closer to Fe2 than are the 5-H or the N-CH_3, and the expected dipolar broadening leads to assignment of the relatively broad feature at ~9 ppm to the unresolved cis and trans 4-CH_3 resonances. We[21] and others[22] have previously shown that the bridging acetate chemical shifts in di- and trinuclear Fe(III) complexes vary monotonically with solution magnetic moments per iron atom and with the pairwise antiferromagnetic coupling constants, $-J$, in the $\hat{H}_{ex} = -2J\hat{S}_1\cdot\hat{S}_2$ formalism. Solution magnetic moments measured at ~296 K in CD_3CN by the Evans method[21] gave effective magnetic moments of 4.00 μ_B/Fe for **1** and 4.01 μ_B/Fe for **2**. These magnetic moments together with the bridging acetate chemical shift of **1** (52.4 ppm) at the same temperature indicate that the pairwise antiferromagnetic coupling between adjacent iron atoms in the cores of **1** and **2** is significantly stronger than that in the isostructural core of $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$ (4.42 μ_B/Fe, 68.7 ppm, $-J$ = 17 cm^{-1} [20]).[23] On the other hand, comparisons of the same parameters indicate that the antiferromagnetic coupling between adjacent iron atoms in the cores of **1** and **2** is significantly *weaker* than that between the iron atom pairs in the "basic iron acetate" cluster $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(N\text{-}MeIm)_3]^+$ (3.34 μ_B/Fe,[21] 30.7 ppm,[21] $-J$ = 30 cm^{-1} [24]). Thus, these comparisons indicate that the pairwise antiferromagnetic coupling strength between adjacent iron atoms in the cores of **1** and **2** is within the range 17 $cm^{-1} < -J < 30$ cm^{-1}.

The ^{57}Fe Mössbauer spectrum of solid **1** (not shown) at 250 K shows a broadened but unresolved doublet with isomer shift (quadrupole splitting) of 0.41 (0.74) mm/s; these values indicate high-spin ferric iron and are close to those of two (μ-hydroxo)-bis(μ-acetato)diiron(III) complexes.[1,4] At 1.8 K in a weak applied field (2.2 kG), the Mössbauer spectrum of **1** shows at least eight resolved components. Such a complex magnetic spectrum is indicative of a paramagnetic ground state. An X-band EPR spectrum at 15 K of a frozen solution of **1** in acetonitrile showed a strong first-derivative feature with zero-crossing at g = 4.29 and a much weaker feature at g = 9.46. This EPR spectrum is consistent with a $S_{tot} = {}^5/_2$ ground state for **1**, as expected for a complex consisting of three paramagnetic centers with $S_1 = S_2 = S_3 = {}^5/_2$ and antiferromagnetic coupling only between adjacent pairs of centers; i.e., $J_{12} = J_{23}$, and $J_{13} = 0$.[25]

The new structure reported here adds to the small but growing list of triiron-carboxylate core types[26] and further illustrates the recently recognized structural flexibility inherent in polynuclear ferric-carboxylate chemistry.[1,2] The trans configuration of the hydroxo bridges around the central iron atoms of **1** and **2** is unusual if not unique in discrete polynulear ferric complexes. The synthetic procedure for **1** is completely analogous to that for $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$, but we have detected no diiron(III) complexes using T1,4DMIP. Examination of space-filling structures of $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$ shows that steric overlap of methyl groups ortho to those coordinating nitrogens which are cis to the oxo bridge on adjacent iron atoms is likely to destabilize the analogous diiron complex with T1,4DMIP. Reactivities of **1** and **2** and synthetic routes to similar trimetal complexes are currently being explored. Preliminary results show that the mixed oxo/hydoxo-bridged complex $[Fe_3(\mu\text{-}O)(\mu\text{-}OH)(\mu\text{-}O_2CR)_4(T1,4DMIP)_2]^{2+}$, whose triiron core is isostructural with that in **1** and **2**, is readily accessible.[28]

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Supplementary Material Available: Listings of X-ray experimental details (Table S1) and atomic coordinates and anisotropic thermal parameters (Table SII) and distances (Table SIII) and angles (Table SIV) for non-hydrogen atoms and figures showing atom numbering and unit cell and packing diagrams (13 pages); a listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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Department of Chemistry
University of Georgia
Athens, Georgia 30602

Vivian A. Vankai
M. Gary Newton
Donald M. Kurtz, Jr.*

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Synthesis and Crystal Structure of a Vanadium(V) Complex with a 2-Hydroxy Acid Ligand, $(NH_4)_2[V(OC(CH_2CH_3)_2COO)(O)_2]_2$: A Structural Model of both Vanadium(V) Transferrin and Ribonuclease Complexes with Inhibitors

Monomeric and polymeric vanadates are potent inhibitors for a variety of enzymes including ATPases, phosphatases, and nucleases.[1-5] V(V) can bind tightly into the active sites of these enzymes in a trigonal-bipyramidal geometry. This interaction is thought to mimic the hydrolytic transition states of their enzymic reactions.[3-5] Such a geometry has been established by X-ray crystallography[6] in the complex formed when ribonuclease A is inhibited by vanadate and uridine. More recently, the first X-ray structure of a V(V) synthetic model that mimics this coordination geometry has been published.[3] However, it contains a trigonal bipyramid of one chloride and four oxygen donors about the V center,[3] unlike the vanadate/uridine/ribonuclease complex.[6] In addition, it is unstable at room temperature, both in the solid state and in solution.[3] We report here the first example of a trigonal-bipyramidal V(V) complex with five oxygen donors which is a good structural model for the vanadate/uridine/ribonuclease complex. It is remarkably stable both in the solid state and in aqueous solutions at room temperature. The complex is also the best structural model that has been reported for the proposed active

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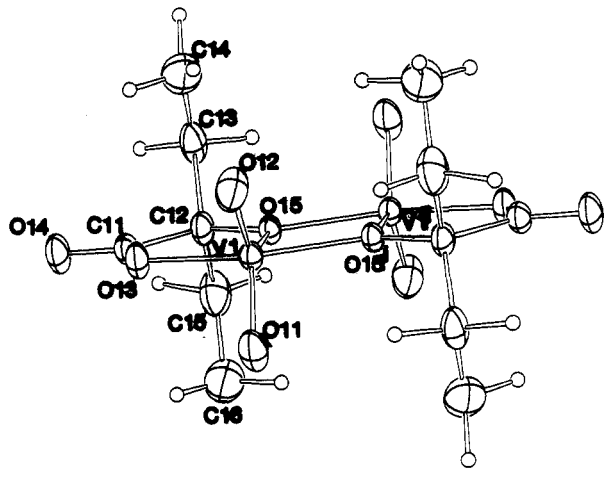

Figure 1. ORTEP view of the anion in the structure of $(NH_4)_2[\{V(O)_2(\eta^2\text{-}O,O''\text{-ehba-}\mu\text{-}O')\}_2]\cdot H_2O$, showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): O(11)–V(1) = 1.605 (2), O(12)–V(1) = 1.617 (2), O(15)–V(1) = 1.973 (1), C(11)–O(13) = 1.280 (3), O(15)–V(1)^i = 1.984 (2), O(13)–V(1) = 1.974 (1), C(11)–O(14) = 1.232 (3), C(12)–O(15) = 1.437 (3), C(12)–C(11) = 1.526 (3); O(12)–V(1)–O(11) = 108.5 (1), O(15)–V(1)–O(11) = 100.6 (1), O(15)–V(1)–O(12) = 99.9 (1), O(15)^i–V(1)–O(15) = 104.0 (2), C(11)–C(12)–O(15) = 104.7 (2), V(1)–O(15)–V(1)^i = 71.9 (1), C(12)–O(15)–V(1) = 131.2 (1), O(13)–V(1)–O(15)^i = 148.2 (1).

site of vanadium(V) transferrin. This complex has been implicated in the metabolism of vanadium both at the very low dietary level and at the toxic level.[7]

Aerial oxidation of an aqueous solution of $(NH_4)[V(O)(ehbaH)(ehba)]$[8] resulted in yellow crystals of the vanadium dimer $(NH_4)_2[\{V(O)_2(\eta^2\text{-}O,O''\text{-ehba-}\mu\text{-}O')\}_2]\cdot H_2O$ (I).[9,10] An ORTEP diagram of one of the symmetry-related independent dimers of the unit cell is given in Figure 1. The geometry about each of the vanadium atoms is a distorted trigonal bipyramid of oxygen atoms with the oxo oxygens occupying equatorial positions (V=O = 1.605 (2), 1.617 (2) Å), together with the alkanolate donor of a chelating ehba ligand (V—O = 1.973 (1) Å). The axial positions are occupied by a terminal carboxylate (V—O = 1.974 (1) Å) and the bridging bond between vanadium and the alkanolate group of the adjacent V center (V—O = 1.984 (2) Å). The structure is the only example of a trigonal-bipyramid geometry with a dioxo moiety and three other oxygen donors. When compared to those of other vanadium(V) alkoxides, bis(μ-pinacolato)bis[chlorooxovanadate(V) (II),[3] $VO(OCH_2CH_2Cl)_3$ (III),[11] and $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ (IV),[12] the V=O bonds in I (V=O = 1.617, 1.605 Å) are longer than the same bonds in II (V=O = 1.576 Å), III (V=O = 1.584 Å), and IV (V=O = 1.581 Å). The V—O(alkanolate) distances in I (1.973, 1.984 Å), where the oxygen bridges two vanadiums, are also longer than equivalent bonds in II (V—O = 1.964, 1.967 Å) and in IV (V—O = 1.957 Å).

In aqueous solution, the ^{13}C NMR spectrum shows that the plane of symmetry observed in the crystal structure is maintained in solution, with only four signals due to the four inequivalent carbons of the ligand being present.[9] No signals were observed that could be attributed to monomers or other decomposition products. The ^1H NMR spectrum also establishes that the geometry is maintained in solution. The inequivalent protons of the methylene group, together with the methyl group, exhibit an ABX_3 coupling pattern.[9] The methyl groups are observed as a triplet because of rapid rotation on the NMR time scale relative to the rigid CH_2 group. The inequivalence of the methylene protons on the same carbon is indicative of limited rotation about the C–C bond connecting the alkanolate group to the methylene group. This in turn mitigates against any rapid dynamic process being present in solution which could act to make two ethyl groups of the ligand equivalent on the ^{13}C NMR time scale. The rigid dimeric structure is remarkably stable toward decomposition in aqueous solutions over a period of hours, since no decomposition products are observed in the NMR spectra over this period of time.

The inhibition of ribonuclease activity occurs through strong binding of vanadium complexes to the uridine moiety of the enzyme, as observed in the crystal structure of the vanadate/uridine/ribonuclease A structure.[6] The geometry around the vanadium atoms is trigonal bipyramidal, which probably simulates the transition state[4,5] in the phosphate ester hydrolyses that the enzyme catalyzes. Presumably, the enzyme is designed to stabilize this transition state in order to maximize the catalytic rate constant. The question of why such a geometry is so stable in the enzyme, when previous structural model complexes readily decompose,[3] is probably related to steric factors that protect the vanadium center when it binds to the protein. The current work offers strong support for this notion because in our structural model, the vanadium center is protected by the bulky ethyl groups to produce a very stable trigonal-bipyramidal geometry. The steric hindrance in this complex is shown by the limited rotation of the ethyl groups on the NMR time scale.

This complex is the first example of a structural model for the proposed active site in vanadium(V) transferrin.[7] The notion that a trigonal-bipyramidal coordination of one carboxylate, two oxo, and two alcoholate (tyrosine) donors is stabilized by steric effects in this protein[7] is strongly supported by the present results, where such a geometry has been shown to be very stable. The only difference between the donor groups of the structural model reported here and the proposed site in the enzyme is the replacement of two aromatic alcoholate donors by two aliphatic donors.

Finally, it should be pointed out that this V(V) complex has very unusual thermodynamic stability compared to other V(V) complexes with oxygen donor ligands.[13,14] Normally, such species exist in solution in equilibrium with substantial amounts of vanadate and polyvanadate ions. Preliminary ^{51}V NMR experiments (δ = 556 for I) establish that the equilibrium quantities of such complexes in aqueous solutions of I are very low (<5%).

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(10) $(NH_4)_2[\{V(O)_2(\eta^2\text{-}O,O''\text{-ehba-}\mu\text{-}O')\}_2]\cdot H_2O$: $C_{12}H_{30}N_2O_{11}V_2$, M_r = 480.3, monoclinic, space group $P2_1/c$, a = 12.446 (2) Å, b = 12.887 (2) Å, c = 13.090 (2) Å, β = 97.59°, V = 2081.1 Å^3, $D_c(Z = 4)$ = 1.482 g cm^{-3}, $F(000)$ = 912, μ_{Mo} = 8.86 cm^{-1}. Range of hkl: −14 to +13, 0 to 9, 0 to 15. R = 0.034 and R_w = 0.043. Residual extrema: 0.46, −0.23. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F four-circle diffractometer employing Mo Kα radiation (0.7017 Å) and a graphite monochromator and operating in the ω–θ scan mode. Data were reduced, and Lorentz, polarization, and decomposition and absorption corrections were applied using the Enraf-Nonius Structure Determination Package. Of the 3423 collected independent reflections not systematically absent, 3082 with $I > 2.5\sigma(I)$ were considered observed and used in the solution of the structure. The structure was solved by direct methods and refined by a full-matrix least-squares analysis using SHELX 76 (Sheldrick, G. M. SHELX-76: A Program for X-Ray Crystal Structure Determination. University of Cambridge, England, 1976). Hydrogen atoms were included at calculated sites (C–H = 0.97 Å) refined with isotropic thermal parameters, and all other atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections for vanadium were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV. For all other atoms the values supplied in SHELX 76 were used.
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Supplementary Material Available: Tables of positional parameters, thermal parameters, torsional angles, bond lengths, and bond angles (3 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Department of Inorganic Chemistry
The University of Sydney
Sydney, New South Wales 2006
Australia

Trevor W. Hambley
Robert J. Judd
Peter A. Lay*

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Articles

Contribution from the Institute for Inorganic Chemistry,
University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, FRG

Kinetics and Mechanism of the Complex Formation Reactions of Diaqua(ethylenediamine)- and Diaqua(tetraethylethylenediamine)palladium(II) with the Purine Nucleosides Adenosine and Inosine

Heribert Hohmann, Björn Hellquist,[1] and Rudi van Eldik*

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The kinetics of the complex formation reactions of $Pd(R_4en)(H_2O)_2^{2+}$ (R = H, Et; en = ethylenediamine) with adenosine and inosine have been studied as a function of nucleoside concentration, temperature, and pressure in a weakly acidic aqueous solution. All systems exhibited two consecutive reaction steps, which each depended on the nucleoside concentration according to the rate law $k_{obs} = k_a + k_b[Nu]$. In the case of adenosine, both k_a and k_b increase significantly with increasing pH, which is ascribed to pronounced participation of the N(1) coordination site. However the produced complex appears to be less stable than the corresponding inosine complex, presumably due to the interference by the exocyclic amine group. The effect of steric hindrance on the en ligand appeas to be more pronounced on the second complex formation reaction, i.e. where one nucleoside molecule is already coordinated to the metal center. The reported activation parameters (especially ΔV^*) underline the operation of an associative ligand substitution mechanism. A detailed comparison with related systems reported in the literature is made.

Introduction

There is presently a significant interest in the interaction of *cis*-Pt^{II}(diamine) and *cis*-Pd^{II}(diamine) with DNA and its constitutents in an effort to improve our understanding of the antitumor activity of such complexes and their use in chemotherapy.[2,3] Many of the quoted studies[3] involve the structural identification of reaction products using NMR and X-ray techniques, such that a good understanding of the bonding modes has been achieved. This is to a lesser degree the case for the reactivity, i.e. kinetics, of the produced species. In our earlier work we have focused on the substitution behavior of diethylenetriamine (dien) and substituted diethylenetriamine complexes of Pd(II) as labile model complexes for the corresponding, more inert Pt(II) complexes.[4] In this work we also investigated the complex formation of $Pd(dien)Cl^+$ and $Pd(dien)H_2O^{2+}$ with typical nucleic bases, nucleosides, and 5'-nucleotides.[4g,h] We have now extended this work to the ethylenediamine(en) and N-substituted tetraethylethylenediamine (Et_4en) dichloro complexes of Pd(II). The Pd(en)Cl_2 complex exhibits aquation and subsequent acid dissociation equilibrium constants very similar to those *cis*-$Pt(NH_3)_2Cl_2$ species,[5,6] although the ligand substitution rate constants (aquation and reverse anation steps) are 5 orders of magnitude larger for

(1) On leave from the Department of Chemistry, Högskolan, 1 Sundsvall/Härnösand, 85124 Sundsvall, Sweden.

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