Preparation and Structure of a Novel Tetranuclear Mixed-Valence Vanadium(IV/V) Complexes Having Alkoxo and Oxo Groups

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Novel tetranuclear complexes, $M_4[V_4O_4(\mu\text{-}O)_2(dptaO)_2]{\bullet}nH_2O$ (M = Na, n = 4; M = Cs, n = 10) (dptaO = 1,3-diamino-2-propanoltetraacetato) having a mixed-valence (V(IV) and V(V)) $V_4O_8{}^{4+}$ core, are first synthesized and characterized by X-ray crystallography, EPR and UV-Vis spectroscopy. The four vanadium atoms reveal octahedral geometry, very close to each other, and afford a nearly square-planar nuclear core.

Polynuclear μ-oxo, μ-hydroxo and/or μ-alkoxo vanadium complexes have received considerable attention in recent years as a consequence of such diverse fields of interest as the role of vanadium in biological systems,[1] metal-mediated oxygen atom transfer reactions,[2] the properties of inorganic solid phases.[7-18] Although several mixed-valence oxovanadium carboxylates have been reported, the structurally characterized V/O/carboxylate chemistry is limited.[6-9]

Our study of the coordination chemistry of the dptaOH ligand stems from our interest in synthesis, structures and properties of oxo and/or alkoxo bridged polynuclear complexes in both solution and solid state.[10-12] The dptaOH uses four carboxylate groups and the deprotonated hydroxy oxygen of the alcohol functional group to bridge two adjacent metal centers.[10-16] As part of our continuing investigations of the polynuclear metal complexes of dptaOH, we have isolated a novel mixed-valence $V_4O_8{}^{4+}$ core with oxo and alkoxo group. In this paper, we report the synthesis, properties and X-ray structural characterization of a mixed-valence tetranuclear complex, $Na_4[V_4O_4(\mu\text{-}O)_2(dptaO)_2]{\bullet}6H_2O$ (**1**).[17]

$VCl_3(thf)_3$ (1.0 g, 2.6 mmol) was dissolved in 4 mL of water. To this solution, the aqueous solution of silver nitrate (1.4 g, 6.9 mmol) was added. The solution mixture was stirred and subsequently filtered to remove AgCl. Aqueous solution of NaOH was added to obtained blue solution, then the solution was transferred to the solution of $H_4dptaOH$ (0.43 g, 1.3 mmol). Ethanol was layered gently on the solution. Blue crystals were obtained within two months. Anal. Calcd for $V_4Na_4O_{30}C_{22}N_4H_{38}$: C, 23.30; H, 3.38; N, 4.94. Found: C, 23.15; H, 3.36; N, 5.13. The corresponding cesium salt was isolated as a decomposition product of $Cs_3[(VO)_2(O_2)_2(dptaO)]$ in acidic solution. Namely, the red peroxo complex gradually turned to a blue species in an acidic solution (pH 3). In this course the charge-transfer band at 434 nm due to the peroxo group disappeared and the new bands due to vanadyl species appeared at 740 and 600 nm, indicating reductive decomposition of $Cs_3[(VO)_2(O_2)_2(dptaO)]$. Deep blue crystals were obtained from the blue solution.[18]

The ligand, dptaOH (dptaOH = 1,3-diamino-2-propanoltetraacetic acid) is often used as a dinucleating ligand.[10-14] The structure of $[V_4O_4(\mu\text{-}O)_2(dptaO)_2]^{4-}$, with the atomic numbering scheme is given in Figure 1.

The crystal of **1** contains four sodium ions per a complex anion and with water molecules of crystallization. The crystal structure shows a 3-dimensional network of $[V_4O_4(\mu\text{-}O)_2(dptaO)_2]^{4-}$ anions, which are linked by sodium ions through the coordination of the oxygen atoms of the dptaO (Na-O distance = av. 2.4Å). Charge balance consideration indicates that the molecule is a mixed-valence V(V)/V(IV) complex having $V_4O_8{}^{4+}$ core. There are several mixed-valence $V_2O_3{}^{3+}$ complexes[6-9,19-21] Although several mixed-valence tetranuclear vanadium complexes have been synthesized and characterized,[22-29] complex **1** is the first compound having square-planar $V_4O_8{}^{4+}$ core characterized by X-ray crystallography. The bond valence calculation[30-32] for V(1) and V(2) provide a bond valence of 4.6

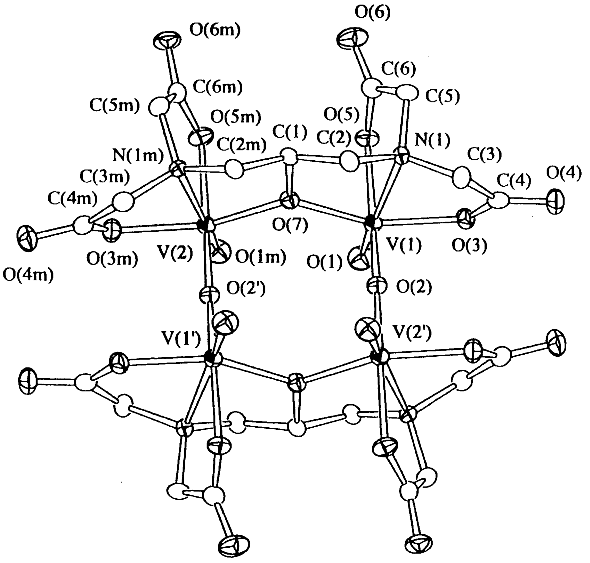

Figure 1. ORTEP drawing of tetranuclear anion of **1** showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity in this figure. Selected Bond Distances (Å) and Angles (deg) are as follows: V(1)-O(1),1.610(3); V(1)-O(2),1.786(3); V(1)-O(3), 2.002(3); V(1)-O(5), 2.075(3); V(1)-O(7), 2.016(3); V(1)-N(1), 2.289(3); V(2)-O(1m), 1.614(3); V(2)-O(2'), 1.846(3); V(2)-O(7), 2.007(3); V(2)-O(3m), 2.014(3); V(2)-O(5m), 2.069(3); V(2)-N(1m), 2.281(3); O(1)-V(1)-O(2), 103.8(1); O(1m)-V(2)-O(2'), 104.3(1); O(1)-V(1)-O(3), 98.3(1); O(1m)-V(2)-O(7), 105.6(1); O(1)-V(1)-O(5), 91.3(1); O(1m)-V(2)-O(3m), 100.5(1); O(1)-V(1)-O(7), 106.7(1); O(1m)-V(2)-O(5m), 90.7(1); O(1)-V(1)-N(1), 165.0(1); O(1m)-V(2)-N(1m), 165.4(1); O(2)-V(1)-O(3), 91.2(1); O(2')-V(2)-O(7), 89.6(1); O(2)-V(1)-O(5), 164.6(1); O(2')-V(2)-O(3m), 88.1(1); O(2)-V(1)-O(7), 89.7(1); O(2')-V(2)-O(5m), 164.9(1); O(2)-V(1)-N(1), 89.8(1); O(2')-V(2)-N(1m), 89.2(1); O(3)-V(1)-O(5), 90.0(1); O(7)-V(2)-O(3m), 153.6(1); O(3)-V(1)-O(7), 154.0(1); O(7)-V(2)-O(5m), 85.0(1); O(3)-V(1)-N(1), 74.7(1); O(7)-V(2)-N(1m), 79.4(1); O(5)-V(1)-O(7), 82.6(1); O(3m)-V(2)-O(5m), 90.6(1); O(5)-V(1)-N(1), 75.7(1); O(3m)-V(2)-N(1m), 74.3(1); O(7)-V(1)-N(1), 79.3(1); O(5m)-V(2)-N(1m), 76.0(1); V(1)-O(2)-V(2'), 174.0(2); V(1)-O(7)-V(2)-127.6(1)

and 4.2, respectively. Consequently, we assigned the V(1) site for V(V) state and V(2) site for V(IV) state, respectively.

A vanadium(IV) and a vanadium(V) center is bridged by a deprotonated alkoxo group of dptaO to afford a mixed-valence $[V_2O_2(dptaO)]$ unit. The two mixed-valence units in the $[V_4O_4(\mu\text{-}O)_2(dptaO)_2]^{4-}$ are linked together by sharing two O^{2-} ligands. The complex has a crystallographic center of symmetry on the midpoint of the V(1) ••• V(1'). The four vanadium atoms, V(1) - V(2) - V(1') - V(2'), are bridged by alkoxo and oxo groups, to afford an approximately square-planar arrangement. The terminal oxygen atoms O(1) and O(2) are in the cis position to each other within the $[V_2O_2(dptaO)]$ unit, on the other hand O(1) and O(2') are in the trans position to each other. Each vanadium ion shows a distorted octahedron with the VNO_5 donor set. The V=O distances (1.610(3) and 1.614(3) Å) are characteristic of oxo-type oxygen atoms with strong π bonding and well agree with those found in six-coordinated complexes.[8,33] Though the V(1) and V(2) are different oxidation state, the corresponding V-N, V-O(carboxyl) and V-O(alkoxo) bond lengths are close to each other. V(1)-O(3)-V(2') angle is 127.6(1)°. The V(1)-O(3) and V(2)-O(3') distances and the V(1)-O(3)-V(2') angle are 1.786(3)Å, 1.846(3)Å and 174.0(2)°, respectively. Several complexes containing the $V_2O_3^{3+}$ unit have been reported with either localized or delocalized vanadium-(IV) and -(V) centers.[6-8,19] The bond distances and angles are falling within normal values of the corresponding mixed-valence oxo-bridged dinuclear complexes.[6-8,19] Although the V-O(alkoxo) distances are close to each other, the V-O(oxo bridge) distances differ from each other. The V(1)-O(3) distance is slightly shorter than that of V(2)-O(3). In mixed-valence oxo bridged dinuclear complexes, $Na[V_2O_3(DL\text{-}salser)_2]$ (salser = *N*-salicylideneserine) and $Na[V_2O_3(S\text{-}peida)_2]$ (S-peida = (S)-[[1-(2-pyridyl)ethyl]imino]diacetate) having localized vanadium-(IV) and -(V) centers have been synthesized and crystallographically characterized.[7,19] It has been reported that the V(IV) atom shows longer V-O(oxo bridge) distance than those at V(V).[7,19]

The reflectance spectrum of complex **1** exhibits bands at 9057, 13120, 16100, 26310 cm^{-1}. The reflectance spectra of mixed-valence dimeric complexes, $Na[V_2O_3(S\text{-}peida)_2]$ and $(NH_4)_3[V_2O_3(nta)_2]$ (nta = nitrilotriacetate), have been measured,[6,7] and the bands near 10000 cm^{-1} are assigned to the intervalence band. For complex **1**, the corresponding band is also found in the region of 10000 cm^{-1}, indicating the similar valence state to those of $Na[V_2O_3(S\text{-}peida)_2]$ and $(NH_4)_3[V_2O_3(nta)_2]$.[34]

The EPR spectrum of polycrystalline sample of complex **1** shows practically isotropic signal from which the g value of 1.97 is obtained. Moreover, the EPR spectrum clearly shows a half-field signal. Indeed, the $\Delta Ms=2$ transition is not completely forbidden due to dipolar coupling.[35] The half-field line at about 1600G also is indicative of the presence of magnetic interactions.

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References and Notes

1 D. Rehder, *Angew.Chem.*, *Int.Ed.Engl.*, **30**, 148, (1991).
2 Y. Zhang and R. H. Holm, *Inorg.Chem.*, **29**, 911, (1990).
3 D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, *Science*, **265**, 1054, (1994).
4 M. T. Pope and A. Mueller, *Angew.Chem.Int.Ed.Engl.*, **30**, 34, (1991).
5 W. G. Klemperer, T. A. Marquart and O. M. Yaghi, *Angew.Chem.Int.Ed.Engl.*, **31**, 49, (1992).
6 M. Nishizawa, K. Hirotsu, S. Ooi and K. Saito, *J.Chem.Soc.Chem.Commun.*, **1979**, 707.
7 A. Kojima, K. Okazaki, S. Ooi and K. Saito, *Inorg.Chem.*, **22**, 1168, (1983).
8 J.-P. Launay, Y. Jeannin and M. Daoudi, *Inorg.Chem.*, **24**, 1052, (1985).
9 K. Okazaki and K. Saito, *Bull.Chem.Soc.Jpn.*, **55**, 785, (1982).
10 S. Kawata, M. Nakamura, Y. Yamashita, K. Asai, K. Kikuchi, I. Ikemoto, M. Katada and H. Sano, *Chem.Lett.*, **1992**, 135.
11 S. Kawata, H. Kosugi, H. Uda, M. Iwaizumi and H. Yokoi, *Bull.Chem.Soc.Jpn.*, **65**, 2910, (1992).
12 K. Kanamori, K. Yamamoto and K. Okamoto, *Chem.Lett.*, **1993**, 1253.
13 J. C. Robles, M. Shimoi and H. Ogino, *Chem.Lett.*, **1992**, 309.
14 J. C. Robles, Y. Matsuzaka, S. Inomata, M. Shimoi, W. Mori and H. Ogino, *Inorg.Chem.*, **32**, 13, (1993).
15 T. Tanase, M. Kato, Y. Yamada, K. Tanaka, K. Lee, Y. Sugihara, A. Ichimura, I. Kinoshita, M. Haga, Y. Sasaki, Y. Yamamoto, T. Nagano and S. Yano, *Chem.Lett.*, **1994**, 1853.
16 M. Kato, Y. Yamada, T. Inagaki, W. Mori, K. Sakai, T. Tsubomura, M. Sato and S. Yano, *Inorg.Chem.*, **34**, 2645, (1995).
17 $Na_4[V_4O_4(\mu\text{-}O)_2(dptaO)_2]\cdot 6H_2O$: Formula weight = 1134.28, monoclinic, *C*2/c, *a* = 28.088(2), *b* = 7.608(2), *c* = 21.227(2) Å, β = 120.422(4)°, V = 120.422(4) Å^3, *Z* = 4, No. of observations = 2901 ($I>2\sigma(I)$), D_{calcd} = 1.929 g/cm^3, F(000) = 2296.00, *R*(*R*w) = 0.041(0.041).
18 $Cs_4[V_4O_4(\mu\text{-}O)_2(dptaO)_2]\cdot 10H_2O$: Formula weight = 823.0, Orthorhombic, *P*mna, *a* = 15.0996(7), *b* = 7.8479(5), *c* = 19.945(1) Å, V = 2363.4(2) Å^3, *Z* = 2, No. of unique reflections = 2749 ($I>3\sigma(I)$), D_{calcd} = 2.313 g/cm^3, F(000) = 1580, *R*(*R*w) = 0.040(0.046). The bond lengths and angles within the complex anion are very similar to the corresponding ones found in the sodium salt. Details will be published elsewhere; K. Kanamori, A. Toda, K, Nishida, and K. Okamoto.
19 J. C. Pessoa, J. A. L. Silva, L. Vilas-Boa, P. O'Brien and P. Thornton, *J.Chem.Soc.Dalton Trans.*, **1992**, 1745.
20 J. Chakravarty, S. Dutta and A. Chakravorty, *J.Chem.Soc.Dalton Trans.*, **1993**, 2857.
21 S. Dutta, P. Basu and A. Chakravorty, *Inorg.Chem.*, **32**, 5343, (1993).
22 D. L. Hughes, U. Kleinkes, G. J. Leigh, M. Maiwald, J. R. Sanders and C. Sudbrake, *J.Chem.Soc.*, *Dalton Trans.*, **1994**, 2457.
23 G. B. Karet, Z. Sun, D. D. Heinrich, J. K. McCuster, K. Folting, W. E. Streib, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg.Chem.*, **35**, 6450, (1996).
24 J. K. Money, J. C. Huffman and G. Christou, *J.Am.Chem.Soc.*, **109**, 2210, (1987).
25 D. D. Heinrich, K. Floting, W. E. Streib, J. C. Huffman and G. Christou, *J.Chem.Soc.,Chem.Commun.*, **1989**, 1411.
26 A. Hills, D. L. Hughes, G. J. Leigh and J. R. Sanders, *J.Chem.Soc.*, *Chem. Commun.*, **1991**, 827.
27 Q. Chen and J. Zubieta, *J.Chem.Soc.,Chem.Commun.*, 2663, (1994).
28 M. I. Khan, Y.-D. Chang, Q. Chen, J. Salta, Y. S. Lee, J. C. O'Connor and J. Zubieta, *Inorg.Chem.*, **33**, 6340, (1994).
29 H. Kumagai, M. Endo, S. Kawata and S. Kitagawa, *Acta Cryst.*, **C54**, 1943, (1996).
30 N. E. Brese and M. O'Keefe, *Acta Cryst.*, **B47**, 192, (1991).
31 I. D. Brown and K. K. Wu, *Acta Cryst.*, **B32**, 1957, (1976).
32 I. D. Brown and D. Altermatt, *Acta Cryst.*, **B41**, 244, (1985).
33 I. Cavaco, C. J. Pessoa, D. Costa, M. T. Duarte, R. D. Gillard and P. Matias, *J.Chem.Soc.Dalton Trans.*, **1994**, 149.
34 The four vanadiumn atoms are X-ray crystallographically equivalent in the cesium salt as in the case of $(NH_4)_3[V_2O_3(nta)_2]$.
35 A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems*; Springer-Verlag: Berlin, 1989.