553(16)	−0.0642(10)	0.066(6)
C51	−0.0645(3)	0.8617(11)	−0.2670(6)	0.037(3)
C52	−0.0940(3)	0.8587(15)	−0.2565(8)	0.055(5)
C53	−0.1042(4)	0.7947(19)	−0.2203(11)	0.077(7)
C54	−0.0842(4)	0.7363(18)	−0.1948(8)	0.064(6)
C55	−0.0556(3)	0.7458(11)	−0.2077(7)	0.038(3)
C56	−0.0331(4)	0.6904(13)	−0.1808(9)	0.056(5)
C57	−0.0401(5)	0.6216(19)	−0.1468(13)	0.105(12)
C58	−0.0177(8)	0.568(3)	−0.125(3)	0.30(5)
C59	0.0115(7)	0.608(5)	−0.118(6)	0.84(15)
C60	0.0151(5)	0.667(2)	−0.1694(14)	0.118(14)
C61	−0.0068(3)	0.9271(12)	−0.3518(6)	0.038(3)
C62	−0.0062(4)	1.0051(17)	−0.3831(6)	0.052(5)
C63	−0.0013(4)	1.0874(16)	−0.3605(7)	0.054(5)
C64	0.0015(3)	1.0979(12)	−0.3082(7)	0.045(4)
C65	−0.0007(3)	1.0170(8)	−0.2789(5)	0.023(2)

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

TABLE III Selected bond distances (Å) and angles (°) for Complex **1**

Bond distances			
Co1–N6	2.110(10)	Co1–N5	2.121(10)
Co1–N2	2.128(12)	Co1–N1	2.151(11)
Co1–N4	2.137(10)	Co1–N3	2.143(11)
Co2–N8	2.115(12)	Co2–N7	2.092(11)
Co2–N9	2.093(12)	Co2–N10	2.108(12)
Co2–O11	2.088(8)	Co2–O1W	2.119(10)
Co3–N11	2.137(14)	Co3–N13	2.107(11)
Co3–N12	2.158(11)	W1–O28	1.717(10)
W1–O31	1.891(9)	W1–O25	1.862(8)
W1–O8	1.913(9)	W1–O18	1.959(8)
W2–O2	1.711(8)	W2–O14	1.900(8)
W2–O23	1.906(8)	W2–O26	1.927(8)
W2–O22	1.947(8)	W3–O9	1.706(8)
W3–O3	1.882(8)	W3–O10	1.909(9)
W3–O14	1.911(8)	W3–O14	1.911(8)
W3–O8	1.939(8)	W4–O11	1.727(8)
W4–O17	1.870(9)	W4–O18	1.903(9)
W4–O24	1.904(9)	W4–O10	1.910(9)
W5–O36	1.696(9)	W5–O19	1.906(8)
W5–O12	1.918(8)	W5–O26	1.931(8)
W5–O25	1.944(8)	W6–O34	1.714(9)
W6–O39	1.906(8)	W6–O22	1.907(8)
W6–O16	1.910(8)	W6–O12	1.924(8)
W7–O1	1.698(9)	W7–O23	1.900(8)
W7–O15	1.902(8)	W7–O4	1.936(9)
W7–O3	1.941(8)	W8–O38	1.708(9)
W8–O21	1.897(9)	W8–O24	1.900(9)
W8–O7	1.911(9)	W8–O4	1.924(9)
W9–O35	1.699(8)	W9–O40	1.898(9)

(*continued*)

TABLE III Continued

Bond distances			
W9–O21	1.905(9)	W9–O29	1.911(9)
W9–O17	1.959(9)	W10–O37	1.703(9)
W10–O16	1.899(8)	W10–O32	1.912(9)
W10–O5	1.920(9)	W10–O40	1.934(9)
W11–O30	1.718(9)	W11–O32	1.896(9)
W11–O39	1.914(9)	W11–O15	1.915(9)
W11–O7	1.936(9)	W12–O13	1.695(9)
W12–O19	1.900(8)	W12–O5	1.906(10)
W12–O31	1.934(9)	W12–O29	1.935(8)
Bond angles			
N2–Co2–N8	77.6(5)	N9–Co2–N10	77.4(6)
O11–Co2–O1W	84.4(4)	W4–O11–Co2	161.1(5)
N6–Co1–N5	77.7(4)	N4–Co1–N3	76.9(4)
N2–Co1–N1	77.0(4)	N11–Co3–N12	75.9(5)
O11–Co2–N7	94.3(4)	O11–Co2–N9	93.2(4)
O11–Co2–N10	88.3(4)	O11–Co2–N8	171.9(4)

RESULT AND DISCUSSION

The hydrothermal reaction of a mixture of H_2MoO_4, $SiO_2{\cdot}12WO_3{\cdot}24H_2O$, $Co(en)_3Cl_3$, 2,2′-bipyridine and water in the mol ratio of 3 : 0.5 : 1 : 1 : 889 at 170°C for six days yielded Complex **1** as the main product. The two-dimensional mixed molybdenum–vanadium polyoxometalate $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}{}_5Mo^{V}{}_3V^{IV}{}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bpy = 2,2′-bipyridine) [3b], was obtained under similar hydrothermal conditions and it appears that mixed molybdenum–tungsten polyoxometalates are more difficult to form than mixed molybdenum–vanadium polyoxometalates. Bands at 914 and 789 cm^{-1} in the IR spectrum of **1** are ascribed to ν(W=O) and ν(W-O-W), respectively.

As shown in Fig. 1, the structure of **1** is composed of $[SiW_{12}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]^{3-}$ heteropolyanions and $[Co(2,2'\text{-bipy})_3]^{2+}$ cations as well as solvent water molecules. The heteropolyanion consists of a reduced α-keggin anion $[SiW^{V}W^{VI}{}_{11}O_{40}]^{5-}$ and a covalently linked $[Co(2,2'\text{-bipy})_2(H_2O)]^{2+}$ fragment, similar to that in $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]{\cdot}0.5H_2O$ [2b]. It is noteworthy that one reduced tungsten atom exists in **1** but there are two reduced tungsten atoms in $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O){\cdot}0.5H_2O$ [2b]. The reduced α-Keggin anion $[SiW^{V}W^{VI}{}_{11}O_{50}]^{5-}$ is formed from twelve WO_6 octahedra and one SiO_4 tetrahedron. W–O distances [W–O_t, 1.695(9)–1.727(8) Å and W-O_b, 1.862(8)–1.959(9) Å are comparable with those in $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O){\cdot}0.5H_2O$. [W–$O_t$, 1.677(5)–1.727(5) Å and W–O_b, 1.780(4)–1.957(5) Å] [2b], but the W–O_a lengths of 2.309(7)–2.370(8) Å are a little shorter than those in $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O){\cdot}0.5H_2O$ [2.378(5)–2.467(5) Å] [2b], because the apical oxygen atoms in **1** are from SiO_4 rather than PO_4, as in $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2\ (H_2O){\cdot}0.5H_2O]$ [2b].

The cobalt atom in the heteropolyanion is coordinated by two 2,2′-bipy ligands, one α-Keggin anion $[SiW^{V}W^{VI}{}_{11}O_{40}]^{5-}$ and one water molecule, while the cobalt atom in the cation is coordinated by three 2,2′-bipy molecules. A μ-oxygen, O11, connects the Keggin unit and Co2; the O11–W4 bondlength (1.727(8) Å) is longer than other W–O_t bond distances but a little shorter than that in $[Ni(2,2'\text{-bipy})_3]_{1.5}$

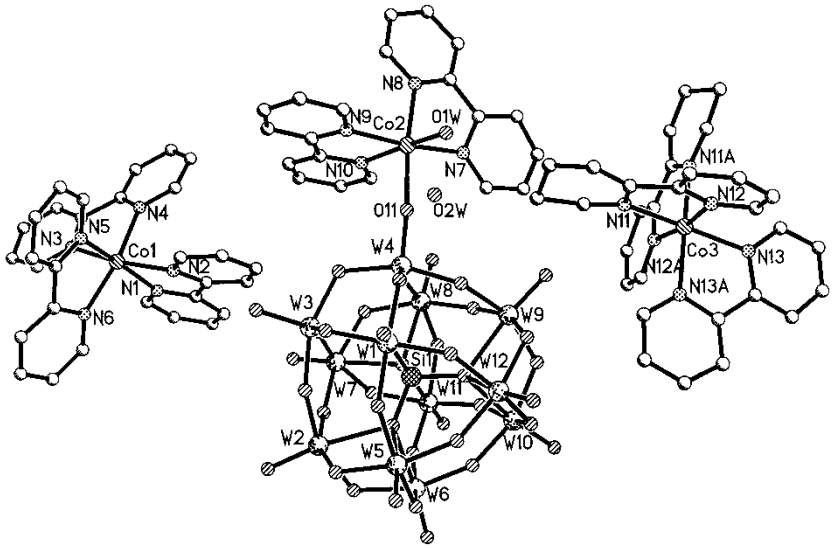

FIGURE 1 Molecular structure of Complex **1**. Hydrogen atoms are omitted for clarity.

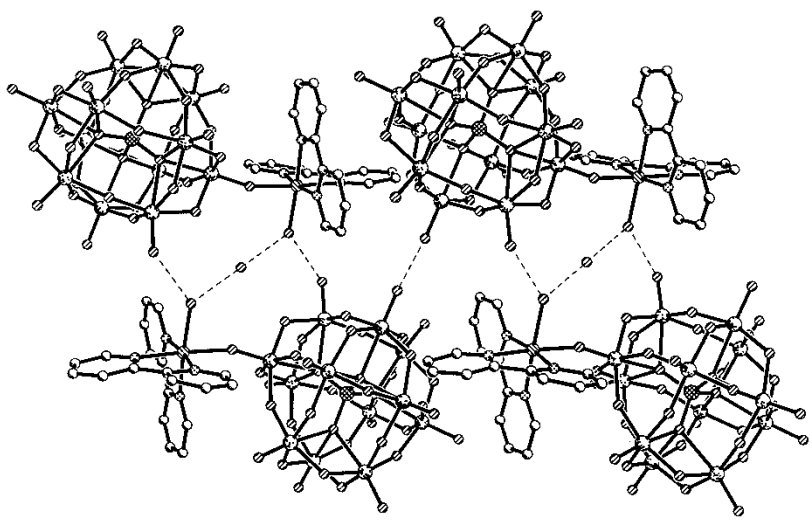

FIGURE 2 Illustration of how discrete $[SiW_{12}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]^{3-}$ heteropolyanions are connected to each other by short O···O contacts and hydrogen bonds to generate a one-dimensional supramolecular array. Cations are omitted for clarity.

$[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)\cdot 0.5H_2O$ [W12–O29 1.780(4) Å] [2b]. The W4–O11–Co2 bond angle (161.1(5)°) is a little larger than that in $[Ni(2,2'\text{-bipy})_3]_{1.5}$ $[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2$ $(H_2O)\cdot 0.5H_2O$ [Ni3-O29-W12 160.6(3)°] [2b].

Each solvent water molecule links a pair of heteropolyanions by hydrogen bonding with a coordinated water molecule (O1w···O2w 2.909 Å; Fig. 2). In addition, the two heteropolyanions also connect with each other through hydrogen bonding interactions between coordinated water molecules and O28 [and symmetry equivalents;

O1w···O28 2.748 Å]. Furthermore, pairs of heteropolyanions are bound to each other through short contacts O···O between O13 and its symmetry equivalents with O13···O13 equal to 3.467 Å. These weak interactions force the structure of **1** into an interesting one-dimensional supramolecular array.

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