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]

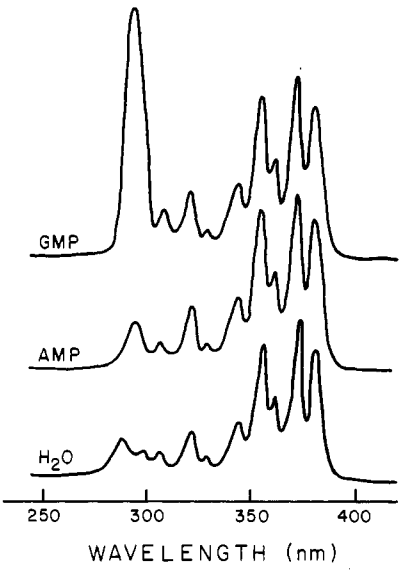

Figure 1. Tb(III) excitation spectra obtained for $Tb(EDTA)(H_2O)_3$ (lower trace), Tb(EDTA)(AMP) (middle trace), and Tb(EDTA)(GMP) (upper trace). The data were obtained while monitoring the $^5D_4 \rightarrow {}^7F_5$ emission band of Tb(III) at 545 nm and are shown in arbitrary units.

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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strong excitation peak at 310 nm. A substantial inner filter effect was observed from a study of the concentration dependence of the excitation spectra. The excitation maximum of the Tb(EDTA)(GMP) complex shifts to lower wavelengths as its concentration is lowered but eventually stabilizes at 293 nm at a Tb(III) concentration of approximately 0.1 mM. This inner filter effect results from the residual absorption of the nucleotide base, but at 0.1 mM nucleotide concentrations the solution absorbance near 300 nm was less than 0.05. Examples of these limiting excitations are provided in Figure 1 for Tb(EDTA)(AMP) and Tb(EDTA)(GMP), as well as the corresponding spectrum for simple Tb(EDTA).[14] It is important to note that the residual absorptions of GMP and AMP between 290 and 310 nm are not significantly different.

One other difference between the Tb(EDTA)(AMP) and Tb(EDTA)(GMP) complexes was noted. Essentially no quenching of Tb(EDTA)(AMP) emission was obtained with use of Eu(EDTA)(AMP) as a quencher, but significant quenching was observed when Eu(EDTA)(GMP) was used to quench Tb(EDTA)(GMP) emission. It has been shown that Tb–Eu energy transfer can be used as a means to study the self-association of lanthanide complexes.[15] These observations suggest that the GMP complexes are self-associated much more extensively than are the AMP complexes.

It is known that the base pairing of guanine is different than that of the other common nucleotides and that this particular compound forms a variety of unique ordered structures.[16] The stacking of GMP is normally observed at concentrations higher than those used in the present work, but complexation of the phosphate group by the lanthanide ion could reduce the influence of this group on the ordering abilities of the aromatic residues. Since AMP does not form the same ordered structures, it is possible that observation of the unique excitation peak might require that the Tb(III) ion exist as part of a polymeric structure. Support for this conclusion is the observation that Tb(EDTA)(7-Me-GMP) does not exhibit a strong excitation band in the 290–310-nm region, a result undoubtably dictated by the different stacking ability of this ligand.[17]

To test this hypothesis, the excitation spectra of a series of Tb(polymer) complexes were obtained. These compounds were chosen so that no aromatic groups of any kind would be present, but where well-defined Tb(III) binding sites had been identified.[18] The spectra are shown in Figure 2.

It is immediately apparent from Figure 2 that a Tb(III) excitation peak at 293 nm is observable in polymers that lack any aromatic residues. It is therefore certain that this band must be an intrinsic Tb(III) absorption. The variability in the intensity of the band is also evident in Figure 2 when one compares the intensity of the 293-nm band to those of the other Tb(III) excitation peaks noted at longer wavelengths. This observation suggests that the intensity effect is extremely dependent on details of the Tb(III) coordination sphere.

Further probing of the Tb(III) photophysics was performed through studies of the luminescence lifetimes, as observed in the various polymer complexes. An interesting correlation was noted between the intensity of the 293-nm band and the Tb(III) emission lifetime. A short Tb(III) luminescence lifetime was observed for the Tb/CMC complex (490 μs), while the Tb/polyacrylate and Tb/heparin complexes exhibited intermediate lifetimes of 680 and 650 μs, respectively. Since the lifetime is roughly determined by the number of water molecules coordinated to the Tb(III) ion,[19]

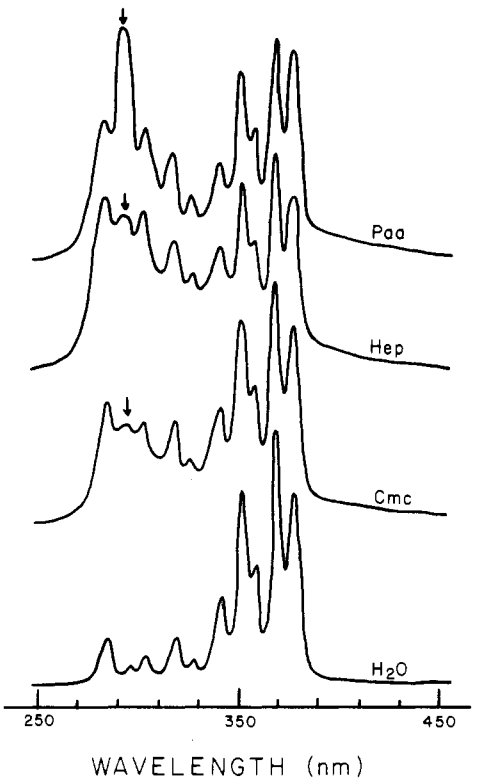

Figure 2. Tb(III) excitation spectra obtained for aqueous Tb(III), Tb/carboxymethyl cellulose, Tb/heparin, and Tb/polyacrylate. The position of the hypersensitive Tb(III) band is marked in each spectrum by an arrow. While the data are shown in purely arbitrary units, one may observe the ratio of the 293-nm band to those found at 350–380 nm to deduce a measure of the intensification of the 293-nm band.

it is possible that the largest degree of enhancement of the 293-nm excitation band takes place when the Tb(III) ion is bound at a site that is deep within the biopolymer.

Since the intensity of the Tb(III) absorption band exhibits such a drastic geometrical dependence, one would predict that the transition should be hypersensitive in nature. Hypersensitive transitions of this type are well-known for lanthanide ions[20] and in many cases correspond to transitions characterized by $\Delta J = 2$. Carnall and co-workers have provided the only assignments for the Tb(III) absorption bands observed in this region.[21,22] According to this analysis, the Tb(III) peak at 303 nm corresponds to the $^7F_6 \rightarrow {}^5H_6$ absorption, the 295-nm peak is the $^7F_6 \rightarrow {}^5H_5$ absorption, and the 286-nm peak is the $^7F_6 \rightarrow {}^5F_5$ absorption. All of these peaks can be identified in the excitation spectra of every Tb(III) compound described in the present work, and the anomalous peak at 293 nm does not correspond to any of these. However, the crystal field calculation of Carnall predicts the presence of a $^7F_6 \rightarrow {}^5H_4$ absorption at 291 nm, a transition that was not observed due to its very low intensity.[22] However, this particular band would correspond to a $\Delta J = 2$ band and thus would fit within the generally accepted view of hypersensitive transitions.[20]

We therefore conclude that the anomalous Tb(III) excitation band observed at 293 nm corresponds to the $^7F_6 \rightarrow {}^5H_4$ absorption. In monomeric Tb(III) compounds this band is too weak to be observed but in certain polymeric environments becomes strongly allowed. While the exact relation between structure and peak intensity is not clear at the present time, it is clear that intramolecular energy transfer from ligand to metal is not the origin of the 293-nm Tb(III) excitation peak in nucleotide or nucleic acid complexes. The ability of the Tb(EDTA)(nucleotide) com-

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plexes to serve as models for Tb(nucleic acid) complexes is evident in the similarity of their spectral properties. The ordering properties associated with guanine residues provide the unique environment that leads to the observation of a strong Tb(III) excitation feature between 290 and 310 nm, the exact energy of which depends on an inner filter effect that is related to base absorption. Other nucleotide bases do not order in the same fashion and hence do not provide the necessary environment required to intensify the $^7F_6 \rightarrow {}^5H_4$ absorption.

A final point concerns the fact that in simple Tb(nucleotide) complexes one may observe conventional energy transfer from the aromatic residues to the Tb(III) ion,[10] while in the Tb(EDTA)(nucleotide) compounds such transfer is not observed. Such a situation would arise if the stereochemical constraints of the ternary complex were such that Forster-type energy transfer could not occur. For example, a 90° rotation of the aromatic residue could result in an unfavorable geometry for which the energy-transfer process could not take place. We are probing such possibilities at the present time through chiroptical techniques. It is clear, however, that the nature of the intrinsic Tb(III) excitation bands does not depend on this latter geometrical constraint.

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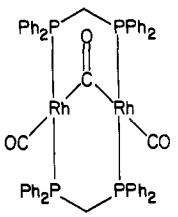
Structural Characterization of the Non-A-frame Complex Tricarbonylbis(bis(diphenylphosphino)methane)dirhodium, $Rh_2(CO)_3(dppm)_2$

Sir:

The complex $Rh_2(CO)_3(dppm)_2$ (**1**; dppm = bis(diphenylphosphino)methane), was first reported in 1980[1] and was assigned the A-frame structure I on the basis of spectroscopic data and



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reaction chemistry. The spectroscopic data included carbonyl stretches at 1940, 1920, and 1835 cm^{-1} and a ^{31}P NMR spectrum that showed a complex but symmetric pattern, indicating equivalence of the phosphorus donor ligands. The spectrum was characteristic of other Rh_2P_4 A-frame structures[2] and symmetric M_2X_4 systems in general.[3,4] In addition, protonation of **1** led to

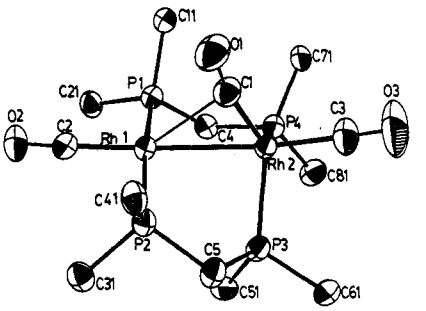
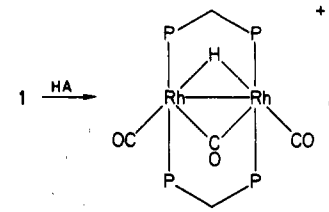


Figure 1. Perspective view of the inner coordination geometry of $[Rh_2(CO)_3(dppm)_2]$ (**1**) in which the phenyl rings have been omitted.

formation of $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2]^+A^-$ (eq 1), which was characterized by an X-ray structural study.[1,5]



(1)

An interesting feature of the spectroscopic data reported for **1** was the observation of only a single resonance for the methylene protons of the dppm ligand. This observation contrasted with ^1H NMR spectra usually seen for A-frame molecules in which two separate resonances for the dppm methylene protons occur[2] and suggested that **1** was fluxional. In the present paper, we report that complex **1** is indeed fluxional and, more importantly, that it possesses a distinctly non-A-frame structure.

The complex $Rh_2(CO)_3(dppm)_2$ (**1**) was prepared and characterized as previously described.[1,5] NMR data were recorded on a Bruker WH-400 spectrometer at 400 MHz for ^1H and at 162 MHz for ^{31}P with samples for the ^1H and ^{31}P NMR experiments in 5- and 10-mm tubes, respectively, flame sealed under vacuum or CO. Dark red-orange crystals suitable for a single-crystal X-ray study were grown from a saturated acetone-d_6 solution of the complex.[6] The X-ray intensity data were corrected for Lorentz, polarization, and background effects, after which an empirical absorption correction (μ_{Mo} = 8.75 cm^{-1}) was applied. The structure was solved by conventional heavy-atom techniques. In the final refinements, all non-hydrogen atoms were refined according to an anisotropic thermal model and all hydrogens were placed in fixed positions, assuming d(C–H) of 0.95 Å and fixed isotropic thermal parameters of 6.0 $Å^2$. This refinement of 559 variables and 5363 observations led to convergence with R and R' of 0.030 and 0.042, respectively. The final difference Fourier revealed no significant features, with the highest residual peak being 0.65 e/$Å^3$. The values of the atomic scattering factors used in the calculations were taken from the usual tabulations, and the effects of anomalous dispersion were included.[7] Tables of final refined positional and anisotropic thermal parameters, observed

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(6) Crystallographic data for $[Rh_2(CO)_3(dppm)_2]$ (**1**): fw 1058.6; monoclinic space group $P2_1/a$; a = 19.070 (5) Å; b = 12.145 (3) Å; c = 20.223 (4) Å; β, 94.88 (2)°; V = 4656 $Å^3$; Z = 4; calcd density 1.51 g cm^{-3}; temp 23 °C; cryst dimens 0.64 × 0.43 × 0.29 mm. Data for intensity measurements: Enraf-Nonius CAD4 diffractometer; Mo Kα (λ = 0.71073 Å); graphite crystal monochromator; ω–2θ scan technique for 4° ≤ 2θ ≤ 46°; octants measured, ±h, +k,+l; final no. of parameters varied, 559; no. of reflections used in least-squares refinement ($I > 3\sigma(I)$), 5363; p = 0.05; R = 0.0304; R_w = 0.0420; goodness of fit, 1.633. All calculations were carried out on a PDP 11/23 computer using the Enraf-Nonius CAD 4-SDP programs and TEXRAY version of Johnson's ORTEP plotting program. In data collection, equivalent reflections other than ±h,k,0 were not measured. The ±h,k,0 reflections were averaged prior to structural refinements.
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