

Dehydrogenative coupling of phenanthroline under hydrothermal conditions: crystal structure of a novel layered vanadate complex constructed of 4,8,10-net sheets: [(2,2'-biphen)Co]V₃O_{8.5}

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2,2'-Biphenanthroline (2,2'-biphen) formed from 1,10-phenanthroline when a new two-dimensional layered vanadium oxide metal coordination complex, [(2,2'-biphen)Co]V₃O_{8.5}, which contains novel 4,8,10-net sheets, was hydrothermally synthesized.

Increasing attention has been paid to organic–inorganic hybrid materials due not only to their intriguing structure diversity but also their potential applications in areas of molecular adsorption, catalysis, electromagnetism and photochemistry.¹ The role of organic components in hybrid materials is of great interest. Usually, organic amines act as structural directors to construct inorganic frameworks, compensating charges and filling space; on the other hand, they may also function as ligands, coordinated directly to the oxide scaffolding or to the secondary metal centers.² As examples of the latter, many hybrid organic–inorganic vanadium oxides have recently been found to be coordinated by transition metal complexes,^{3–7} which have discrete cluster, one-dimensional (1D) chain and layer structures. However, few examples involving the self-reaction of the organic component have been reported. Herein, we present a novel two-dimensional (2D) layered vanadium solid state complex [(2,2'-biphen)Co]V₃O_{8.5} **1**, where 2,2'-biphenanthroline (2,2'-biphen) formed automatically from 1,10-phenanthroline (phen) under hydrothermal reaction conditions. To our knowledge, the dehydrogenative coupling of 1,10-phenanthroline during hydrothermal reaction has not been described to date though there are hybrid organic–inorganic structures reported in which 1,10-phenanthroline coordinates to metal centers.^{7,8} Complex **1** is the first vanadate complex containing a tetradentate ligand.

Dark red block crystals of **1** were synthesized hydrothermally from a mixture of NH₄VO₃, H₃BO₃, Co(NO₃)₂·6H₂O, phen and H₂O (molar ratio 1:1.5:1:2:1000) in a polyfluoroethylene-lined stainless steel bomb (25 ml capacity) under autogenous pressure heated to 160 °C for five days (yield 50% based on vanadium).[‡] H₃BO₃ is necessary for this reaction though boron is not incorporated into the structure of **1**. H₃BO₃ might have adjusted the pH value of the mixture (the pH value changed from 6 to *ca.* 5 after adding of H₃BO₃), however, **1** did not form in the presence of other acids such as H₂C₂O₄ or HCl instead of H₃BO₃.

The formation mechanism for 2,2'-biphenanthroline is not yet known, but probably arises from the polymerization catalysis role of the cobalt complex.⁹ High temperature and pressure have also been proved to be effective for the dehydrogenation of pyridine when suitable transition metal salts are present,¹⁰ but require strictly anhydrous conditions^{10a} or dioxygen as oxidant.^{10b} Gillard and Hall suggested the 2-(or 4-) position of pyridine becomes polarized upon coordination to metal ions and so facilitating oxidation.^{10b} A similar situation

may occur in the formation of 2,2'-biphenanthroline in our reaction system. Interestingly, no 2,2'-biphenanthroline was observed in the products when Ni(NO₃)₂ instead of Co(NO₃)₂ was used under the same hydrothermal conditions.¹¹

The coordination sphere of the cobalt(II) site in **1** is defined by four nitrogen donors of a biphen ligand and two vanadate oxygen donors in the apical position leading to a distorted CoN₄O₂ octahedron (Fig. 1).[§] The two phenanthroline planes of the 2,2'-biphenanthroline ligand are coplanar (mean deviation from the plane defined by N1, C12, C11, N2, C10, C13, N3, C24, C23 and N4 is 0.0209 Å; all 2,2'-biphenanthroline planes are parallel to the *ab* plane) with a C10–C13 bond distance of 1.459(7) Å. The N1–Co1, N4–Co1 bond distances (2.197(2) and 2.189(2) Å, respectively) are slightly larger than those for N2–Co1 (2.111(2) Å) and N3–Co1 (2.110(2) Å), and the bond angle of N1–Co1–N4 (135.40(9)°) is larger than that of N2–Co1–N3 (72.49(10)°) for the tetradentate 2,2'-biphenanthroline ligand. Similar bond angle trends have also been observed in tetradentate Schiff base complexes.¹²

The structure of **1** consists of a 2D neutral framework, where (2,2'-biphen)Co units are covalently linked to the vanadium oxide V₆O₁₇ chains (Fig. 2). Each V₆O₁₇ chain is constructed from V₄O₁₂ tetramer rings and V₂O₇ units arranged alternately by edge- and corner-sharing interactions, while (2,2'-biphen)Co units connect, in a *trans* fashion, V₄O₁₂ tetramer rings and V₂O₇ units of neighboring V₆O₁₇ chains to form an extended 2D network structure with a unique 4,8,10-net as shown in Fig. 3. It is noteworthy that **1** is the first 2D layered vanadium oxide metal coordination complex constructed of 4,8,10-net sheets.

[(bipy)₂Zn]V₆O₁₇ also possesses a V₆O₁₇^{4–} component but this exhibits a quite different 2D layer structure,^{3a} where within each VO layer there are roughly circular rings, defined by

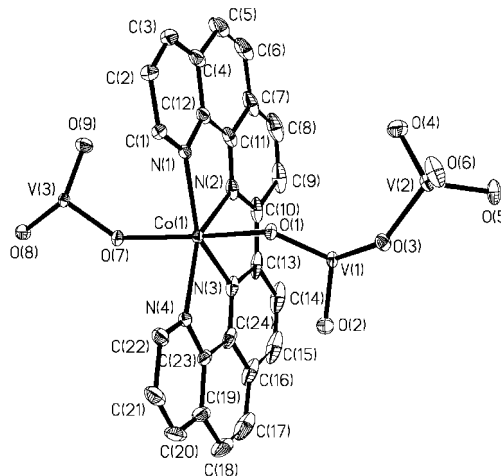


Fig. 1 A fragment of the net with the atomic labeling scheme (30% probability ellipsoids) in complex **1**.

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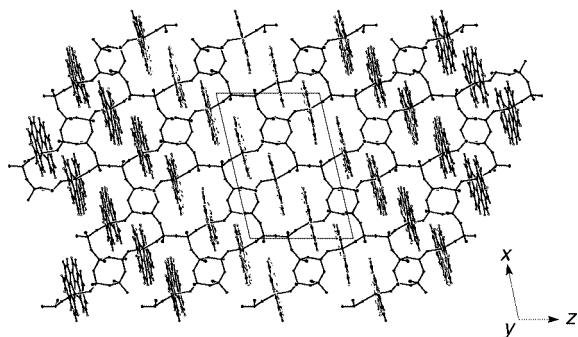


Fig. 2 View of the 2D layer in **1** along the *b*-axis direction.

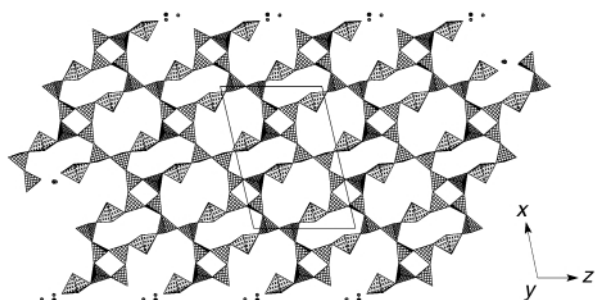


Fig. 3 Polyhedral representation of complex **1** packed along the *b*-axis; all C and H atoms are omitted for clarity.

fourteen corner-sharing VO_4 tetrahedra and two $\text{Zn}(\text{bpy})_2$ moieties which are bonded in a *cis* fashion to two second-nearest neighbor VO_4 groups on opposite sides of each ring. It is clear that two oxygen atoms of vanadate connected to the $\text{Zn}(\text{bpy})_2$ moiety adopting *cis*- rather than *trans*-orientation give rise to the structure difference of $[(\text{bipy})_2\text{Zn}]_2\text{V}_6\text{O}_{17}$ from **1**. Another quite recently reported vanadium solid state complex with a $\text{V}_6\text{O}_{17}^{4-}$ component is $[\text{Co}_4(2\text{-pzc})_4(\text{V}_6\text{O}_{17})] \cdot x\text{H}_2\text{O}$ (2-*pzc* is the anion of 2-pyrazinecarboxylic acid),¹³ where $\text{V}_6\text{O}_{17}^{4-}$ forms double chains, and each chain connects four $[\text{Co}_4(2\text{-pzc})_4]$ chains to form a 3-D chiral structure.

In conclusion, this study illustrates that even organic ligands can undergo self-reaction under hydrothermal conditions, which suggests more novel structures can be obtained by hydrothermal or solvothermal methods even with common ligands.

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Notes and references

‡ Other products are amorphous materials. Anal. Calc. for $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}_{8.5}\text{CoV}_3$ **1**: C, 40.82; H, 2.00; N, 7.93. Found: C, 40.50; H, 2.03; N, 7.80%. IR (KBr, cm^{-1}) for **1**: 1674(w), 1608(m), 1517(w), 1425(m), 968(s), 946(m), 894(s), 853(s), 835(s), 796(m), 727(s), 667(vs).

§ Crystal data for **1**: $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}_{8.5}\text{CoV}_3$, monoclinic, space group $C2/c$, $M_r = 706.14$, $a = 19.660(4)$, $b = 18.430(4)$, $c = 13.640(3)$ Å, $\beta = 103.20(3)^\circ$, $V = 4811.7(17)$ Å³, $Z = 8$, $D_c = 1.950$ g cm^{-3} , $T = 293(2)$ K, Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu = 1.870$ mm⁻¹, $R_1 = 0.0420$, $wR_2 = 0.1046$ for 5750 observed reflections from 6778 independent reflections, GOF = 1.014, Nonius Kappa-CCD diffractometer.

CCDC reference number 163766.

See <http://www.rsc.org/suppdata/cc/b1/b103304m/> for crystallographic data in CIF or other electronic format.

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