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# Construction of an unusual 3D framework based on V-shaped imidazolyl and oxalate ligands

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**A new polymer $\{[Co(BIDPE)_2(ox)_{0.5}(NO_3)]\cdot 3H_2O\}_n$ has been prepared, and X-ray diffraction study shows that it is a non-interpenetrated 3D framework containing rare $[N_4Co(C_2O_4)CoN_4]$ unit.**

The design of metal-organic frameworks from V-shaped building blocks is of considerable current interest.[1–8] Recently, V-shaped ligands based on diphenyl ether have been widely employed to construct coordination polymers with fascinating architectures and interesting properties.[9,10] 4,4′-Bis(imidazol-1-yl)diphenyl ether (BIDPE) is a V-shaped imidazolyl ligand, which can be regarded as a half-flexible ligand.[11] To test the ability of this ligand to give new architectures and topologies, the BIDPE, oxalate, and bivalent cobalt salt were selected to solvothermally synthesize new coordination polymers with intriguing structures, namely, $\{[Co(BIDPE)_2(ox)_{0.5}(NO_3)]\cdot 3H_2O\}_n$ **1**.[†] Compound **1** is a non-interpenetrated 3D framework containing a rare $[N_4Co(C_2O_4)CoN_4]$ unit.

An X-ray crystallography analysis[‡] revealed that a crystal of **1** is solved in monoclinic space group *C*2/*c*, the asymmetric unit contains one independent $Co^{II}$ cation, half an oxalate ion, two types of BIDPE ligands, and one free nitrate ion. In Figures 1 and 2, only the nitrate positions with higher occupation are shown. Large voids in the structure and diffuse electron density regions in the Fourier maps suggested the presence of disordered crystallization water. In TGA experiments (see below), the presence of three $H_2O$ molecules per formula unit has been established. As no sensible point atom model could be refined for it, the contribution of the solvent region to the structure factors has been removed by the Back-Fourier-Transform method.[13] As shown in Figure 1, the $Co^{II}$ center is six-coordinated with four N atoms from four BIDPE and two O atoms from one oxalate ion to form an

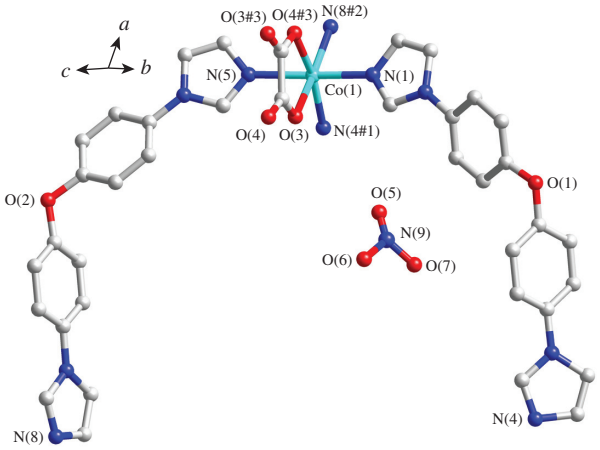


**Figure 1** Coordination environment of complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 1 – *x*, *y*, 0.5 – *z*; #2 = 0.5 + *x*, 0.5 + *y*, *z*; #3 = 1.5 – *x*, 1.5 – *y*, 1.5 – *z*. Selected bond lengths (Å): Co(1)–N(4#1) 2.097(4), Co(1)–N(8#2) 2.106(3), Co(1)–O(4#3) 2.114(3), Co(1)–N(1) 2.135(4), Co(1)–O(3) 2.144(3), Co(1)–N(5) 2.159(4); selected bond angles (°): N(4#1)–Co(1)–N(8#2) 102.51(15), N(4#1)–Co(1)–O(4#3) 165.77(13), N(8#2)–Co(1)–O(4#3) 91.43(12), N(4#1)–Co(1)–N(1) 95.48(15), N(8#2)–Co(1)–N(1) 89.75(14), O(4#3)–Co(1)–N(1) 87.34(14), N(4#1)–Co(1)–O(3) 87.61(13), N(8#2)–Co(1)–O(3) 169.51(13), O(4#3)–Co(1)–O(3) 78.62(11), N(1)–Co(1)–O(3) 86.50(14), N(4#1)–Co(1)–N(5) 90.70(15), N(8#2)–Co(1)–N(5) 95.10(14), O(4#3)–Co(1)–N(5) 85.15(14), N(1)–Co(1)–N(5) 171.15(15), O(3)–Co(1)–N(5) 87.43(13).

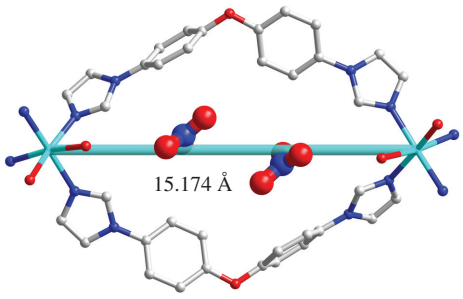


**Figure 2** $[Co_2(BIDPE)_2]$ metallocyclic ring occupied by two nitrate ions; the adjacent distance of Co···Co is 15.174 Å.

[†] Commercial reagents and solvents were used as received.

*General procedure for the preparation of complex* **1**. A mixture of $Co(NO_3)_2$ (0.15 mmol), BIDPE (0.2 mmol) and oxalate (0.1 mmol) was dispersed in 8 ml of $H_2O$. The pH was adjusted to 7.0 by the addition of a 1 M NaOH solution. The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 ml) and heated at 130 °C for 3 days. Purple crystals were obtained (47% yield based on BIDPE).

[‡] *Crystallographic data for* **1**. Crystal of **1** ($C_{37}H_{34}CoN_9O_{10}$, $M$ = 823.66) is monoclinic, space group *C*2/*c*, at 296 K: $a$ = 29.641(3), $b$ = 11.9922(11) and $c$ = 25.453(2) Å, $\beta$ = 118.613(2)°, $V$ = 7942.6(13) Å$^3$, $Z$ = 8, $d_{calc}$ = = 1.287 g cm$^{-3}$, $\mu$(MoKα) = 0.489 mm$^{-1}$, $F$(000) = 3168. 19276 reflections were measured and 6975 independent reflections ($R_{int}$ = 0.054) were used in further refinement. The refinement converged to $wR_2$ = 0.1831 and GOF = 0.98 for all independent reflections [$R_1$ = 0.063 was calculated against $F$ for 4611 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on $F^2$ values.[12] Hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 945325 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2013.

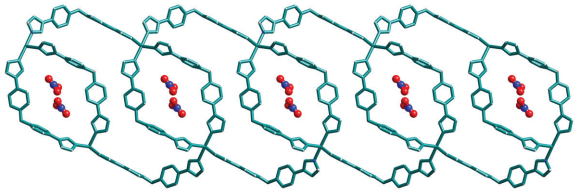

**Figure 3** 2D two-double sheet, the spaces of grids were occupied by free nitrate ions as counteranions.

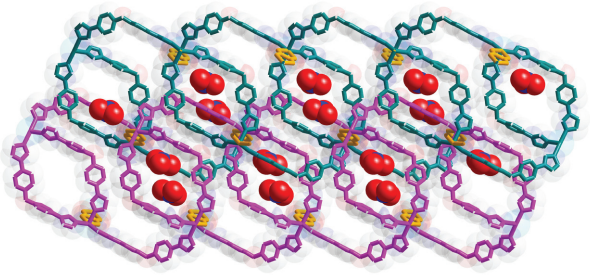

**Figure 4** 3D framework constructed by 2D two-double sheet and oxalate ions.

octahedral geometry. The angles N(1)–O(1)–N(4) and N(5)–O(2)–N(8) are 116.1 and 120.1°, respectively.

The neighbouring $Co^{II}$ ions are linked by one type of BIDPE [N(1) and N(4)] to form a 32-membered $[Co_2(BIDPE)_2]$ metallocyclic ring; the adjacent Co···Co distance is 15.174 Å. A similar 32-membered $[Co_2(BIDPE)_2]$ ring with a Co···Co distance of 16.019 Å has been reported previously.[11] In complex **1**, the spaces of metallocyclic rings were occupied by nitrate ions (Figure 2). Another type of BIDPE [N(5) and N(8)] linked these metallocyclic rings to generate an infinitely 2D two-double sheet (Figure 3). The adjacent sheets were linked by oxalate anions to form a 3D framework containing $[N_4Co(C_2O_4)CoN_4]$ units (Figure 4). Only a few coordination polymers containing a $[N_4M(C_2O_4)MN_4]$ (M = metal ions) unit have been documented, most of which are 0D coordination compounds, only four examples are polymers: $\{[Ni_2(dpt)_2(\mu\text{-ox})(\mu\text{-}N_3)]\}_n\cdot(PF_6)_n$ and $\{[Ni_2(Medpt)_2(\mu\text{-ox})(\mu\text{-}N_3)]\}_n\cdot\{(ClO_4)\cdot 0.5H_2O\}_n$ [dpt = bis-(3-aminopropyl)amine, Medpt = methyl-bis(3-aminopropyl)-amine] are 1D chains,[14,15] and the bridge ligands are all $\mu\text{-}N_3$ anions. While $[Mn(N_3)(ox)_{0.5}(phen)]_n\cdot 2H_2O$ and $\{Mn(u\text{-ox})(H_2O)_{0.5}[Cr(bpy)(CN)_4]\}_n\cdot 2nH_2O\cdot xn$MeOH (bpy = 2,2′-bipyridine) are 2D sheets,[16,17] the bridge ligands are $\mu\text{-}N_3$ and CN anions. However, a 3D framework has not been reported, complex **1** is the first example of a 3D framework containing the $[N_4Co(C_2O_4)CoN_4]$ unit. The results demonstrate that this V-shaped ligand can produce various unusual coordination frameworks.

A better insight into the nature of this intricate framework is provided by a topology analysis. The $[Co(C_2O_4)Co]$ can be regarded as a four-connected node with BIDPE as the linker. By analysis, the whole structure is represented as a $CdSO_4$ network topology (Figure 5).

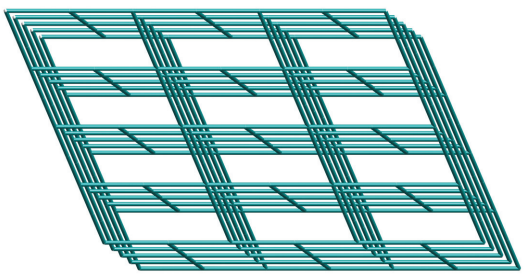

**Figure 5** View of non-interpenetrated $CdSO_4$ network in complex **1**.

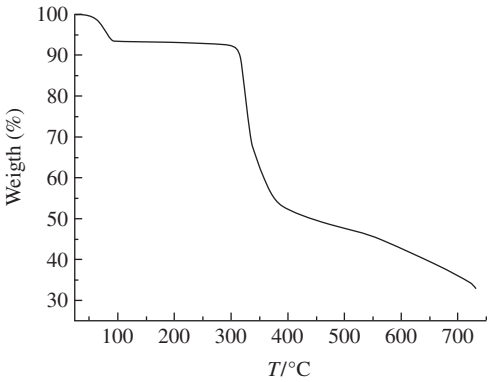


**Figure 6** The TGA pattern of complex **1**.

The numbers of solvent molecules were obtained by thermogravimetric analysis. A weight loss of 6.41% (calc. 6.56%) is observed from 30 to 102 °C, which is attributed to the loss of three lattice water molecules, and the structure decomposed starting from 350 °C (Figure 6).

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