lations with the cis-carbonyl, phenyl C(1), phenyl C(2,6), phenyl C(3,5), and phenyl C(4) data are respectively -1.33, -0.70, -1.01, -1.00, and -1.53. The variation in these numbers is considerably greater than the error of the calculations, and these values are also considerably different from the E_s parameter of -0.90, which has been reported for the phenyl group.[10] Thus, this method allows for the separation of steric from electronic effects by multiple measurement of the E_s parameter.

Since this method appears to be extremely useful for the measurement of E_s parameters, this study is currently being extended to determine the limits of the method. Included in this study are complexes in which the R group is a long-chain alkyl group or a polyhaloalkyl group and complexes in which the diphenylphosphino group is replaced by a 1,3,2-dioxaphosphorinane group. The results of this research will be reported in a subsequent communication.

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A Polymeric Peroxo Heteroligand Vanadate(V). Synthesis, Spectra, and Structure of $M^I[VO(O_2)(C_4H_5O_4N)]$

Sir:

Vanadium peroxo complexes are known to act as catalysts[1,2] and have been proposed as one of the model systems for the biochemistry of vanadium.[3,4] Although recently recognized as an essential element for mammals,[5] the vanadium function remains unknown.[6,7] Some of the peroxo heteroligand vanadates(V) have shown antitumor activity against L1210 murine leukemia, and the biological activity of these complexes[4] strongly depends upon the heteroligands. We have been interested in the peroxovanadates(V) before[8] and have now decided to investigate such complexes containing amino carboxylato or polycarboxylato ligands, to find out some general trends regarding the influence of the heteroligand on the mode of coordination, the bond distances and the bond angles, the charge-transfer bands, the stability, and the reactivity of coordinated peroxides.

We report now our work with the iminodiacetic acid, $C_4H_7NO_4$, which reacts with V(V) in the presence of hydrogen peroxide to form crystalline compounds[9] of the formula $M^I[VO(O_2)IDA]$ (M^I = K, NH_4; IDA = $[C_4H_5NO_4]^{2-}$). Unlike other analogous oxo peroxo heteroligand vanadates[8,10] these complexes crystallize anhydrous from the aqueous solutions and are remarkably stable toward decomposition. Aqueous solutions of the compounds show a band centered at 420 nm, as observed for some other monoperoxovanadates.[11] This absorption remains constant over a wide pH range of 2-8 but shifts at pH ≤1 to 450-460 nm, and a new band appears at 280 nm. In such acid solutions the complexes obviously rearrange, but the peroxo group remains coordinated to the metal.[11-13] In aqueous solutions the potassium and the ammonium complexes show identical cyclic voltammograms with characteristic irreversible cathodic and anodic peaks. Study of the electrochemical behavior of these complexes is in progress. The ammonium complex has shown marginal antitumor activity against L1210 murine leukemia.[4]

The significant features in the IR spectra of the potassium and the ammonium compounds involve bands of coordinated IDA, peroxo frequencies, and V=O stretchings. The NH stretchings of the three-coordinated ligand shift to higher energy, and a sharp strong band occurs at 3215 cm^{-1} as compared to strong absorption found at 3100 cm^{-1} in the acid. The coordinated carboxylato groups cause a distinct shift of antisymmetric CO stretchings,[14] which occur as strong bands at 1680 to 1660 and 1560 cm^{-1}. Very strong absorption in addition to the organic ligand bands is observed in the region of 980 and 920 cm^{-1} and assigned to the V=O and O—O stretchings, respectively.[8,15]

Only a few well-refined X-ray structure analyses of peroxovanadates were reported.[1,16-19] The vanadium is seven-coordinated in all but one,[17] which is described as a distorted pentagonal pyramid. The distorted pentagonal bipyramid used as model in the other four structures invariably shows V=O on an apical position and the peroxo group(s) in the equatorial planes. Such seven-coordination is also common in peroxo complexes of Mo(VI)[21] and Ti(IV),[22] while Nb(V) prefers eight-coordinated dodecahedral structures.[23] The complexes are usually monomeric, and a few dimeric ones exist.[16,24] The coordination of the peroxo group, the O-O distance, and the MOO bond angles depend upon the metal ion, the symmetry of the ligand field, and the heteroligand. With only little sufficiently precise structural data available, some common trends expected within the family of the peroxometal coplexes cannot be detected. More accurate structure determinations of these compounds are needed, and we therefore looked for conditions to prepare crystals of $M[VO(O_2)IDA]$ adequate for X-ray structure analysis. The potassium salt precipitated invariably in small irregular crystal clusters. Acceptable crystals were obtained of $NH_4[VO(O_2)IDA]$, and we now report the structure of this compound, which represents the first polymeric structure of a transition-metal peroxo heteroligand complex.

X-ray diffraction data were collected on a crystal grown from aqueous solutions,[25] and the structure was solved by standard

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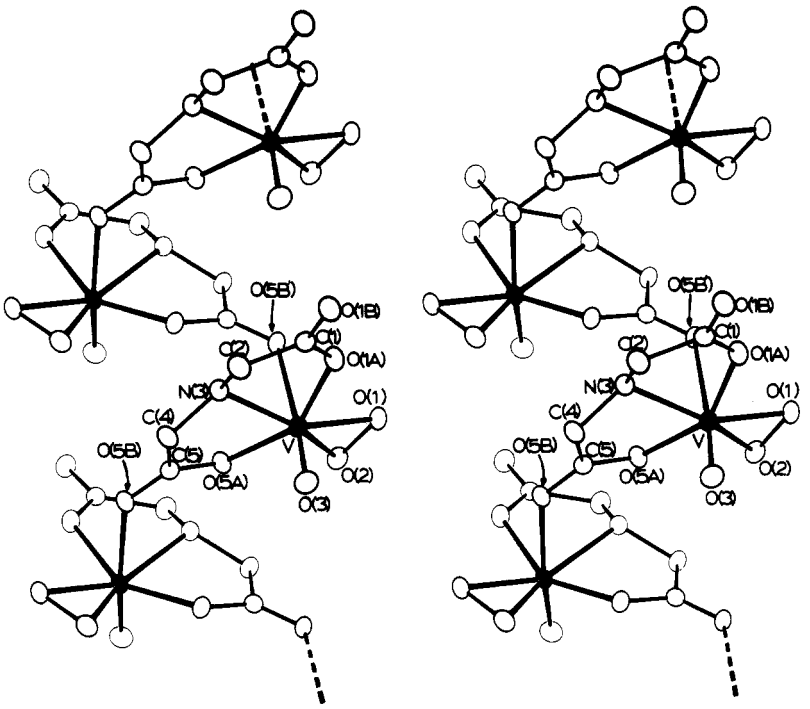

Figure 1. Stereoview of the anionic chains present in $NH_4[VO(O_2IDA]$. Principal bond distances (Å): O(1)–O(2) = 1.435 (5); V–O(1) = 1.876 (3); V–O(2) = 1.886 (3); V–O(3) = 1.587 (3); V–O(1A) = 2.008 (3); V–O(5A) = 2.023 (3); V–N = 2.138 (4); V–O(5B) = 2.375 (3). Selected bond angles (deg): O(1)–V–O(2) = 44.85 (15); V–O(1)–O(2) = 67.9 (2); V–O(2)–O(1) = 67.2 (2); O(3)–V–O(5B) = 175.35 (15).

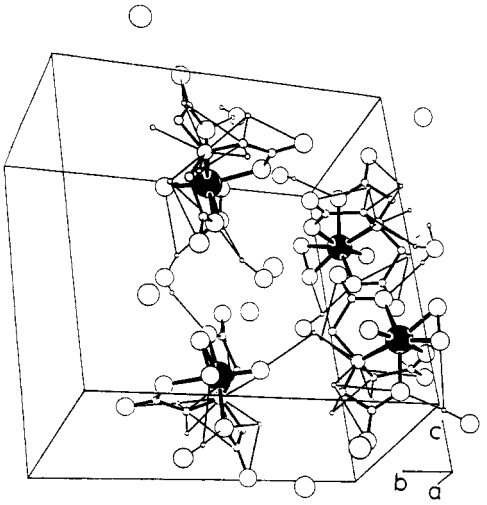

Figure 2. Ionic packing of $NH_4[VO(O_2)IDA]$ in the unit cell. Ammonium cations connect adjacent anion chains via hydrogen bonds to two coordinated oxygens, one peroxo group oxygen and a noncoordinated carboxylato oxygen.

Patterson and Fourier procedures.[26,27] Crystal data: space group $P2_12_12_1$, $Z = 4$, $a = 6.145$ (2) Å, $b = 8.408$ (2) Å, $c = 17.268$ (3) Å, 1076 reflections; $R = 2.8\%$, $R_w = 2.8\%$. Figure 1 shows the stereoview of four units of the anion chain, and Figure 2, the ionic packing in the unit cell. The structure consists of $[VO(O_2)IDA]^-$ polyhedra linked by relatively weak, 2.375 (3) Å, interionic V–O bonds to form a polymeric chain. The bridging occurs via a carboxylato group (V–O(5B)–C(5)–O(5A)–V), where the oxygen farthest from vanadium occupies the apical position (2.375 (3) Å), trans to the relatively short (1.587 (3) Å) oxovanadium bond. The other oxygen (shorter V–O bond of 2.023 (3) Å) is a part of the pentagonal plane. The two C–O distances within the bridging carboxylato group remain unsymmetrical (C(5)–O(5B) = 1.226 (5) Å; C(5)–O(5A) = 1.290 (5) Å), within the expected bond length range. The possibility of an oxo, a peroxo, or another carboxylato bridge is excluded because of the lack of the intermolecular V–O contacts (e.g., V′–O(5A) = 3.635 Å). NH_4 cations connect anion chains via hydrogen bonds to ligand oxygen atoms O(1A), O(1B), and O(1) of two adjacent chains. The vanadium environment can be viewed in two ways. The complex polyhedron can be regarded as a distorted pentagonal bipyramid, with V=O and intermolecular V—O at the apical positions and with an equatorially coordinated peroxo group, positioned trans to the coordinated nitrogen, with two carboxylato oxygens closing the pentagonal ring. The vanadium atom is 0.28 Å above the ring plane toward the vanadyl oxygen and the V–O bond at the other apex is considerably elongated: 2.375 (3) Å. In this view the structure resembles that of the oxodiperoxoamminevanadate(V)[17] ion, except that the latter is only six-coordinated without the additional seventh bond that creates the polymeric link. Another view of the structure is a distorted rectangular bipyramid, formed by coordinated carboxylato oxygens and the oxo group in the rectangular plane, with the peroxo group at one apex and nitrogen at the other. The vanadium atom is again displaced 0.28 Å out of the rectangular base toward the peroxo group, and the V–N bond is slightly elongated compared to the other end of the axis. The peroxo coordination is only slightly unsymmetrical, 1.876 (3) and 1.886 (3) Å, possibly due to hydrogen bonding. The V–O bond length of 1.587 (3) Å falls in

(25) Crystal dimensions (in mm of faces from centroid): (100) 0.125, ($\bar{1}$00) 0.125, (010) 0.075, (0$\bar{1}$0) 0.075, (001) 0.125, (00$\bar{1}$) 0.125. Mo radiation 0.71073 Å) was used. Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-cycle CAD-4 diffractometer. The principal programs used were previously described.[26] The row intensity data were corrected for Lorenz–Polarization and absorption effects (the absorption coefficient was 12.0). Of the 1398 independent intensities, 1076 were used ($\geq 3\sigma$) in the final refinement of the structural parameters. A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier synthesis. Full-matrix least-square refinement was carried out.[27] Anisotropic temperature factors were introduced for the non-hydrogen atoms, and further Fourier difference functions permitted location of the hydrogen atoms. The test for the chirality was done. A final Fourier difference map was featureless. Listings of positional parameters, thermal parameters, and bond distances and angles are available as supplementary material.

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the range of 1.58–1.62 Å observed before for analogous complexes. The O=V—O angle of 175.4° is nearest to the ideal 180° observed in vanadium peroxo complexes of pentagonal-bipyramidal stereochemistry so far, where deformation up to 164.4° were found.[19] The OVO and VOO angles of the coordinated peroxo group are almost symmetrical: 67.2 and 67.9°. The peroxo O–O bond of 1.435 (4) Å is definitely shorter than in hydrogen peroxide (1.47 ± 0.02) or ionic peroxides (1.49 ± 0.04),[28] and also shorter than in the diperoxo vanadates.[16,17,19,20] It agrees well, however, with the bond length found in the monoperoxo complex of formula $[VO(O_2)PicH_2O]$, reported recently,[1] and is essentially the same as that in $K_2[VO(O_2)NTA]\cdot 2H_2O$.[24]

The stability of these complexes, which have exhibited no sign of decomposition on standing in air for more than 1 year, seems to illustrate the ability of a specific heteroligand, in this case iminodiacetate, to stabilize the coordinated peroxo group in the ligand spheres of vanadium(V), but it may be due also to the polymeric nature of the complex. Investigations in this area are continuing.

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Registry No. $NH_4[VO(O_2)IDA]$, 95533-38-3; $K[VO(O_2)IDA]$, 95533-36-1.

Supplementary Material Available: Listings of positional parameters, bond distances and angles, and thermal parameters (Tables I-III) (3 pages). Ordering information is given on any current masthead page.

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Nature of the Terbium(III) Excitation Band Observed near 300 nm in Certain Nucleotide or Nucleic Acid Complexes

Sir:

It is known that Tb(III) can be used as a luminescence probe for the study of RNA,[1,2] DNA,[3,4] and ribosomes.[5] At micromolar concentrations Tb(III) in buffer exhibits no detectable emission, but the luminescence intensity increases by several orders of magnitude upon formation of the Tb/nucleic acid complex. It was learned that certain aromatic residues (primarily guanine-containing nucleotides) would sensitize the Tb(III) emission, and consequently luminescence methods based on this energy transfer were developed to monitor the chemical modification of guanine residues.[6] This latter application is of extreme importance to the study of how mutagenic agents interest with DNA. When nucleic acids are treated with alkylating agents (all of which are known mutagens), substitution at the 7-position of guanine ordinarily results.[7] However, Ringer has shown that 7-substituted guanine residues are incapable of sensitizing Tb(III) emission,[8] even though the triplet levels of guanosine and 7-methylguanosine lie at exactly the same energy.[9]

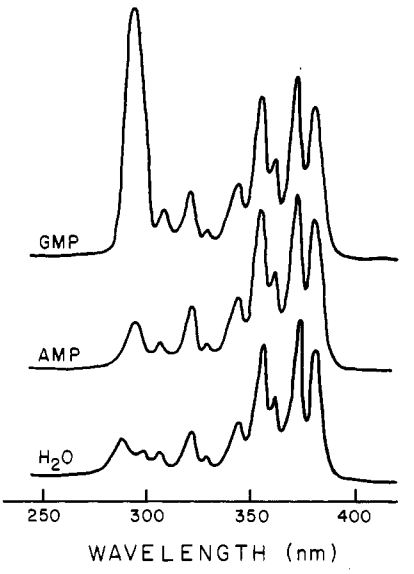

Figure 1. Tb(III) excitation spectra obtained for $Tb(EDTA)(H_2O)_3$ (lower trace), Tb(EDTA)(AMP) (middle trace), and Tb(EDTA)(GMP) (upper trace). The data were obtained while monitoring the $^5D_4 \rightarrow {}^7F_5$ emission band of Tb(III) at 545 nm and are shown in arbitrary units.

All the studies that have been reported indicate that Tb(III) emission is sensitized by an aromatic base, which is either guanine or xanthine. This sensitization process is characterized by the presence of a relatively sharp, strong Tb(III) excitation peak appearing between 290 and 310 nm. This feature is markedly different than the excitation spectra (observed between 240 and 300 nm) characteristic of energy transfer from the nucleotide aromatic residue to the Tb(III) ion.[10] The 300-nm peak is unusual since none of the nucleotides exhibit appreciable absorption within this wavelength region. While the most important feature associated with the Tb(III) emission studies is that of enhanced emission, little evidence exists which indicates that the origin of the 300-nm excitation peak is due to any sensitization process. The question to be answered is therefore: What is the mechanism leading to the enhancement of the 300-nm excitation band in the Tb(III) nucleic acid complexes? Recent work concerning the luminescence properties of Tb(III) complexes with nucleotide and polymer ligands has enabled us to answer this question.

While it is accepted that lanthanide/nucleotide complexes may serve as useful model systems for the characterization of lanthanide/nucleic acid complexes,[3,11,12] the solubility of these complexes is low. We have found during the course of our investigations that ternary Tb(EDTA)(nucleotide) complexes are far easier to work with and provide the same type of spectroscopic information as do the Tb(nucleotide) complexes. The advantages associated with using these ternary complexes are threefold: (1) the complexes are stable over much wider pH ranges; (2) no apparent upper limit on complex solubility exists; (3) the Tb(III)/nucleotide stoichiometry is limited to that of 1:1 complexes.

The Tb(III) excitation peaks between 275 and 450 nm correspond to f–f absorption bands, and Tb(III) spectra obtained within this region (at 15 mM Tb(III) levels) for Tb(EDTA)(AMP) and Tb(EDTA)(GMP) complexes exhibited many analogous features.[13] The main difference noted in the spectra was the presence of a major excitation peak at 310 nm for the GMP complex and the weakness of that feature in the other excitation spectra. The Tb(EDTA)(7-Me-GMP) complex was not found to exhibit a

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