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Raman Spectroscopic Evidence for Side-On Binding of Peroxide Ion to Fe^{III}(edta)

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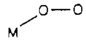
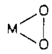
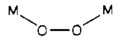
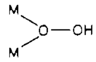
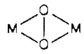
Resonance Raman spectra of the complex of Fe^{III}–ethylenediaminetetraacetate with hydrogen peroxide have been obtained in the region of the peroxidic O–O stretching vibration that occurs at 815 cm^{-1} in frozen solution. When the complex was prepared from nearly neat, mixed-isotope hydrogen peroxide, $H_2{}^{16}O^{18}O$, a single O–O vibration was observed at 794 cm^{-1}. This observation establishes that the two oxygen atoms of the bound peroxide are equivalent and that the peroxide is ligated in an η^2 side-on configuration in this mononuclear complex. The absence of any shift in ν(O–O) when the complex was prepared in D_2O solvent provides further support for the side-on Fe(O–O) geometry and rules out the alternative η^1 end-on Fe–OOH configuration. In contrast, ν(O–O) of free hydrogen peroxide in the frozen state occurs at 877 cm^{-1} in H_2O and at 879 cm^{-1} in D_2O. The 2-cm^{-1} upshift in D_2O is similar to that observed previously with oxyhemerythrin and appears to be characteristic of a hydrogen-bonded or protonated peroxide species.

Introduction

The bonding of dioxygen to transition-metal complexes has been of interest for some time because of the biological and industrial importance of oxygen activation by metals.[2] The common modes of dioxygen binding to metal ions are illustrated in Table I. In mononuclear superoxo complexes, η^1 (end-on) geometries predominate, whereas η^2 (side-on) structures are favored for mononuclear peroxides. In binuclear complexes, $\eta^1{:}\eta^1$ is the most common geometry for both peroxo and superoxo species, but $\eta^2{:}\eta^2$ coordination has also been observed.[3,4]

Information on the electronic structure and binding geometry in metal–dioxygen complexes can be obtained from the O–O stretching vibration. The frequency of this vibration, ν(O–O), is indicative of the O–O bond order,[5] with bands in the 1030–1180-cm^{-1} region being characteristic of superoxides and those in the 750–950-cm^{-1} region being diagnostic of peroxides.[6] The splitting and shift in ν(O–O) upon substitution of the bound dioxygen with an asymmetrically labeled isotope, i.e., $^{16}O^{18}O$, can provide definitive evidence for an η^1 or η^2 type structure.[7] In a mononuclear complex of type η^1, $\nu(^{16}O–^{18}O)$ shifts down in energy relative to $\nu(^{16}O–^{16}O)$ and is split into two closely spaced bands of equal intensity reflecting the two species that result from metal coordination to the isotopically distinct oxygens atoms. In a mononuclear complex of type η^2, ν(O–O) also shifts down in energy, but yields only a single vibrational component. Examples of these two cases are seen for the η^1 ferric peroxide complex of oxyhemerythrin [$\nu(^{16}O–^{16}O)$ at 845 cm^{-1}; $\nu(^{16}O–^{18}O)$ at 825 and 818 cm^{-1}][8] and for the η^2 matrix-isolated complex derived from the reaction of Fe vapor with O_2 [$\nu(^{16}O–^{16}O)$ at 946 cm^{-1}; $\nu(^{16}O–^{18}O)$ at 931 cm^{-1}].[9]

Table I. Experimentally Observed Modes of Dioxygen Binding in Metal Complexes

structure type	dioxygen coordination[a]	dioxygen classification[b]
	η^1	superoxo
	η^2	peroxo
	$\eta^1{:}\eta^1$	superoxo/peroxo
	η^1	peroxo
	$\eta^2{:}\eta^2$	

[a] Reference 3. [b] Reference 4.

The purpose of the present study is to determine the mode of dioxygen binding in the purple complex formed from the reaction of excess hydrogen peroxide with Fe^{III}(edta) in alkaline solution. Previous studies have shown that the stoichiometry of the formation of the purple complex is 1:1 in Fe(edta) and peroxide, that the iron is fully paramagnetic high-spin Fe(III), and that the complex is best formulated as $[Fe^{III}(edta)O_2]^{3-}$ or some stoichiometric equivalent.[10] Although η^2 side-on binding of dioxygen is more likely for a mononuclear peroxide complex (Table I) and has been suggested as such by Bull et al.,[11] NMR proton relaxation studies have been interpreted as favoring an η^1 end-on, protonated structure for the Fe(edta)–peroxo complex.[12] A resolution of this controversy is of interest in view of the potential role of Fe^{III}(edta) complexes with hydroperoxides as model systems for nonheme-iron-containing oxygenases[13] and respiratory proteins such as hemerythrin.[14]

The Fe(edta)–peroxo complex is amenable to study by resonance Raman spectroscopy, and a vibration at 824 cm^{-1} has been identified as the O–O stretch of the bound peroxo group.[15] Further vibrational characterization has now been made possible through the availability of $H_2{}^{16}O^{18}O$ prepared as a nearly neat reagent from an $H^{18}OF$ intermediate.[16] Earlier vibrational spectroscopic studies with hemerythrin and matrix-isolated $Fe(O_2)$ with mixed isotopes of dioxygen were complicated by using a statistical mixture of $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{18}O^{18}O$ species.[8,9] A neat sample of gaseous $^{16}O^{18}O$ was first used to elucidate the η^1 binding of dioxygen in oxyhemoglobin.[17] In the present study,

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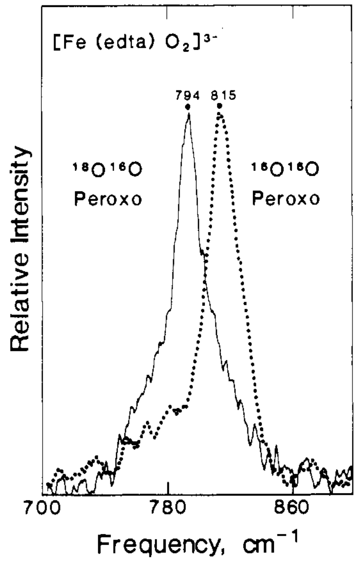

Figure 1. Resonance Raman spectrum of $[Fe(edta)O_2]^{3-}$ prepared from $H_2{}^{18}O^{16}O$ (—) or $H_2{}^{16}O^{16}O$ (- - -). Samples contained 50 mM Fe and a 3-fold excess of H_2O_2. Spectra were obtained from samples in capillaries at 90 K with 514.5-nm excitation (100 mW at the sample) and a slit width of 5 cm^{-1}. A total of 10 scans of the $^{16}O^{16}O$-containing sample were collected at 1 cm^{-1}/s and subjected to a 25-point smooth. Data for the $^{16}O^{18}O$-containing sample were collected at 0.5 cm^{-1}/s, 18 scans, and given a 25-point smooth.

a similarly neat sample of mixed-isotope hydrogen peroxide has enabled us to determine the mode of peroxo coordination to Fe^{III}(edta).

Experimental Section

$NaFe(edta){\cdot}3H_2O$ was prepared by mixing a solution of 250 mM $FeCl_3{\cdot}6H_2O$ with a 3-fold excess of NaOH and an equimolar amount of Na_2H_2(edta), heating for 10 min at 80–90°, and slowly evaporating to yield yellow-brown crystals.[18] The peroxo complex, $[Fe(edta)O_2]^{3-}$, was prepared by dissolving $NaFe(edta){\cdot}3H_2O$ in 1 M Na_2CO_3 followed by the addition of 30% H_2O_2 (Sigma) to give a solution 50 mM in Fe and 150–200 mM in peroxide with a pH between 9.5 and 10.5. The resulting purple solution had the expected absorption maximum at 520 nm[10] and was stable for about 1 h at 4 °C. $[Fe(edta)O_2]^{3-}$ was also prepared in deuteriated solvent by dissolving $NaFe(edta){\cdot}3H_2O$ in 1 M Na_2CO_3 in D_2O (Aldrich 99.8 atom % D) followed by the addition of 30% H_2O_2 in H_2O. The isotopic composition of the final solution was 97% deuterium and 3% hydrogen.

Isotopically labeled hypofluorous acid, $H^{18}OF$, was prepared by reacting F_2 with $H_2{}^{18}O$ ice (Norsk Hydro, 99+ atom % ^{18}O) as described previously.[16] The labeled $H^{18}OF$ was then transferred into $H_2{}^{16}O$ water yielding a solution 0.3 M in $H_2{}^{16}O^{18}O$ and 0.5 M in HF, which was frozen to minimize further decomposition. This material was later reacted with $NaFe(edta){\cdot}3H_2O$ as described above to produce the mixed isotope peroxide complex. The 1 M Na_2CO_3 was adequate to neutralize the HF and maintain the final solution above pH 9 in the region of maximal stability for the peroxo complex.[12]

Resonance Raman spectra were recorded on a computer-interfaced Jarrell-Ash spectrophotometer[19] equipped with a Spectra-Physics 164-05 (Ar) ion laser, a Spectra-Physics 2025-11 Kr ion laser, an RCA C31034A photomultiplier tube, and an ORTEC Model 9302 amplifier/discriminator. Samples studied at 15 K were directly frozen onto a gold-plated copper cold finger in a closed-cycle helium Displex (Air Products). Samples at 90 K were frozen either directly on an aluminum sample holder attached to a cold finger or inside a glass capillary inserted into a copper cold finger,[20] which was immersed in a Dewar cooled with liquid N_2. The integrity of samples at ~278 K was maintained by flowing the solutions in capillary tubing through a chilled bath.[21] Data from frozen samples were collected in a 150° backscattering geometry, whereas 90° scattering was used on cooled solution samples. Isotope comparisons were carried out on spectra collected under identical conditions and acquired in sequential order. Reported peak frequencies are accurate to ±0.5 cm^{-1}.

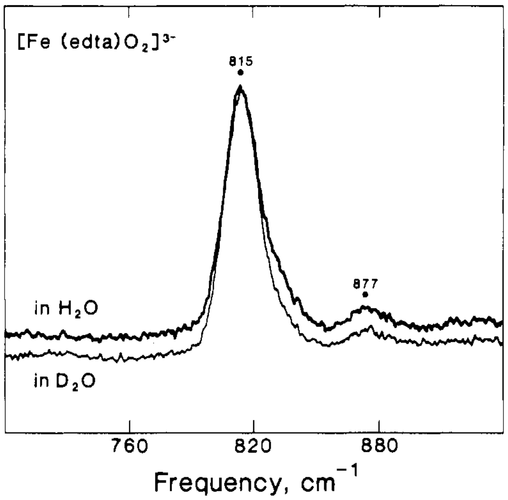

Figure 2. Resonance Raman spectrum of $[Fe(edta)O_2]^{3-}$ in H_2O and in D_2O. Samples (50 mM in Fe) were prepared by using a 4-fold excess of H_2O_2. Spectra were obtained at 15 K with 514.5-nm excitation (60 mW at the sample) and a slit width of 5 cm^{-1}. Six scans were collected at 0.5 cm^{-1}/s followed by a 13-point smooth.

Results

In the previously reported resonance Raman spectrum of $[Fe(edta)O_2]^{3-}$, peaks were observed at 472 and 824 cm^{-1} by using a spinning sample at room temperature.[15] The 824-cm^{-1} band was assigned as the O–O stretch of a bound peroxide on the basis of its frequency and its enhancement profile tracking the 520-nm $O_2{}^{2-} \rightarrow Fe^{III}$ charge-transfer band.[15] Lowering the temperature to 90 K gives increased sample stability and a shift in ν(O–O) to 815 cm^{-1} (Figure 1). Although the purple solution gains an orange tinge upon freezing, the enhancement maximum for ν(O–O) remains at ~520 nm. The color change most likely arises from a sharpened electronic absorption band with diminished intensity in the long-wavelength shoulder. The broad feature at ~470 cm^{-1} is still noted for samples frozen in glass capillaries, but it is markedly diminished in samples frozen directly onto cold fingers at either 90 or 15 K where the glass windows of the chamber are considerably farther removed from the scattering surface. Since glass alone displays a broad band centered at ~470 cm^{-1}, it seems likely that the previous assignment to an Fe–L vibration[15] was incorrect and that this spectral feature arises mainly from the glass capillary. It is only prominent in the spectrum of the $[Fe(edta)O_2]^{3-}$ because ν(O–O) is so weakly resonance enhanced.

When mixed-isotope hydrogen peroxide is used to form the Fe^{III}(edta)–peroxo complex, the O–O stretch at 815 cm^{-1} shifts cleanly to 794 cm^{-1} with no detectable splitting (Figure 1). The single peak is diagnostic of an η^2 configuration in which the two oxygens are equivalent.[7] A simple Hooke's law calculation gives a value of 23 cm^{-1} for the expected downshift in ν(O–O) upon isotopic substitution with $^{16}O^{18}O$, which agrees well with the experimental value of 21 cm^{-1}.

The alternative proposed structure for the Fe^{III}(edta)–peroxo complex has the dioxygen coordinated as an end-on bound hydroperoxide.[12] In this structure, ν(O–O) would be expected to exhibit a deuterium isotope effect. The spectra of $[Fe(edta)O_2]^{3-}$ in H_2O and D_2O obtained at 15 K are shown in Figure 2. There is no detectable shift of the 815-cm^{-1} ν(O–O) peak in the D_2O sample. The small feature at 877 cm^{-1} is due to ν(O–O) of unreacted H_2O_2. A similar lack of a deuterium isotope effect was observed for samples at 5 °C. Thus, the bound dioxygen shows no indication of protonation in the Fe^{III}(edta)–peroxo complex.

A control experiment was performed on hydrogen peroxide to quantitate the deuterium sensitivity of ν(O–O) in a species known to be protonated at neutral pH. Previous studies of the vibrational

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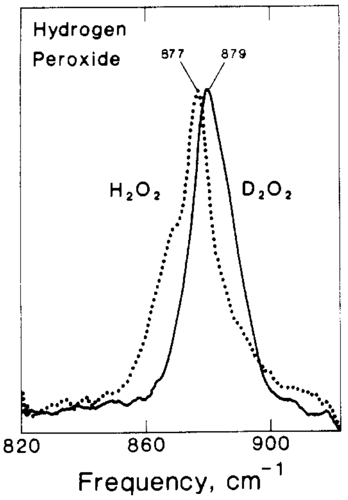


Figure 3. Raman spectrum of hydrogen peroxide (1.5 M) in H_2O and D_2O. Samples were prepared by mixing 170 μL of a 30% solution (aqueous) of H_2O_2, 10 μL of glycerol, and 820 μL of H_2O or D_2O to give a total volume of 1 mL. Spectra were obtained at 15 K with 647.1-nm excitation (60 mW at the sample) and a slit width of 5 cm^{-1}. The data were collected at 0.5 cm^{-1}/s and were given a 17-point smooth.

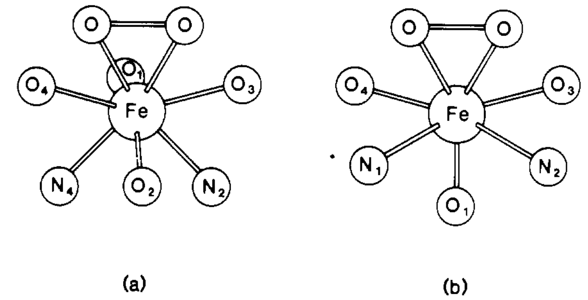
spectrum of H_2O_2 reported ν(O–O) at 878–880 cm^{-1} with little or no shift in deuterium.[22,23] Figure 3 shows Raman spectra of 1.5 M solutions of hydrogen peroxide in H_2O and D_2O obtained at 15 K. The high resolution achieved with low-temperature samples makes it clear that the O–O stretch occurs at 877 cm^{-1} in H_2O and shifts up to 879 cm^{-1} in D_2O.

The Raman spectrum of hydrogen peroxide in the frozen state is complicated by the appearance of shoulders at higher and lower energy relative to the principal O–O vibration. The intensities of these minor components were found to vary with sample temperature and rate of freezing. They were not observed in liquid samples and were considerably diminished by the addition of 1% glycerol prior to freezing. Since glycerol alters the structure of the frozen solvent, it is likely that the appearance of multiple O–O vibrations is related to hydrogen-bonding properties of the solvent in the frozen state. The frequency of the major Raman peak and its 2-cm^{-1} shift to higher energy in D_2O was unaffected by the addition of glycerol. In liquid samples at room temperature, the O–O stretching mode was observed at 875 cm^{-1} in H_2O_2 and at 876 cm^{-1} in D_2O_2.

The shift of the hydrogen peroxide ν(O–O) to higher energy in D_2O is anomalous in view of the expected decrease in frequency with increasing mass. The upward shift most likely relates to the hydrogen-bonding interactions between the peroxide oxygens and solvent protons. If deuterium forms a weaker hydrogen bond than hydrogen, this causes a relatively greater bonding electron density to remain in the O–O bond, thereby accounting for the increase in frequency. Such deuterium-dependent upshifts in hydrogen-bonded moieties have been observed for the Fe–O–Fe symmetric stretch in oxyhemerythrin and the C–O–C asymmetric stretch in 2-methoxyethanol.[24] Alternatively, since deuterium tends to form stronger σ bonds than hydrogen, the O–O bond of D_2O_2 or DO_2^- could be strengthened if the σ bonding involved significant withdrawal of electron density from the filled antibonding π^* orbitals on the oxygen atoms. The latter explanation has been invoked for the deuterium-dependent upshift in ν(O–O) of the iron-bound peroxide in oxyhemerythrin.[21,25]

Discussion

The observation of ν(O–O) for the Fe(edta)–peroxo complex at 824 cm^{-1} in solution and at 815 cm^{-1} in the frozen state establishes that the bound dioxygen species is a peroxide. Similar peroxide vibrations have been reported at 766 cm^{-1} in Na_2O_2 and at 806 cm^{-1} in the Fe^{III}OEP–peroxo complex.[26,27] The η^2 side-on binding of peroxide in the $[Fe(edta)O_2]^{3-}$ complex is conclusively demonstrated by our isotope substitution experiments. Other established examples of side-on binding of dioxygen include $[Mn^{III}TPP(O_2)]^-$ and $[V^VO(IDA)(O_2)]^-$ whose structures have been verified by X-ray crystallography and whose O–O vibrations are at 983 and 920 cm^{-1}, respectively.[28,29] Infrared and EXAFS data on $[Fe^{III}TPP(O_2)]^-$ and $[Ti^{IV}TPP(O_2)]^-$ indicate that the bound dioxygen is also in a side-on peroxo configuration.[27,30] Furthermore, the η^2 structure has been proposed as an intermediate in the oxidation of Fe^{II}(edta) by H_2O_2,[31] and the present results with Fe^{III}(edta) make this a likely probability.



(a) (b)

Figure 4. Possible structures of $[Fe^{III}(edta)O_2]^{3-}$: (a) derived from the peroxide displacement of the water in the seven-coordinate $[Fe^{III}(edta)(OH_2)]^-$ complex (N_1, N_2, and O_1–O_4 from edta ligands with atom positions similar to those in $[Fe^{III}(edta)OH_2]^{3-}$ [32]); (b) derived from the displacement of a carboxylate oxygen as well as the water molecule.

The structures of the reactive forms of Fe^{III}(edta) and hydrogen peroxide as well as the resultant peroxo complex have been the subject of much conjecture. In the crystal structure of $[Fe(edta)OH_2]^-$ reported by Lind et al.,[32] the seven-coordinate iron has a distorted pentagonal-bipyramidal geometry. The two amine nitrogens, two monodentate carboxylate oxygens (one from each N–), and the water molecule occupy the pentagonal plane, whereas the remaining two carboxylates coordinate to the axial positions. Nucleophilic ligands seem to be capable of displacing the water molecule to form $[Fe^{III}(edta)L]^{2-}$ complexes.[33] If a similar structure formed with peroxide, it would have the configuration shown in Figure 4a. Alternatively, the side-on binding of peroxide could be accompanied by the displacement of both the water and a carboxylate ligand, resulting in a more nearly octahedral geometry (Figure 4b).

There is reasonably good agreement that the predominant solution species between pH 8.0 and 10.0 is $[Fe^{III}(edta)OH]^{2-}$, which then reacts with either H_2O_2 or HO_2^- to produce the peroxo complex.[11,12] The $[Fe^{III}(edta)OH]^{2-}$ species is likely to have a seven-coordinate geometry similar to that of its protonated analogue, $[Fe^{III}(edta)OH_2]^-$. The overall reaction can be written as

$$[Fe^{III}(edta)OH]^{2-} + H_2O_2 \rightleftarrows [Fe^{III}(edta)O_2]^{3-} + H_3O^+ \quad (1)$$

According to Bull et al.,[11] reaction 1 proceeds via the initial dissociation of hydroxide, followed by the formation of the peroxide adduct and the concomitant release of protons. The sensitivity of the forward reaction to general-acid/base catalysis is explained as H^+ assistance of hydroxide dissociation and general-base assistance of peroxide deprotonation. The second-order rate constant

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in the absence of general-acid catalysis is $\sim 3 \times 10^2$ M^{-1} s^{-1}.[11,34] Interestingly, the reaction

$$[Fe^{II}(edta)]^{2-} + O_2^{\bullet -} \rightleftarrows [Fe^{III}(edta)O_2]^{3-} \qquad (2)$$

forms the identical product by oxidative addition without the apparent need for hydroxide or proton dissociation and proceeds $\sim 2 \times 10^4$-fold faster.[11] Although it has been proposed on the basis of water proton relaxation rates that the OH^- ligand is still present in the peroxo complex and that it is an edta carboxyl group which is displaced,[12] hydroxide displacement seems more likely to account for the difference in peroxide and superoxide reaction rates as well as for the observed single proton dependence of the back-reaction in (1).[11] Thus, the species in Figure 4a is the more probable structure for the Fe^{III}(edta)–peroxo complex.

Since the η^2 configuration is the generally observed mode of dioxygen binding in mononuclear metal–peroxo complexes, the protein oxyhemerythrin appears to represent an exception. The combination of X-ray crystallographic,[35] spectroscopic,[36] and resonance Raman[8,37] results makes it certain that the dioxygen is reduced to peroxide and is coordinated to a single Fe(III) in an η^1 end-on fashion. The O–O stretch at 844 cm^{-1} in oxyhemerythrin shifts 4 cm^{-1} to higher energy in D_2O, implying that the bound peroxide is protonated.[21] The end-on binding of hydroperoxide appears to be enforced by steric restrictions at the oxygen binding site and by the presence of an Fe–O–Fe moiety (a suitable hydrogen bond acceptor), which anchors the hydroperoxide ion in place.[24,35] These conditions allow the protein to override the preferred η^2 orientation of metal-coordinated peroxides.

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Registry No. H_2O_2, 7722-84-1; $H_2{}^{16}O^{18}O$, 13813-07-5; Fe(edta)$^-$, 15275-07-7; $[Fe(edta)O_2]^{3-}$, 12558-61-1.

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Electron Paramagnetic Resonance Studies of Vanadium Tetrachloride Adducts with Oxygen-, Nitrogen-, Phosphorus-, and Arsenic-Donor Ligands[†]

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Vanadium tetrachloride reacts in hydrocarbon solvents with O-, N-, P-, and As-donor ligands such as phosphines, arsines, pyridines, amines, tetrahydrofuran, and dioxane to give paramagnetic molecular adducts. Studies by electron paramagnetic resonance performed on liquid and frozen solutions show that these adducts have the stoichiometry 1/2 (VCl_4/ligand L); the molecular geometry is assumed to be octahedral with tetragonal distortion, the four chlorine atoms lying in the basal plane and the two ligands in a trans position along the 4-fold axis. Superhyperfine interaction of the unpaired electron with the P and As nuclei was neatly resolved in most cases. It is shown that the magnitude of the hyperfine interaction with the V nucleus exhibits some dependence on the donor character of the ligand. Slow hydrolysis gives vanadyl compounds of the formula $VOCl_2{\cdot}2L'$ (L' = L for N and O donors and the corresponding phosphine oxide for P donors). Some data of optical absorption measurements are also given.

Introduction

The chemistry of vanadium(IV) coordination compounds is largely dominated by that of the vanadyl ion VO^{2+} because of its unusually high stability. In contrast to the case for other transition-metal halides which have well-developed chemistry with electron donor ligands, vanadium compounds having the formula $VX_4{\cdot}nL$ (X = halogen; L = nucleophile ligand) remained hitherto virtually ignored although they could be of high potential value in the search for vanadium organometallic compounds. This obviously serious gap in our knowledge of some fundamental aspects of the chemistry of group V halides has already been recognized.[1]

The very high lability of these compounds impeded extensive research in this area. In some instances tetrachlorides are reported to be reduced by the ligand to give complexes of lower oxidation states. In most other cases they hydrolyze readily, giving rise to the corresponding vanadyl compounds.

Electron paramagnetic resonance is a very convenient tool to study V(IV) compounds (V: $I = {}^7/_2$, 99.75%; $S = {}^1/_2$). It has been put to trial in the case of $NbCl_4$ adducts with trialkylphosphines. In a previous work in this area[2] we used EPR techniques to identify in solution the adducts of formula $NbCl_4{\cdot}2PR_3$ and postulated a distorted-octahedral geometry with the phosphines lying in trans positions. Subsequently, the compound where R = Et was isolated and gave the predicted structure by X-ray diffraction studies;[3] its EPR spectrum was perfectly consistent with our observations.

We report herein our results concerning the identification by EPR of some vanadium tetrachloride adducts with O–, N–, P–, and As-donor ligands. It is shown that this technique is particularly suitable to give information on the molecular geometry and the influence of ligand donor character on electron delocalization within the metal–ligand bond.

Experimental Section

VCl_4 (Alfa Inorganics) was used without further purification. All solvents were rigorously dried by the usual methods. Toluene was freed from olefins by treatment with H_2SO_4 and then dried and distilled over $AlLiH_4$. All manipulations were carried out under argon and samples transferred via syringe–septum systems. Samples for EPR were handled in sealed tubes. Liquid phosphines were freshly distilled before use.

In a typical experiment, VCl_4 (0.2 mL) was introduced into 10 mL of toluene in a round-bottomed flask to which was added dropwise a solution of 0.5 mL of phosphine diluted in 5 mL of solvent at −30 °C.

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