

Dinuclear manganese and cobalt complexes with cyclic polyoxovanadate ligands: Synthesis and characterization of $[\text{Mn}_2\text{V}_{10}\text{O}_{30}]^{6-}$ and $[\text{Co}_2(\text{H}_2\text{O})_2\text{V}_{10}\text{O}_{30}]^{6-}$

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Dinuclear Manganese and Cobalt Complexes with Cyclic Polyoxovanadate Ligands: Synthesis and Characterization of $[\text{Mn}_2\text{V}_{10}\text{O}_{30}]^{6-}$ and $[\text{Co}_2(\text{H}_2\text{O})_2\text{V}_{10}\text{O}_{30}]^{6-}$

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An all-inorganic complex, $[\text{Mn}_2\{\text{VO}_3\}_2]^{6-}$ (**1**) is synthesized and the structure determination reveals a dinuclear manganese complex coordinated by two cyclic pentavanadate ligands. The cyclic pentavanadate units sandwich the edge-sharing octahedral dimanganese core through coordination of the oxo group of the pentavanadate. A dinuclear cobalt complex with a cyclic decavanadate, $[\text{Co}_2(\text{OH}_2)_2(\text{VO}_3)_{10}]^{6-}$ (**2**), is also synthesized. The structure analysis reveals a dinuclear cobalt complex with a macrocyclic decavanadate which is composed of ten VO_4 units joined by the vertex sharings. The CoO_6 octahedrons are edge-shared, with each cobalt octahedron coordinated to five oxo groups in the decavanadate. The remaining site is occupied by water.

The coordinated water molecules are supported with hydrogen bonds in two directions. The complex **2** in acetonitrile shows no reactivity with dioxygen even at low temperature, and the cyclic voltammogram of **2** shows no redox chemistry in acetonitrile. Complex **2** exhibits chromism by water exposure both in the solid state and in acetonitrile. Complex **2** is a green yellow color, and the addition of water causes the complex to turn brown. After heating the sample, it returns to its original color in a reversible manner. The EXAFS data in acetonitrile is also reported and is consistent with the solid state structure.

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Introduction

Polyoxometalates exhibit a variety of coordination abilities as building blocks of molecular-based materials with a diverse range of structural versatility.^[1] The negatively charged polyoxometalate can serve as an inorganic ligand which is able to form a metal complex through the coordination of the oxo groups. The typical heteropolyoxometalates, such as Anderson type compounds, may be regarded as all-inorganic metal complexes (Figure 1). Other examples of all-inorganic complexes have been reported for $[\text{Mn}(\text{Nb}_6\text{O}_{19})_2]^{12-}$ and its Ni^{IV} isomorph.^[2] Since the discovery of cation–anion complex formation in polyoxometalate chemistry, a variety of complex formations have been investigated.^[3] The introduction of heteroatoms in the polyoxometalate frameworks can produce chirality in the structure and recently the chirality of sandwich and substituted lacunary type polyoxometalate derivatives has been reviewed.^[4] The lacunary polyanions are good ligands at their vacant sites, and they have been utilized as all-inorganic ligands for lanthanide ions.^[5] Recently, we studied the coordination chemistry of polyoxometavanadate species which have the capability to coordinate to Cu^{2+} , Ni^{2+} , and Pd^{2+} cations.^[6] The large cyclic polyoxovanadates act as macrocyclic ligands for transition metal cations. In the all-inorganic complex, the ligands are constructed by a $[(\text{VO}_3)_n]^{n-}$ anion which is composed of a ring of vertex-shared VO_4 units forming a crown ether type cyclic

structure. The coordination of the oxo groups to the heterometal ion produces the all-inorganic polyoxovanadate complex. The chemistry between cyclic metavanadates and heterometal cations defines a new class of heteropolyoxometalates.^[7] We describe here two types of structurally novel dinuclear complexes of manganese and cobalt with cyclic $[(\text{VO}_3)_n]^{n-}$ ligands. Both complexes have an edge-shared dinuclear octahedral unit, and the coordination mode of the polyoxovanadates shows a striking contrast between the dimanganese and dicobalt complexes. The dimanganese unit has a sandwich structure between the two cyclic pentavanadates through the coordination of the oxo groups of the pentavanadates. On the other hand, the dicobalt unit is surrounded by the cyclic decavanadate which resembles a crown ether type macrocyclic complex. Both compounds are thermally stable and soluble in acetonitrile. The cobalt complex shows chromism by the exposure of water and removal of water returns the complex to its original color. The extended X-ray absorption fine structure (EXAFS) studies are also performed in acetonitrile solution.

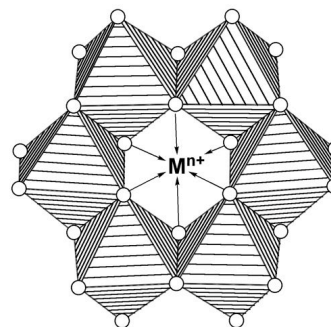


Figure 1. Alternative view of Anderson-type polyoxometalate. MO_6 units are represented by hatched octahedrons. Oxygen atoms are represented by plain circles.

Results and Discussion

Synthesis

Reactions of metavanadate with Mn^{2+} , Fe^{2+} , and Co^{2+} were surveyed in this paper. Treatment of $[\text{Mn}(\text{CH}_3\text{CN})_4]^{2+}$ and $[\text{VO}_3]^-$ ions^[8] in acetonitrile formed $[\text{Mn}_2\{(\text{VO}_3)_5\}_2]^{6-}$ (**1**) in 75% yield. If aqueous manganese ions were used in the synthesis, insoluble materials precipitated and **1** was not formed. The formation of the sandwich type complex contrasts with the case of Cu^{2+} , Ni^{2+} , and Pd^{2+} cations where all the obtained complexes were crown ether type macrocyclic complexes.^[6] In Cu^{2+} and Pd^{2+} complexes, the heteropolyoxovanadate complexes incorporated the metal cations without the coordination of hydroxide or water ligands. In the Ni^{2+} complex, the hydrolysis reaction caused the formation of a hydroxo bridged nickel(II) tetramer and the resulting heteropolyoxometalate incorporated the hydroxo bridged tetramer with the coordination of water ligands. In complex **1**, instead of incorporating a heteroatom at the center of the ring, the small cyclic pentavanadate acted as a sandwich ligand to the dimanganese core. The reaction between $[\text{Co}(\text{CH}_3\text{CN})_6]^{2+}$ and $[\text{VO}_3]^-$ in acetonitrile produced the novel complex, $[\text{Co}_2(\text{H}_2\text{O})_2(\text{VO}_3)_{10}]^{6-}$ (**2**), which has a macrocyclic decavanadate ligand. When Co(II) aqua complex was employed, the reaction produced the cobalt complex, $[\text{CoCl}(\text{V}_4\text{O}_{12})]^{3-}$, where the CoCl group was attached on the surface of the cyclic tetravanadate anion.^[9] The tetravanadate ring was too small to be a macrocyclic ligand. The nonaqueous condition is required for the synthesis of these complexes. In both complexes, the electrostatic charges built up on the cyclic vanadate rings were compensated by the dinuclear transition metal cations. The synthesis of an iron(II) complex was not successful. The addition of $[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+}$ to the acetonitrile solution of $[\text{VO}_3]^-$ immediately produced a purple color solution. Iron(II) acted as a reducing reagent to the vanadate species, which resulted in the isolation of the reduced decavanadate ion, $[\text{V}_{10}\text{O}_{26}]^{4-}$.^[10]

IR Spectroscopy

The IR spectra of **1** and **2** showed similar characteristic features of the macrocyclic polyoxovanadate complexes with the multiple appearance of V–O stretches in the region of $500\text{--}1000\text{ cm}^{-1}$. The strong bands in the range of $900\text{--}970\text{ cm}^{-1}$ correspond to the $\nu(\text{V}=\text{O}_{\text{terminal}})$ stretching frequencies (Figure 2). A notable feature is the splittings of those peaks over a wide range.

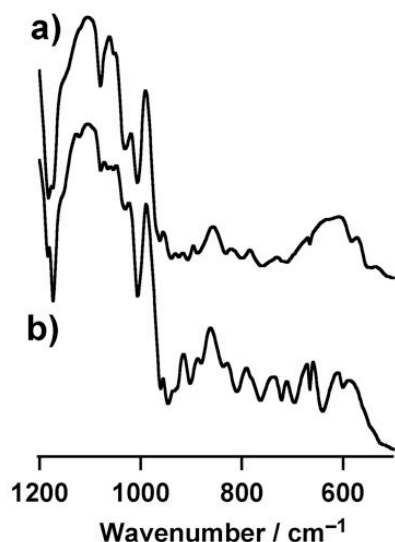


Figure 2. Infrared spectra of (a) complex **1**; (b) complex **2**.

The typical isopolyoxovanadates only show a single $\nu(\text{V}=\text{O}_{\text{terminal}})$ peak, reflecting the uniform VO_x polyhedron. The distortion of the VO_4 units by coordination to the different sites of the heterometals is responsible for these splittings. The coordination of the cyclic vanadate ligands causes the formation of two types of μ^2 -O bridges, e.g., V–O–V and V–O–M, where M is a heteroatom. The multiple stretchings spanning the range of $600\text{--}900\text{ cm}^{-1}$ are consistent with the structures of complexes **1** and **2** which contain the two types of μ^2 -O bridges.

Structures

Figure 3 shows the structure of the anion **1** in ORTEP and polyhedral views. An inversion center relates the sandwiched molecule. The MnO_6 octahedrons of the dinuclear manganese cores are edge-shared and bridged by O2. The remaining manganese coordination sites are occupied by the oxo groups from the cyclic pentavanadate. Each VO_4 unit has one terminal oxygen, two bridging oxygens between the vanadium atoms, and one bridging oxygen to the manganese atom. The pentavanadate rings are composed of the vertex-shared tetrahedrons of VO_4 units and they act as a pentadentate ligand that coordinates to the dimanganese unit through O1, O2, O3, O6 and O7 atoms. The Mn–O distances of the μ^3 -O bridging oxygen are longer (2.211(2) and 2.213(2) Å) than the Mn–O distances of the μ^2 -O oxygen (average distance is 2.151 Å). The separation of manganese atoms is 3.308(2) Å. The vanadium atoms of V1, V3, V4 and V5 lie on the same plane and the V2 unit is inclined toward the manganese octahedron and the distance to the least square plane is 0.737 Å. The distance between the plane and Mn1 is 2.993 Å. The packing water molecule has a close contact with O14 (O14 \cdots O16 is 2.895(3) Å). Two acetonitrile molecules are located in the asymmetric unit and the methyl group is pointing in the direction of anion **1**. The short intermolecular interactions of the methyl carbon and terminal oxygens are observed in the length of 3.016(5) Å (O15 \cdots C20) at the manganese bridging VO_4 group. The others have lengths of 3.260(4) Å (O14 \cdots C20).

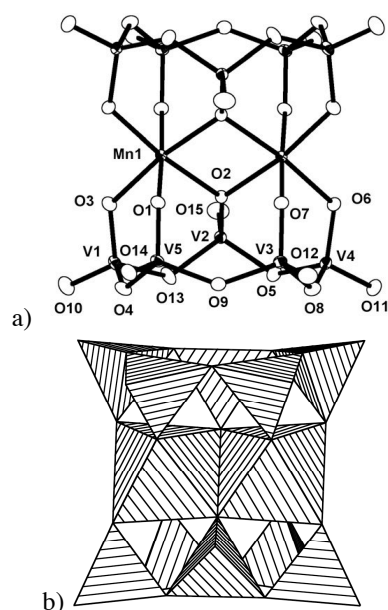


Figure 3. a) Thermal ellipsoidal plot of anion **1** with the atom numbering scheme; b) Polyhedral representation of anion **1**. Octahedrons are MnO_6 units and tetrahedrons are VO_4 units.

In complex **2**, the edge-shared octahedrons of the Co(II) centers are coordinated by the eight oxo groups from the cyclic decavanadate as shown in Figure 4. An inversion center relates the dinuclear complex **2** with the macrocyclic decavanadate. Two of the tetrahedrons out of the ten VO_4 units are not involved in the coordination to cobalt atoms (V2 units). The O9 oxygen is assigned to a H_2O ligand which is deduced from bond valence sum calculations^[11] and the positions of these protons are successfully located from the difference Fourier map and refined. The water ligands have close contacts along two directions indicating hydrogen bonds. One is to the terminal oxo (O16) of the V1 unit where the $\text{O9}\cdots\text{O16}$ distance is 2.812(2) Å. The other is to the *cis*-axial oxygen (O3) of the edge-shared dinuclear cobalt units and the distance between the water oxygen and the *cis*-axial oxygen at the octahedron is 2.711(3) Å. These hydrogen bonds in two directions seem to bind the water molecules effectively. In fact, complex **2** could be formed in the reaction system containing a trace amount of water in distilled acetonitrile. Although the highest oxidation polyoxometalate core provides a robust structural framework for the potential use of cobalt(II) complex **2** for a dioxygen activation site,^[12] **2** shows no reactivity to dioxygen. This is due to the high negative charges on the anion, unlike the traditional cationic dinuclear cobalt complexes which have been known to show various type of reactivities to dioxygen.^[13] The complex shows no redox waves by means of cyclic voltammetry in the range of ± 2 V vs Ag/Ag^+ .

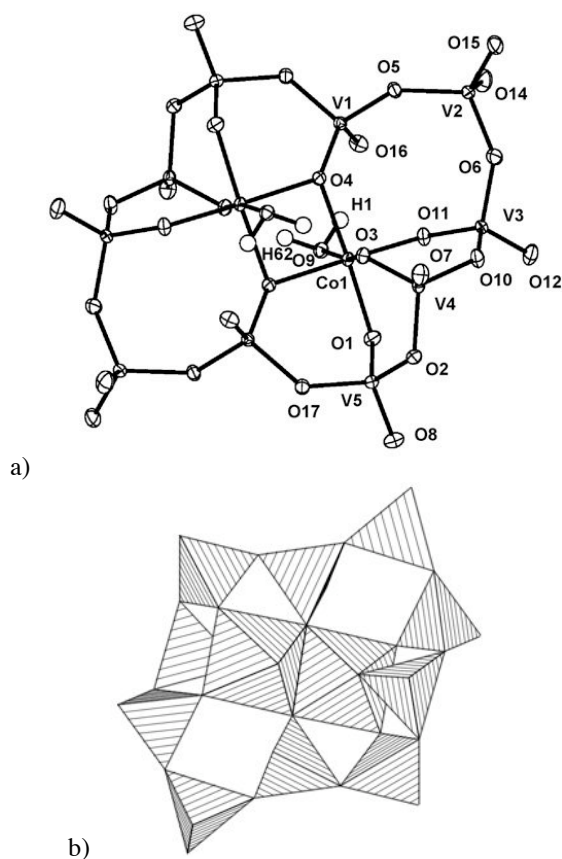


Figure 4. a) Thermal ellipsoidal plot of anion **2** with the atom numbering scheme; b) Polyhedral representation of anion **2**. Octahedrons are $\text{CoO}_5(\text{OH}_2)$ units and tetrahedrons are VO_4 units.

Complex **2** has a green yellow color in the solid state under dry air and its reflectance spectrum at room temperature shows a broad absorption band in the region of 550–800 nm as shown in Figure 5. The exposure of water vapor to the solid of **2** resulted in a change

in color to brown. The intensity of the absorption at $\lambda_{\text{max}} = 731$ nm was greatly diminished. After heating the water exposed sample, the original green yellow color was restored. Complex **2** is substantially stable thermally as well as to exposure of water. The color change may be interpreted by the partially dissociated crown like decavanadate ligands which provide additional coordination sites to the water.

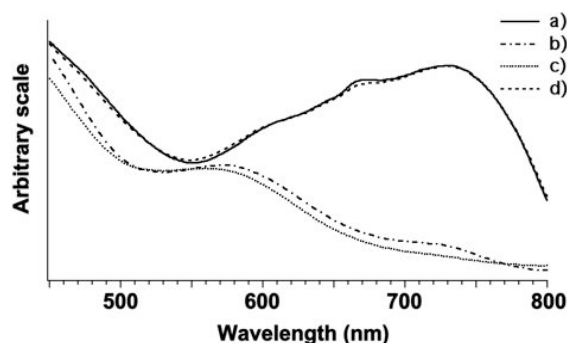


Figure 5. Electronic reflectance spectral changes of **2** demonstrating the quasi-reversible chromism of the solid by exposure to water vapor. The band at $\lambda_{\text{max}} = 731$ nm is decreased by the exposure to water vapor. a) complex **2**; b) after exposure of water vapor to the solid; c) after second exposure of water vapor to d); d) after heating the water exposed sample of b).

The UV/Vis spectrum recorded in acetonitrile solution displays the typical spectrum of an octahedral Co(II) complex with a band at 744 nm ($\epsilon = 170 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). The addition of water also caused the decrease of the band at 744 nm and the color of the solution changed from green yellow to brown. The complete removal of the solvents and the heating of the powder at 100°C retrieves the color to green yellow. The powder sample of **2** shows two weight loss steps in the TG curve. The first weight loss of 2% in the temperature range of 40–130 °C is attributed to the loss of two coordinated water molecules (calcd. 1.9%). The loss of these two water molecules causes an increase in brightness of the green yellow color, but the process was highly sensitive to water even in air and we were unable to record a spectrum of dried sample. The second weight loss of 40% in the temperature range of 210–370 °C may be due to decomposition of the Et_4N^+ counter cations.

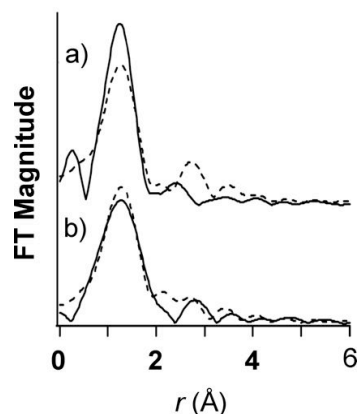


Figure 6. V *K*-edge Fourier transform of **1** (a) and **2** (b) in acetonitrile. Experimental data are shown as solid lines and simulated data are in dotted lines.

Figure 6 shows the Fourier transforms of the EXAFS data of **1** and **2** in acetonitrile solution. The fitting parameters of the EXAFS results are presented in Table 1. The coordination numbers are

fixed to the number of neighbors for each combination of the coordination spheres from single crystal X-ray studies. The V *K*-edge analyses of the complexes are consistent with the VO₄ tetrahedral geometry of the first coordination spheres. The V–O bond lengths of the fitted data correspond to the average of the V–O distances from the terminal and bridging oxygens, and the lengths between complexes **1** and **2** coincide. The structure of the cyclic inorganic framework may be less rigid than that of the spherical structures.^[14] The structural fluctuation may be the cause of the weak intensities of the peaks in the range of 2–4 Å, and the larger Debye-Waller factor. The fitted data exhibits similar V···V lengths in **1** and **2** and indicates that both complexes are composed of cyclic structures based on the linkages of VO₄ tetrahedra. The solubility requirements and the quality of the data limit us from drawing a definite conclusion of the structures of these complexes in solution, but the fits of the EXAFS results were consistent with the structure in the solid state. The longer V···Co distances compared to the V···Mn distances are in good agreement with the structural requirements that **1** has the shorter V···Mn lengths and **2** has a non-coordinated VO₄ (V2) group that causes the longer average distances between Co and V. To monitor the chromism of complex **2**, we attempted to collect data on the water diluted sample of **2** in acetonitrile. Unfortunately, the solubility of the diluted sample prevented us from collecting high resolution data. Further studies should reveal the hydrated structures of **2** by means of elongation of the average V···Co distances by varying the amount of water in the solution.

Table 1. EXAFS best-fit parameters for **1** and **2** in acetonitrile. ΔE is the edge position relative to the photoelectron wavevector (eV); *R* is the distance in Angstroms and DW are the Debye-Waller Factor terms in Å².

Shells	CN	<i>R</i> (Å)	ΔE (eV)	DW (Å ²)
complex 1				
V–O	4	1.70	–0.3	0.11
V–V	2	3.18	–7.0	0.11
V–O	2	3.32	–6.4	0.09
V–Mn	1	3.38	32	0.15
complex 2				
V–O	4	1.70	–4.2	0.11
V–V	2	3.20	3.2	0.2
V–Co	1	3.43	–3.8	0.2
V–O	1	3.47	–5.2	0

Conclusions

In conclusion, two types of all-inorganic complexes of cyclic polyoxovanadate, bis-pentavanadate dimanganese complex (**1**) and cyclic decavanadate dicobalt complex (**2**), have been synthesized and characterized. The structure analyses reveal that complex **1** has a dinuclear framework sandwiched by cyclic petavanadates and complex **2** was also a dinuclear cobalt complex of cyclic decavanadate ligand which resembles a crown ether. Both of the all-inorganic ligands are constructed from cyclic polyoxovanadates via linkages of the tetrahedral VO₄ units. This new approach to all-inorganic synthesis has considerable promise for the assembly of various types of robust transition metal complexes without organic ligands. The synthetic and chemical flexibility of heteropolyoxometalates allow the tunings of metal compositions and structures exactly. The all-inorganic complex may be regarded as an ultimate basic precursor of metal oxides for electronic devices.^[15]

Experimental Section

General Methods: IR spectra were recorded by mineral oil with a HORIBA FT720 FTIR spectrophotometer. UV/Vis spectra and diffuse reflectance spectrum were recorded with a HITACHI U3500 spectrophotometer. Electrochemical data were recorded in acetonitrile, with 0.1 M tetra-*n*-butylammonium tetrafluoroborate salt as the supporting electrolyte. Cyclic voltammetry was carried out with an ALS Model 600A instrument by using a standard three-electrode cell with a glassy carbon electrode, a Pt counter electrode, and a Ag/Ag⁺ reference electrode. TG measurements were conducted in a Seiko TA station SSC 5000 system. Elemental analyses were performed by the Research Institute for Instrumental Analysis at Kanazawa University.

Synthesis: All reagents were reagent grade and used without further purification. Solvents were dried and distilled, then stored under nitrogen. (Et₄N)[VO₃], [Mn(CH₃CN)₄](BF₄)₂, and [Co(CH₃CN)₆](BF₄)₂ were synthesized by the literature procedure.^[16] All synthetic procedure were performed in glove box under nitrogen gas.

(*n*-Et₄N)₆[Mn₂{(VO₃)₅}₂] (1**):** (Et₄N)[VO₃] (206 mg, 0.9 mmol) was dissolved in 3 mL acetonitrile. To the stirred solution, [Mn(CH₃CN)₄](BF₄)₂ (39 mg, 0.1 mmol) in 3 mL acetonitrile was added dropwise. Slow addition of the solution was required to prevent the formation of undissolved materials. The red solution was filtered and concentrated to 2 mL. The red crystals were collected after 2 day. Yield 70 mg (74.8% based on Mn). IR(Nujol, 500–1000 cm^{−1}) 962(m), 939(s), 923(s), 906(s), 889(s), 831(s), 800(s), 759(s), 711(s), 665(m), 582(m), 549(s). (Et₄N)₆[Mn₂{(VO₃)₅}₂]·2CH₃CN·2H₂O (1998.9) calcd. C 31.25, H 6.55, N 5.60; found C 31.00, H 6.39, N 5.40.

(*n*-Et₄N)₆[Co₂(H₂O)₂(VO₃)₁₀] (2**):** (Et₄N)[VO₃] (130 mg, 0.56 mmol) was dissolved in 2 mL acetonitrile. To the solution, [Co(CH₃CN)₆](BF₄)₂ (46 mg, 0.96 mmol) in 2 mL acetonitrile was added dropwise with stirring. The green solution was filtered and concentrated to 2 mL. The green crystals were collected after 2 day. Yield 70 mg (75.6% based on Co). IR(Nujol, 500–1000 cm^{−1}) 960(m), 944(s), 933(sh), 902(m), 881(w), 836(w), 809(m), 763(s), 721(s), 696(s), 665(m), 640(s), 599(w). (Et₄N)₆[Co₂(H₂O)₂(VO₃)₁₀] (1924.8) calcd. C 29.95, H 6.49, N 4.37; found C 29.89, H 6.44, N 4.53.

EXAFS Studies: The extended X-ray analysis fine structure (EXAFS) data were collected with the synchrotron beamline BL01B1 at SPring-8 (Himeji, Japan). The spectra for V-*K* edges (5.464 keV) were recorded in transmission mode at room temperature using a double-crystal Si(111) monochromator. X-rays were detected by two ion chambers, which were purged with a mixture of 70% He and 30% N₂ in I0 and 100% N₂ in I1, respectively. The samples in acetonitrile were sealed in a transparent plastic bag with approximate thickness of 3 mm through a hand made cell. The data analysis and handling were performed with the program package REX2000 (Rigaku). The EXAFS spectra were analyzed using the FEFF8 code of the University of Washington analysis programs for *ab initio* calculation of scattering paths.^[17]

X-ray Crystallography: The intensity data were collected at −150 °C on a Rigaku/MS Mercury diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å) using 0.5° ω-scans at 0° and 90° in φ. The crystal data were summarized in Table 1.

Data were collected and processed using the CrystalClear program (Rigaku).^[18] The data were corrected for Lorenz and polarization effects Absorption Corrections were applied based on the face-indexing. The structures were solved by direct methods (SHELXS-86). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water in **2** were located in the difference map, and were refined. The hydrogen atoms of the counter cations and solvent molecules were positioned with

idealized geometry and refined by using a riding model. The SHELX-97 program^[19] was used for full-matrix least-squares refinements against F^2 .

Table 1. Crystal data for **1** and **2**.

compound	1	2
Formula	(Et ₄ N) ₆ [Mn ₂ (V ₅ O ₁₅) ₂]·2CH ₃ CN·2H ₂ O	(Et ₄ N) ₆ [Co ₂ (H ₂ O) ₂ V ₁₀ O ₃₀]
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	14.044(2)	13.981(2)
<i>b</i> [Å]	24.465(3)	19.701(2)
<i>c</i> [Å]	13.820(2)	14.261(2)
α [°]	90	90
β [°]	118.968(2)	96.663(2)
γ [°]	90	90
<i>V</i> [Å ³]	5669(1)	3901.5(8)
<i>Z</i>	2	4
No. of data collected	41158	39752
No. of data used	9053	8508
No. of variables	470	451
<i>R</i> (<i>R</i> _w)	0.0355(0.0386)	0.0351(0.0925)
GOF	1.028	1.04

CCDC-737790 (for **1**) and -737791 (for **2**) contain 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.

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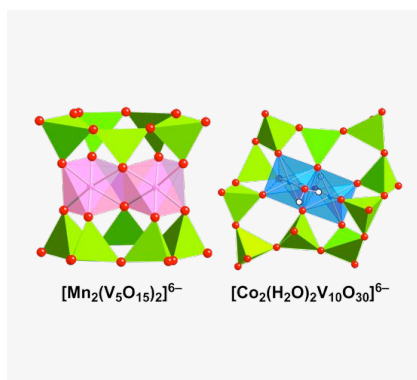
- [1] M. T. Pope in *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, **1983**, Chapter 5.
- [2] (a) B. W. Dale, M. T. Pope, *Chem. Commun.* **1967**, 792–793; (b) C. M. Jr. Flynn, G. D. Stucky, *Inorg. Chem.* **1969**, *8*, 332–334.
- [3] (a) Hill, C., Ed. in *Polyoxometalates*, *Chem. Rev.* **1998**; (b) J. J. Borrás-Almenar, E. Coronado, A. Müller, M. T. Pope (Eds.), *Polyoxometalate Molecular Science*, NATO Science Series, Kluwer Academic Publishers, Dordrecht, **2003**, vol. 98.
- [4] B. Hasenknopf, K. Micoine, E. Lacôte, S. Thorimbert, M. Malacria, R. Thouvenot, *Eur. J. Inorg. Chem.* **2008**, 5001–5013.
- [5] (a) B. S. Bassil, M. H. Dickman, B. Von Kammer, U. Kortz, *Inorg. Chem.* **2007**, *46*, 2452–2458; (b) C. Zhang, R. C. Howell, Q-H. Luo, H. L. Fieselmann, L. J. Todaro, L. C. Francesconi, *Inorg. Chem.*

- 2005**, *44*, 3569–3578; (c) Q. Luo, R. C. Howell, J. Bartis, M. Dankova, W. D. Horrocks, Jr, A. L. Rheingold, L. C. Francesconi, *Inorg. Chem.* **2002**, *41*, 6112–6117; (d) Q. Luo, R. C. Howell, M. Dankova, J. Bartis, C. W. Williams, W. D. Horrocks, V. G. Young, A. L. Rheingold, L. C. Francesconi, *Inorg. Chem.* **2001**, *40*, 1894–1901.
- [6] T. Kurata, A. Uehara, Y. Hayashi, K. Isobe. *Inorg. Chem.* **2005**, *44*, 2524–2530.
- [7] Y. Hayashi, T. Shinguchi, T. Kurata, K. Isobe, in *Vanadium: The Versatile Metal* (Eds.: K. Kustin, J. C. Pessoa, D. C. Crans), Oxford University Press, **2007**, Chap. 29, 408–423.
- [8] (a) H. Nakano, T. Ozeki, A. Yagasaki, *Inorg. Chem.* **2001**, *40*, 1816–1819; (b) H. Nakano, T. Ozeki, A. Yagasaki, *Acta Cryst.* **2002**, *C58*, m464–m465; (c) P. Román, A. S. José, A. Luque, J. M. Gutiérrez-Zorrilla, *Inorg. Chem.* **1993**, *32*, 775–776.
- [9] a) A. Bino, S. Cohen, C. Heitner-Wirguin, *Inorg. Chem.* **1982**, *21*, 429–431; b) S. M. Baxter, P. T. Wolczanski, *Inorg. Chem.* **1989**, *28*, 3263–3264; c) C. Heitner-Wirguin, J. Selbin, *Inorg. Nucl. Chem.* **1968**, *30*, 3181–3188.
- [10] T. Kurata, Y. Hayashi, K. Isobe, *Chem. Lett.* **2009**, 218–219.
- [11] I. D. Brown, in *The Chemical Bond in Inorganic Chemistry*, Oxford University Press, New York, **2002**.
- [12] (a) M. Volpe, H. Hartnett, J. W. Leeland, K. Wills, M. Ogunshun, B. J. Duncombe, C. Wilson, A. J. Blake, J. McMaster, J. B. Love, *Inorg. Chem.* **2009**, *48*, 5195–5207; (b) M. Risch, V. Khare, I. Zaharieva, L. Gerencser, P. Chernev, H. Dau, *J. Am. Chem. Soc.* **2009**, *131*, 6936–6937.
- [13] D. H. Busch, N. W. Alcock, *Chem. Rev.* **1994**, *94*, 585–623.
- [14] K. Domae, D. Uchimura, Y. Koyama, S. Inami, Y. Hayashi, K. Isobe, H. Kameda, T. Shimoda, *Pure Appl. Chem.* **2009**, *81*, 1323–1330.
- [15] T. Shimoda, Y. Matsuki, M. Furusawa, T. Aoki, I. Yudasaka, H. Tanaka, H. Iwasawa, D. Wang, M. Miyasaka and Y. Takeuchi, *Nature*, **2006**, *440*, 783–786.
- [16] D. Coucouvanis, *Inorg. Synth.* Wiley Interscience, New York, **2002**, *33*, 75–83.
- [17] S. I. Zabinsky, J. J. Rehr, J. J. Ankudinov, R. C. Albers, M. J. Eller, *Phys. Rev. B*, **1995**, *52*, 2995–3009.
- [18] *CrystalClear*. Version 1.3.5. Rigaku Corporation, Tokyo, Japan.
- [19] G. M. Sheldrick, *SHELXL-97, Program for the refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

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Entry for the Table of Contents

A ferrocene-like dinuclear manganese complex sandwiched by bis-cyclopentavanadate and a dinuclear cobalt complex with a crown ether-type macrocyclic decavanadate have been synthesized and characterized.



((Polyoxovanadate Complexes))

Shinnosuke Inami, Masaki Nishio, Yoshihito Hayashi,* Kiyoshi Isobe, Hiroyuki Kameda, and Tetsuya Shimoda Page No. – Page No.

Dinuclear Manganese and Cobalt Complexes with Cyclic Polyoxovanadate Ligands: Synthesis and Characterization of $[\text{Mn}_2\text{V}_{10}\text{O}_{30}]^{6-}$ and $[\text{Co}_2(\text{H}_2\text{O})_2\text{V}_{10}\text{O}_{30}]^{6-}$

Keywords: Polyoxometalates / Oxide ligands / Vanadates / Cobalt / Manganese