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# A novel bimetallic cage complex constructed from six $V_4Co$ pentatomic rings: hydrothermal synthesis and crystal structure of $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$†

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**A bimetallic cluster complex, $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$ ($2,2'\text{-}Py_2NH$ = 2,2′-dipyridylamine) 1, has been hydrothermally synthesized; X-ray crystallography reveals that 1 possesses a novel cage topology structure in which the metal cluster core is constructed from six $V_4Co$ pentatomic rings.**

The hydrothermal synthesis of organic–inorganic hybrid vanadium oxides and polyvanadate clusters is of great interest due to their intriguing structural diversity and their potential functions as microporous solids for molecular adsorption, ion exchange and heterogeneous catalysis,[1–3] and as anode candidates in secondary lithium batteries and electrochromic devices.[4,5] Besides acting as a charge-compensating and space-filling constituent, the organic structure-directing component of such hybrid materials may also function as a ligand, the resulting transition metal complexes or fragments are then covalently bonded to metal framework or polyanion clusters.[6] Up to now, the study of vanadium solid state complexes has largely focused on infinite chains and layer structures.[7–10] Only a few discrete clusters have been reported, they are limited to $V_4O_{12}^{4-}$, [11] and $V_{10}O_{29}^{8-}$,[12] the latter formed through combination of two $V_4O_{12}^{4-}$ and one $V_2O_7^{4-}$ building unit by sharing oxygen atoms. Herein, we report the structure of a novel bimetallic cage complex, $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$ ($2,2'\text{-}Py_2NH$ = 2,2′-dipyridylamine**)** **1**, which is based upon a new vanadium cluster $V_8O_{23}^{6-}$. To our knowledge, **1** is the first heterometallic cage complex composed of six pentatomic rings.

Complex **1** was obtained as red blocks in 20% yield by a hydrothermal reaction. A mixture of $V_2O_5$, 2,2′-dipyridylamine, $Co(OAc)_2{\cdot}4H_2O$ and $H_2O$ in the mol ratio of 1 : 2 : 1 : 889 was stirred for 20 min, then transferred to a 25 ml Teflon-lined stainless steel bomb, which was kept at 140 °C under autogenous pressure for three days.‡ The IR spectrum of **1** exhibits characteristic bands at 922vs $cm^{-1}$ for the terminal V=O stretch and at 800–770 $cm^{-1}$ for the V–O–V stretch.

As shown in Fig. 1, the crystal structure§ of **1** consists of isolated neutral undecanuclear heterometallic clusters $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$ which are built up from a $V_8O_{23}^{6-}$ cluster and three $[(2,2'\text{-}Py_2NH)_2Co]^{2+}$ fragments. The cobalt atom has a distorted octahedral environment. It coordinates to four N atoms from two 2,2′-dipyridylamine ligands and two oxygen atoms from vanadium oxides, which adopt *cis*-orientation.

The core of **1** is $V_8O_{23}^{6-}$, which can be regarded as a pseudo-cube octanuclear vanadium cluster though there are three V–O–V edges replaced with three V–O–Co–O–V long edges (Fig. 2). The anionic vanadium cluster is composed of corner-sharing $VO_4$ tetrahedra, all $VO_4$ tetrahedra have one terminal oxygen atom. There are two crystallographically independent vanadium atoms: the V1 atom shares oxygen atoms with one $CoN_4O_2$ octahedron and two $VO_4$ tetrahedra while the V2 atom only shares oxygen atoms with three $VO_4$ tetrahedra. The cobalt atoms connect with neighboring vanadium atoms *via* O1 and its symmetry equivalents to finish the empty ‘edges’ of the pseudo-cube, thus a unique cage topology structure is formed, which is constructed from six $V_4Co$ pentatomic rings. This cage topology feature has not been described in other heterometallic clusters to date.[11,12]

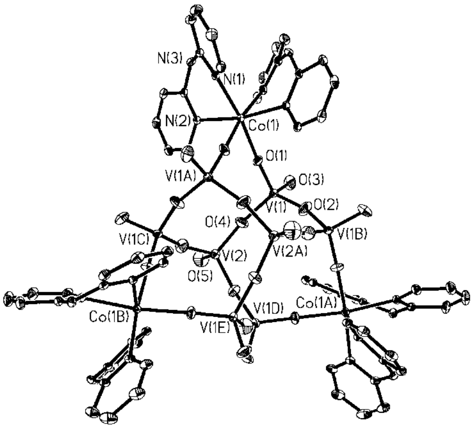

**Fig. 1** A diagram showing the molecular structure of **1** with 10% thermal ellipsoids.

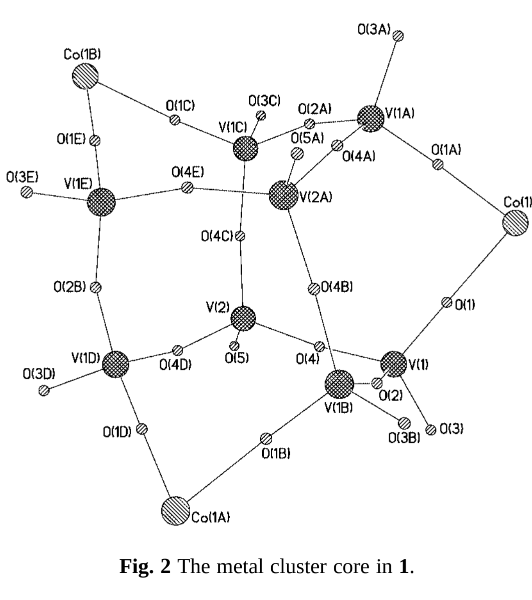

**Fig. 2** The metal cluster core in **1**.

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams of **1** in CHIME format. Fig. S1: another view of the packing of cage **1** in three-dimensional space. See http://www.rsc.org/suppdata/cc/b1/b104273b/

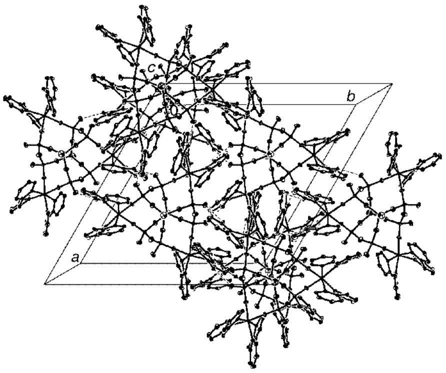

**Fig. 3** The three-dimensional supramolecular array formed through intermolecular hydrogen bonding interactions in the solid state of **1**.

It is noteworthy that there is a $C_3$ symmetry axis along the O5=V2···V2A=O5A vector, the cluster, therefore, looks like a paddle with six 2,2′-dipyridylamine ligands corresponding to the paddles. The Co···Co separation along the edge of the cobalt triangle is 8.832 Å while the V2···V2A separation is 5.765 Å. The intermolecular hydrogen bonds play a significant role in stabilization of the structure of **1**. Each uncoordinated amino group of the 2,2′-dipyridylamine ligand links to O3 or its symmetry equivalents of the neighboring $V_8O_{23}^{6-}$ clusters *via* hydrogen bonding with a corresponding N···O distance of 2.787 Å. These hydrogen bonding interactions force the undecanuclear cages $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$ into an interesting three-dimensional supermolecular array, as shown in Fig. 3.

The cube-based cage compounds related to silsesquioxanes have been studied extensively for modeling framework metal zeolite centers.[13,14] This work demonstrates that a hydrothermal method is another optional route for obtaining new metal oxide cage materials. The formation of this type of heterometallic cage suggests that there will be many potential implications of such materials as new candidates for models of zeolites or catalyst.

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## Notes and references

‡ The other product is very thin yellow plate. *Anal. Calc.* for $C_{60}H_{54}N_{18}O_{23}Co_3V_8$ **1**: C, 36.41; H, 2.75; N, 12.74. Found: C, 36.20; H, 2.91; N, 12.53%; IR(KBr, cm$^{-1}$) for **1**: 1638m, 1582m, 1528w, 1475vs, 1434m, 1420w, 1362w, 1238w, 1158w, 922vs, 879s, 863s, 790s, 773s, 752m, 741m, 672w, 665w.

§ *Crystal data* for **1**: $C_{60}H_{54}N_{18}O_{23}Co_3V_8$, rhombohedral, space group $R\bar{3}c$, $M_r$ = 1979.52, $a$ = 22.596(3), $b$ = 22.596(3), $c$ = 27.515(6) Å, $\alpha = \beta$ = 90, $\gamma$ = 120°, $V$ = 12167(3) Å$^3$, $Z$ = 6, $D_c$ = 1.621 g cm$^{-3}$, $T$ = 293(2) K, $\mu$ = 1.551 mm$^{-1}$, $R_1$ = 0.0532, $wR_2$ = 0.1397 for 2259 observed reflections [$I > 2\sigma(I)$] from 3107 independent reflections, GOF = 1.055. The data were collected on a Nonius Kappa CCD with Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods and refined by a full matrix least-squares technique based on $F^2$ using the SHELXL 97 program. The V2 atom and O5 atom are disordered over 90:10 sites. All non-hydrogen atoms except V2′ and O5′ were refined anisotropically and hydrogen atoms were allowed for as riding atoms.

CCDC reference number 167670. See http://www.rsc.org/suppdata/cc/b1/b104273b/ for crystallographic data in CIF or other electronic format.

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