All of the present structures contain lattice water molecules. Most of these are strongly hydrogen bonded to either carboxylate groups or to other water molecules. Where no hydrogen bond exists, we were unable to locate the hydrogen atoms and the thermal parameters of the water oxygen atoms were significantly higher. One further consequence of the hydrogen bonding is the compactness of the crystal packing, as evidenced by the high values for the crystal densities.

In conclusion we find that iron(III) forms interesting complexes with the poly(aminocarboxylate) ligand DTPA as a function of solution pH. Further, the low-pH solution of Fe^{III}DTPA represents an example of an iron complex incorporating biologically relevant ligand atoms (N, O) that has some of the spectroscopic properties that are characteristic of the iron environment in lipoxygenases. In extending the present results to the enzyme, we hypothesize that the active form has a structure in the first-coordination sphere of the iron that is very similar to the low-pH form of Fe^{III}DTPA, while at high pH the axial component of the cis-octahedral coordination is reduced in magnitude, possibly by ligand addition as it is in the case of FeDTPA.

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Supplementary Material Available: For compounds I-III, text describing data collection and reduction and structure solution and refinement and tables giving crystallographic details, positional parameters, and bond distances and angles (64 pages); listings of structure factor amplitudes (39 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and Magnetic Properties of a Unique Diamagnetic Binuclear μ-Oxo Vanadium(IV) Complex. Crystal Structure of $[(tpa)VO(\mu\text{-}O)VO(tpa)](ClO_4)_2$ (tpa = Tris(2-pyridylmethyl)amine)

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Introduction

Oxo-bridged transition-metal complexes have received much attention in recent years, as these complexes may serve as structural models for metalloproteins involved in oxygen transport and oxygen metabolism.

Examples of homobinuclear single-oxo-bridged metal complexes are known for the first elements of the transition periods. Reviews covering the newer literature[2,3] have been published. Although there are a few examples of single-μ-oxo binuclear vanadium complexes reported in the literature, there are no reports on mono(μ-oxo) vanadium(IV) complexes. Four binuclear V(III) systems have been reported.[4,5] Mixed-valence IV,V systems having tripodal doubly or triply negatively charged ligands have been characterized.[6-9] Binuclear vanadium(V) complexes of enolato-[10] or phenolato-based[11] ligands are known also. This paper reports the synthesis, physicochemical properties, and crystal structure of the first example of a diamagnetic mono(μ-oxo) vanadium(IV) complex. The nonbridging donor atoms are provided by the quadridentate tripodal ligand tris(2-pyridylmethyl)amine (tpa). The fact that this is a neutral ligand with good σ-donor properties seems to be essential for the stabilization of the V(IV) oxidation state in a binuclear structure.

Table I. Crystallographic Data and Refinement Results for $[(tpa)VO(\mu\text{-}O)VO(tpa)](ClO_4)_2$

formula	$V_2C_{36}Cl_2H_{36}N_8O_{11}$	γ, deg	81.41 (3)
fw	929.53	V, Å^3	1935 (1)
space group	$P\bar{1}$	Z	2
T, K	110	λ, Å	0.710 73
a, Å	12.244 (6)	d_{calc}, g cm^{-3}	1.595
b, Å	12.299 (2)	μ, cm^{-1}	6.75
c, Å	13.370 (2)	$R(F_o)$	0.037
α, deg	77.418 (13)	$R_w(F_o)$	0.044
β, deg	83.15 (2)		

Experimental Section

Syntheses. Tris(2-pyridylmethyl)amine (tpa). This ligand was prepared by the method described by Højland et al.[15] The crude product was purified by recrystallization of the $tpaH_3(ClO_4)_3$ salt.

(μ-Oxo)bis[(tris(2-pyridylmethyl)amine)vanadyl(IV)] Perchlorate. Tris(2-pyridiniumylmethyl)amine perchlorate (1.2 g, 2,0 mmol) was dissolved in a 1:1 mixture of acetonitrile and 0.5 M aqueous sodium hydroxide (24 mL). An aqueous solution of oxovanadium(IV) sulfate (10 mL, 0.2 M) was added with stirring at room temperature. The solution immediately turned dark purple and became strongly acidic. During 1 h an aqueous sodium hydroxide solution (1 mL, 1 M) was added dropwise with stirring. The reaction mixture yielded dark maroon crystals of the title compound over 18 h. The product was filtered out and dried in air. Yield: 0.73 g (78.6%). The crude product was recrystallized from a 1:2 mixture of acetone and water. Anal. Found: C, 42.66; H, 3.87; N, 10.98; Cl, 7.22. Calc for $[V_2O_3C_{36}H_{36}N_8](ClO_4)_2 \cdot 2H_2O$: C, 44.78; H, 4.17; N, 11.60; Cl, 7.34.

Physical Measurements. Infrared spectra were recorded on a Hitachi 270-30 infrared spectrophotometer, UV-visible absorption spectra on a Cary 219 spectrophotometer at room temperature, and ^1H NMR spectra on a Bruker 250-MHz spectrometer at room temperature in a 1:1 mixture of $(CD_3)_2CO$ and D_2O. Magnetic susceptibilities were measured (at Monash University) down to liquid-helium temperature on an automated Faraday balance using a superconducting magnet.[12] The molar susceptibilities were corrected for ligand diamagnetism by using Pascal's constants. C, H, N, and Cl analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

X-ray Crystallography. The compound forms compact crystals. Room-temperature Weissenberg photographs showed that they belong to the triclinic system. Low-temperature diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation obtained from a graphite monochromator. An Enraf-Nonius gas-flow low-temperature device was used to cool the crystal (0.15 × 0.2 × 0.2

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Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors

atom	x	y	z	B_{eq},[a] Å^2
V1	0.02632 (3)	0.35966 (3)	0.07559 (2)	0.795 (5)
O1	−0.0881 (1)	0.3343 (1)	0.1453 (1)	1.28 (3)
O1B	0.00000	0.50000	0.00000	0.96 (3)
N10	0.2001 (1)	0.3486 (1)	−0.0112 (1)	1.00 (3)
C110	0.2525 (2)	0.4399 (2)	0.0132 (2)	1.19 (3)
N11	0.1187 (1)	0.4280 (1)	0.1643 (1)	1.00 (3)
C111	0.2176 (2)	0.4587 (2)	0.1208 (2)	1.09 (3)
C112	0.2791 (2)	0.5150 (2)	0.1690 (2)	1.52 (4)
C113	0.2354 (2)	0.5456 (2)	0.2610 (2)	1.70 (4)
C114	0.1337 (2)	0.5138 (2)	0.3056 (2)	1.56 (4)
C115	0.0787 (2)	0.4535 (2)	0.2563 (2)	1.21 (4)
C120	0.2649 (2)	0.2356 (2)	0.0154 (2)	1.30 (4)
N12	0.1143 (1)	0.2001 (1)	0.1493 (1)	1.06 (3)
C121	0.2159 (2)	0.1629 (2)	0.1099 (2)	1.01 (3)
C122	0.2732 (2)	0.0598 (2)	0.1535 (2)	1.33 (4)
C123	0.2265 (2)	−0.0049 (2)	0.2414 (2)	1.50 (4)
C124	0.1234 (2)	0.0362 (2)	0.2847 (2)	1.47 (4)
C125	0.0701 (2)	0.1375 (2)	0.2363 (2)	1.28 (4)
C130	0.1780 (2)	0.3725 (2)	−0.1211 (2)	1.21 (4)
N13	0.0094 (1)	0.2922 (1)	−0.0534 (1)	1.09 (3)
C131	0.0887 (2)	0.3051 (2)	−0.1330 (2)	1.22 (4)
C132	0.0854 (2)	0.2632 (2)	−0.2206 (2)	1.62 (4)
C133	−0.0041 (2)	0.2095 (2)	−0.2288 (2)	1.92 (4)
C134	−0.0870 (2)	0.1987 (2)	−0.1492 (2)	1.82 (4)
C135	−0.0775 (2)	0.2397 (2)	−0.0619 (2)	1.44 (4)
V2	0.51818 (3)	0.86803 (3)	0.45820 (3)	0.947 (6)
O2	0.4123 (1)	0.8679 (1)	0.3972 (1)	1.58 (3)
O2B	0.50000	1.00000	0.50000	0.91 (3)
N20	0.6805 (1)	0.8325 (1)	0.5354 (1)	1.12 (3)
C210	0.6461 (2)	0.8361 (2)	0.6445 (2)	1.27 (4)
N21	0.4702 (1)	0.7905 (1)	0.6104 (1)	1.05 (3)
C211	0.5418 (2)	0.7821 (2)	0.6818 (2)	1.21 (4)
C212	0.5156 (2)	0.7356 (2)	0.7842 (2)	1.82 (4)
C213	0.4129 (2)	0.7003 (2)	0.8151 (2)	2.10 (5)
C214	0.3375 (2)	0.7114 (2)	0.7423 (2)	1.95 (4)
C215	0.3698 (2)	0.7551 (2)	0.6406 (2)	1.44 (4)
C220	0.7458 (2)	0.7233 (2)	0.5237 (2)	1.72 (4)
N22	0.5914 (2)	0.7040 (1)	0.4326 (1)	1.25 (3)
C221	0.6922 (2)	0.6605 (2)	0.4627 (2)	1.18 (4)
C222	0.7468 (2)	0.5600 (2)	0.4389 (2)	1.64 (4)
C223	0.6946 (2)	0.5031 (2)	0.3843 (2)	2.22 (5)
C224	0.5902 (2)	0.5476 (2)	0.3533 (2)	2.36 (5)
C225	0.5411 (2)	0.6479 (2)	0.3786 (2)	1.82 (4)
C230	0.7414 (2)	0.9284 (2)	0.4833 (2)	1.58 (4)
N23	0.6367 (2)	0.9296 (2)	0.3397 (1)	1.51 (3)
C231	0.7309 (2)	0.9526 (2)	0.3692 (2)	1.74 (4)
C232	0.8115 (2)	1.0007 (2)	0.2982 (2)	2.94 (6)
C233	0.7938 (3)	1.0261 (3)	0.1960 (2)	3.70 (6)
C234	0.6988 (3)	1.0017 (2)	0.1643 (2)	3.56 (6)
C235	0.6216 (2)	0.9526 (2)	0.2383 (2)	2.42 (5)
Cl1	0.08297 (4)	0.73709 (4)	0.50466 (4)	1.302 (9)
O11	0.0229 (1)	0.6444 (1)	0.5043 (1)	2.08 (3)
O12	0.1159 (1)	0.7259 (2)	0.6070 (1)	2.28 (3)
O13	0.1791 (1)	0.7344 (2)	0.4316 (1)	2.43 (4)
O14	0.0109 (1)	0.8410 (2)	0.4774 (1)	2.47 (4)
Cl2	0.42427 (4)	0.77417 (4)	0.08466 (4)	1.576 (9)
O21	0.4927 (2)	0.6733 (2)	0.0661 (2)	2.94 (4)
O22	0.3276 (2)	0.7907 (2)	0.0292 (1)	2.90 (4)
O23	0.4837 (2)	0.8687 (2)	0.0482 (2)	4.14 (5)
O24	0.3879 (2)	0.7628 (2)	0.1913 (1)	3.84 (5)

[a] $B_{eq} = {}^1/_3(8\pi^2\sum_i\sum_j U_{ij}\bar{a}_i\bar{a}_j a_i^* a_j^*)$.

mm^3). The temperature was monitored during the experiment with a thermocouple placed in the exhaust pipe a few centimeters above the crystal. The temperature was constant within 1 K. The unit cell parameters were determined from least-squares refinement of the setting angles for 22 reflections (17.5° < θ < 21.0°). An analysis of reflection profiles provided the basis for the selection of scan type (ω-scan) and range. Intensities of three standard reflections were measured after every 10 000 s. The orientation of the crystal was checked after every 300 reflections. These measurements showed that no misalignment or deterioration had occurred during the data collection. Data reduction included correction for background, Lorentz, and polarization effects. Crystal data and a summary of experimental results are presented in Table I.

Table III. Bond Lengths (Å) and Angles (deg) in the Two Independent $[(\text{tpa})\text{VO}(\mu\text{-O})\text{VO}(\text{tpa})]^{2+}$ Ions

	i = 1	i = 2
V*i*–O*i*	1.6193 (12)	1.6123 (13)
V*i*–O*i*B	1.8045 (3)	1.8039 (3)
V*i*–N*i*0	2.2993 (14)	2.2892 (14)
V*i*–N*i*1	2.105 (2)	2.105 (2)
V*i*–N*i*2	2.1816 (14)	2.163 (2)
V*i*–N*i*3	2.113 (2)	2.109 (2)
O*i*–V*i*–O*i*B	106.36 (5)	106.71 (5)
O*i*–V*i*–N*i*0	165.84 (6)	168.00 (6)
O*i*–V*i*–N*i*1	106.24 (6)	103.63 (6)
O*i*–V*i*–N*i*2	92.08 (6)	92.74 (6)
O*i*–V*i*–N*i*3	101.12 (6)	103.08 (7)
O*i*B–V*i*–N*i*0	87.38 (4)	85.28 (4)
O*i*B–V*i*–N*i*1	86.73 (4)	88.20 (4)
O*i*B–V*i*–N*i*2	161.02 (4)	160.54 (4)
O*i*B–V*i*–N*i*3	90.17 (4)	88.71 (4)
N*i*0–V*i*–N*i*1	77.39 (5)	76.73 (5)
N*i*0–V*i*–N*i*2	74.55 (5)	75.26 (5)
N*i*0–V*i*–N*i*3	74.90 (5)	75.93 (6)
N*i*1–V*i*–N*i*2	84.74 (5)	87.89 (6)
N*i*1–V*i*–N*i*3	152.23 (6)	152.66 (6)
N*i*2–V*i*–N*i*3	90.66 (5)	85.08 (6)

The structure was solved by standard Patterson and difference Fourier methods and refined by least-squares methods, minimizing $\sum w(F_o - F_c)^2$ by using 8009 reflections that were considered observed, $F^2 > 2\sigma(F^2)$. The positions of the hydrogen atoms were shown clearly on a difference Fourier map. Positional parameters for the hydrogen atoms were also refined, and they were given a common fixed isotropic thermal parameter of 3 Å^2. A total of 643 parameters were included in the final refinement; the maximum shift was 0.076σ. Crystallographic computations were performed on a MicroVAX II computer using the Enraf-Nonius Structure Determination Package.[13] Atomic scattering factors and anomalous dispersion corrections for V, Cl, O, N, and C were taken from ref 14 and used as contained in the program system. The positional parameters for the non-hydrogen atoms are listed in Table II. Additional experimental details, anisotropic thermal parameters, positions for the hydrogen atoms, and observed and calculated structure amplitudes are provided as part of the supplementary material.

Results and Discussion

Synthesis. The (μ-oxo)bis[tris(2-pyridylmethyl)amine)oxovanadium(IV)] cation was formed spontaneously in solution from a mixture of tpa and oxovanadium(IV) sulfate. However, 1 equiv of base was added in order to avoid contamination with monomer. Quite remarkably, 2,2′-bipyridine is reported only to form monomeric green V(IV) complexes.[5c]

IR Data. In the infrared spectrum of the title compound the bands at 943 and 807 cm^{-1} are assigned to the terminal V–O stretching mode and the antisymmetric V–O stretching mode of the V–O–V moiety, respectively. Typical values for the terminal V–O stretching frequency[4,5] are about 40 cm^{-1} higher than the value observed here, suggesting that the V=O bond is influenced by the trans-N (tertiary) atom.

Description of the Structure. The compound crystallizes with one formula unit per asymmetric unit. It is remarkable that the crystal contains two centrosymmetric, crystallographically inequivalent complex cations, as the asymmetric unit contains two half binuclear cations placed with their oxygen atoms on crystallographic inversion centers.

The coordination around vanadium in the two binuclear complexes is apparent from Table III, which lists the bond lengths and angles. The molecular geometries of the tpa ligands are virtually identical in the two compounds; the coordination geometries of the cations display some small differences, as shown in Table III. The distance between vanadium and the nitrogen atom from pyridine ring 2 is longer in molecule 1 (i = 1) than in the one labeled 2. Likewise the angles O*i*–V*i*–N*i*0 and O*i*–V*i*–N*i*1 differ significantly in the two complexes.

The conformations of the tpa ligands are slightly different in the two binuclear cations, as is apparent from Figure 1. In the cation (i = 2) the pyridine planes of the tpa ligand are oriented with pyridine rings 1 and 3 virtually perpendicular to the plane defined by V*i*, O*i*, and O*i*B and pyridine ring 2 almost (6°) in

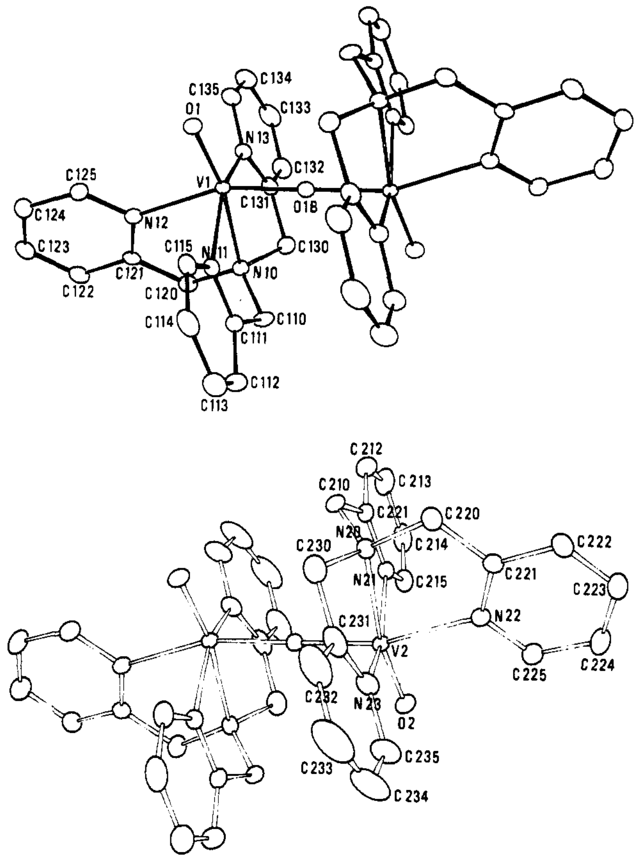

Figure 1. ORTEP drawings of the two crystallographically independent $[(\text{tpa})\text{VO}(\mu\text{-O})\text{VO}(\text{tpa})]^{2+}$ ions, illustrating the atomic labeling. The thermal ellipsoids are scaled to include 50% probabilities. The molecule with dark bonds is molecule 1 ($i = 1$), and the one with open bonds, molecule 2 ($i = 2$).

the plane. The conformation of cation 1 is less regular; the three pyridine planes make angles of 84, 13, and 87°, respectively, with the V*i*, O*i*, O*i*B plane.

The coordination around the two vanadium centers deviates significantly from octahedral geometry due to the strain in the three connected five-membered chelate rings of the coordinated tpa ligand. As a consequence, the vanadium atoms in both complexes are displaced 0.41 Å toward the oxo group relative to the plane defined by N*i*1, N*i*2, N*i*3, and O*i*B. This is in the high end of the range observed for other similar systems.[4-9]

The V=O distances of 1.6123 and 1.6193 Å agree well with the V=O bond lengths observed in other mononuclear oxovanadium(IV) complexes.

Only one other μ-oxo oxovanadium(IV) complex has been reported in the literature, but in this case the bridging system is so asymmetric that the complex is regarded as two weakly interacting five-coordinated oxovanadium(IV) species.[6]

The V–O(bridge) distance of 1.804 Å in the present structure is virtually identical with the equivalent distance in other centrosymmetric V–O–V moieties in binuclear V(III) and V(V) complexes, which previously have been characterized structurally.[4-5,7-11] It appears to be a general trend among vanadium complexes that vanadium to ligand distances are very little influenced by the formal oxidation state. More variation in the V–N distances seem to be caused by the trans ligand than by the oxidation state of vanadium. The coordination of vanadium to the pyridine nitrogen atoms in the present structure displays a pattern similar to that observed in the structures of V(III), V(IV), and V(V) complexes of 2,2′-bipyridine.[5c] The longest V–N distance, 2.294 Å, is found trans to the V=O group. It compares well with the V–N distances of 2.29–2.32 Å trans to V(V)=O groups.[5,7-11] Similarly, the V*i*–N*i*2 distance of 2.17 Å trans to the bridging oxygen atoms is significantly longer than the equivalent V*i*–N*i*2 and V*i*–N*i*3 distances.

Electronic Spectrum. The UV-vis spectrum of the title compound in a 1:1 mixture of acetonitrile and water is very unusual for an oxovanadium(IV) complex. It exhibits at least three overlapping very strong absorption bands with molar absorptions $>10^3$ M^{-1} cm^{-1} in the visible region ($\lambda_{\max}$ (ϵ): 437 (3260), 520 (6170), 568 sh). Because of their very high intensity, none of these bands are assigned as d–d bands. They can be due to μ-oxo to vanadium(IV) charge-transfer transitions or vanadium(IV) to pyridine charge transfer. The former assignement is supported by resonance Raman spectroscopy, as vibrations in the V–O–V moiety (at 804 cm^{-1}) are resonance enhanced with excitation in the band around 520 nm.[16]

Magnetic Properties. Measurements of the molar susceptibility were carried out on solid samples by using the Faraday method between 4.2 and 300 K. A tiny positive susceptibility (ca. 20×10^{-6} cgsu per V) was observed at 300 K, and this follows a Curie-like dependence down to 4.2 K. This is assumed to arise from a 1.5% contamination with a monomeric vanadyl complex. Likewise, the frozen-glass EPR spectrum only gave a very weak signal typical for a monomeric vanadyl complex. This again is attributed to a slight contamination with monomer.

These results show that the two oxovanadium(IV) centers in the title compound are very strongly antiferromagnetically coupled. When the susceptibility of the monomer impurity is subtracted from the observed values, the susceptibility due to the binuclear complex is essentially zero at all temperatures. Assuming a temperature-independent paramagnetic contribution to VO^{2+} of zero and using the Bleaney–Bowers equation for a $S = {}^1/_2$ dimer yield a lower limit for $2J$ of about -1000 cm^{-1}. This is by far the strongest coupling ever observed for a binuclear vanadium(IV) complex.

A value of -354 cm^{-1} has been reported for a dihydroxo-bridged system[17,18] with 1,4,7-triazacyclononane as the nonbridging ligand. As the unpaired electron on each oxovanadium(IV) center is situated in one of the three orbitals d_{xy}, d_{xz}, and d_{yz}, the dominating magnetic exchange pathway must be through a π orbital via oxygen and not through the σ backbone. Such an exchange pathway is known to be quite efficient in chromium(III) complexes, e.g. in the basic rhodo system ($2J = -450$ cm^{-1})[19] or in $[\text{SCN}(\text{tpa})\text{Cr-O-Cr}(\text{tpa})\text{NCS}](\text{ClO}_4)_2$ ($2J = -509$ cm^{-1}).[20]

Glerup has shown how a strong antiferromagnetic coupling in these kinds of μ-oxo systems can be explained by interactions between the ligand field states and excited charge-transfer states.[21] Assuming that a similar mechanism is operating in the present case, a singlet–triplet separation of the same order of magnitude as the singlet–heptet separation in Cr(III)–O–Cr(III) (ca. 3000 cm^{-1}) is expected.

The diamagnetism and the intense purple color of $[(\text{tpa})\text{VO}(\mu\text{-O})\text{VO}(\text{tpa})]^{2+}$ are shared by a long list of *anti*-$[\text{LMo}^{\text{V}}\text{O}(\mu\text{-O})\text{Mo}^{\text{V}}\text{OL}]^{4+}$ systems.[22]

^{1}H NMR Spectrum. The very strong antiferromagnetic coupling in the title compound allows the 250-MHz ^{1}H NMR spectrum to be recorded without any complications from the 3d^1 paramagnetic VO^{2+} centers.

Some of the signals are shifted a few parts per million compared to those of the free ligand, but no line broadening is observed. The spectrum clearly shows that the structure found in the solid state is retained in solution. Thus there are two sets of pyridyl signals (each consisting of two doublets and two triplets) with a 1:2 intensity ratio: H*i*25, 10.10 ppm, $J = 5.0$ Hz; H*i*15, H*i*35, 8.15 ppm, $J = 4.9$ Hz.

One set of the CH$_2$ signals observed at 4.34 ppm arises from equivalent protons H*i*20 showing that the molecule has a symmetry

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plane through this carbon atom, whereas the other set H*i*10, H*i*30 is split into two doublets (6.20 ppm, J = 15.7 Hz; 4.78 ppm, J = 15.8 Hz) due to their nonequivalent positions and geminal H_A,H_B coupling.

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Supplementary Material Available: Tables SI–SIV, listing details of the crystal data collection, anisotropic thermal parameters, positional parameters for the hydrogen atoms, distances, and angles, a packing diagram, and a UV–vis spectrum (6 pages); a listing of observed and calculated structure amplitudes (54 pages). Ordering information is given on any current masthead page.

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Structure and Properties of Bis(D-penicillaminato-*N*,*S*)nickelate(II) Tetrahydrate: A Monomeric Nickel Complex of D-Penicillamine, the Antidote for Nickel Toxicity

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Introduction

For some time D-penicillamine (D-H_2Pen)[1] has been in use for removing excess copper from patients with Wilson's disease.[2,3] In recent years, D-H_2Pen has also afforded promising results in the treatment of acute intoxication with other metals, especially nickel.[4–7] We report here the structure and spectral parameters of a genuine $[NiL_2]^{2-}$ complex of D-H_2Pen formed under the condition of excess drug (therapeutic level). In addition, the structural features of this complex, namely potassium bis(D-penicillaminato-*N*,*S*)nickelate(II) tetrahydrate (**1**) are compared with those of potassium bis(L-cysteinato-*N*,*S*)nickelate(II) sesquihydrate (**2**), recently reported by this group.[8] Since (a) solution studies by us as well as other groups[9–15] have demonstrated the existence of only the $[NiL_2]^{2-}$ species and (b) the complex **1** is extremely stable in aqueous and saline solutions in the pH range 6–10, it is quite possible that excess nickel is excreted from the body in this form.[16]

Experimental Section

Preparation of Compounds. D-Penicillamine was purchased from Aldrich Chemical Co. In the following preparation, all manipulations were performed under a pure dinitrogen atmosphere.

$K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$ (1). To a solution of dipotassium D-penicillaminate ($KSC(CH_3)_2CH(NH_2)COOK$), prepared from 1.0 g (6.7 mmol) of D-H_2Pen and 0.75 g (13.4 mmol) of KOH in 25 mL of 1-butanol, was added with stirring a solution of 0.4 g (1.68 mmol) of $NiCl_2\cdot 6H_2O$ in 20 mL of 3:1 1-butanol/methanol when a cloudy red solution was obtained. After 1 h of stirring, the reaction mixture was filtered to remove KCl. Next, the filtrate was heated to 50 °C and 0.5 mL of water was added to it. The clear red solution was then allowed to slowly cool and stand at room temperature for 24 h. The red crystals thus obtained were collected by filtration and dried under dinitrogen. Yield: 0.65 g (73%). Selected IR bands (KBr pellet, cm^{-1}): 3400 (s, br), 3200 (s), 2960 (s), 1595 (s), 1577 (s), 1400 (s), 1360 (s), 1135 (m), 1050 (m), 930 (m), 790 (m). Anal. Calcd for $C_{10}H_{26}N_2O_8S_2K_2Ni$: C, 23.84; H, 5.21; N, 5.56. Found: C, 23.71; H, 5.23; N, 5.70.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$ (**1**)

formula (mol wt)	$C_{10}H_{26}N_2O_8S_2K_2Ni$ (503.26)	β, deg	117.50 (3)
		V, Å^3	2139.7 (14)
T, K	130	Z	4
cryst syst	monoclinic	d_{calcd}, g cm^{-3}	1.57
space group	$P2_1$	abs coeff, μ, cm^{-1}	15.20
a, Å	10.949 (3)		
b, Å	19.292 (7)	R^a	6.48
c, Å	11.420 (5)	$R_w{}^b$	6.84

[a] $R = (\sum||F_o - F_c||)/\sum|F_o|$. [b] $R_w = \{[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrometer. Absorption spectra were monitored on a Perkin-Elmer Lambda 9 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a General Electric GN-300 (300 MHz) instrument. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

X-ray Data Collection, Structure Solution, and Refinement. Dark red blocks were obtained from a solution of **1** in moist butanol. Diffraction experiments were performed on a Siemens R3m/V machine equipped with graphite monochromator and a modified LT-1 low-temperature apparatus. Mo Kα radiation was employed. The intensities of two standard reflections, recorded after every 198 reflections, remained unchanged during the period of data collection. The structure was solved by direct methods (SHELXTL PLUS (VMS)). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions, and a riding model was used with fixed isotropic thermal parameters. A total of 4479 reflections with $F > 4\sigma(F)$ were used in the refinement (full-matrix least squares), and the data were corrected for absorption effects by the use of the program XABS.[17]

Machine parameters, crystal data, and data collection parameters are summarized in Table I. Positional parameters are listed in Table II, while selected bond distances and angles are collected in Table III. The rest of the crystallographic data have been submitted as supplementary material.

Results and Discussion

Cysteine[8,10,13,14] and other S-containing ligands[18] form $[NiL_2]^{2-}$ type of complexes with bivalent nickel in the presence of large excess of L—at lower L:Ni^{2+} ratios, the propensity of thiolato

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