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

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

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.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM 18865 to T.M.L. and J.S.-L.) and the Division of Chemical Sciences, U.S. Department of Energy (to E.H.A.).

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

---

(34) Orhanović, M.; Wilkins, R. G. *Croat. Chim. Acta.* **1967**, *39*, 149.
(35) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 713.
(36) Gay, R. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1978**, *100*, 1972.
(37) Dunn, J. B. R.; Shriver, D. F.; Klotz, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2582.

Contribution from the Laboratoire de Chimie Organique Industrielle de l'ENSCP (URA 403, CNRS),
11 rue P. et M. Curie, 75005 Paris, France, and Laboratoire de spectrochimie du solide (URA 302, CNRS),
Université P. et M. Curie, 75005 Paris, France

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

J. Zah-Letho,[‡,§] E. Samuel,*[,‡] and J. Livage[||]

Received July 16, 1987

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.

---

* To whom correspondence should be addressed.

[†] Dedicated to Prof. J. Tirouflet on the occasion of his retirement.

[‡] Laboratoire de Chimie Organique Industrielle de l'ENSCP.

[§] Present address: Laboratoire de chimie minérale, Faculté des Sciences, Abidjan, Côte d'Ivoire.

[||] Université P. et M. Curie.

(1) Kepert, D. L. *The Early Transition Metals*; Academic: New York, 1972.
(2) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* **1980**, *19*, 1384.
(3) Cotton, F. A.; Duray, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *24*, 3592.

0020-1669/88/1327-2233$01.50/0

A vigorous reaction took place accompanied by a change in color, which progressively became dark violet. In some cases a crystalline solid and in other cases a sticky material deposited at the bottom of the flask. An aliquot of the supernatant solution was transferred into the EPR tube under argon and sealed under vacuum or into the UV–visible cell under argon after dilution.

In the case of triphenylphosphine, the solid phosphine was dissolved in toluene and a stoichiometric amount of VCl_4 in toluene was introduced via a syringe to the solution. An abundant violet precipitate immediately formed, which increased in volume upon addition of the rest of the tetrachloride. The supernatant solution was mauve. The solid could be isolated by filtration under argon.

Blank experiments were made to ensure that no EPR signals were present in toluene solutions of VCl_4 down to 130 K, so that all the observed signals are due to the reaction products.

EPR spectra were recorded on a JEOL ME 3X X-band spectrometer with a Bruker B-A6 accessory for field calibration.

Abbreviations used: Et = ethyl; Ph = phenyl; Cy = cyclohexyl; THF = tetrahydrofuran; py = pyridine; Diox = dioxane; DMPE = (dimethylphosphino)ethane; diars = *o*-phenylenebis(dimethylarsine). Other abbreviations have their usual meaning.

Results

1. Chemistry of the Compounds. (a) P Donors. In general, phosphorus-donor ligands give a dark violet to mauve coloration of the supernatant solution with separation of a rather sticky noncrystalline solid. It was not possible to isolate well-defined compounds because of the extreme sensitivity to air and moisture of these reaction products and the difficulty of their handling. However, in some cases well-shaped mauve crystals were found to separate from the solutions when these were kept in a sealed tube in the cold (−20 °C) for several days. The case of PPh_3, however, deserves special attention. Previous attempts have been made[4] to prepare a VCl_4 adduct with this ligand. It was reported that in CCl_4 and after several months the reaction proceeds with formation of reduction products, and the compound obtained was supposed to have a salt structure such as $(Ph_3PH)(VCl_4{\cdot}PPh_3)$. We found that, immediately after the reaction, a violet precipitate was formed that could be separated by filtration but could not be redissolved in toluene; it was slightly soluble in dichloromethane. Elemental analysis gave a formula approaching that of the bis(phosphine) adduct; we believe that the discrepancy is due to the simultaneous formation of some monoadduct or reduction products. However, the supernatant solution of the reaction mixture showed by EPR (see below) the presence of the bis(phosphine) adduct only. The IR spectrum of the violet precipitate showed the characteristic bands due to PPh_3. By slow controlled hydrolysis, for instance if the compound is allowed to stand for several days in methylene chloride, a light green crystalline compound can be isolated; it was identified from its analytical data as $VOCl_2{\cdot}2OPPh_3$ (II). Its IR spectrum showed the characteristic band due to $\nu(V{=}O)$ stretching at about 1000 cm^{-1}, the assignment of which was confirmed by vanadyl-^{18}O labeling, which shifts the band to 962 cm^{-1} (Figure 1). This is the order of magnitude of the shift already observed for similar vanadyl-^{18}O compounds.[5] The geometry of II prepared through a different route was determined recently by X-ray diffraction.[6] A property common to all these phosphine complexes was oxidation of the phosphine to phosphine oxide within the vanadium coordination sphere, with simultaneous hydrolysis of VCl_4.

(b) As Donors. $AsPh_3$ seems to react in a manner similar to that of the phosphorus analogue. $AsMe_3$ gave an orange-brown precipitate. The solution showed an EPR spectrum consistent with the formation of a bis(arsine) adduct. The behavior toward hydrolysis appears to be similar to that of the phosphine compounds.

(c) N Donors. Reactions with this type of ligand (pryidines and amines) gave generally a strong maroon-red coloration with the formation of an abundant precipitate, which was presumed to be the adduct. A dark red pyridine compound having the formula $VCl_4{\cdot}2py$, also insoluble in organic solvents, was previously described.[7] The adducts we obtained as solids hydrolyzed slowly to give deliquescent green materials, except for 3-Etpy, which yielded a well-defined compound having the formula $VOCl_2{\cdot}2(3\text{-Etpy}){\cdot}H_2O$, confirmed by the X-ray structure.[8] A remarkable difference therefore from the P donors is the resistance to oxidation of the ligand upon hydrolysis on the one hand and the tendency to form aqua–vanadyl complexes on the other. It appears that, with soft donors such as pyridines, the vanadium atom can still act as an electrophile and seeks to accommodate the oxygen doublet of a water molecule in a hexacoordinate structure. With NMe_3, the compound $VOCl_2{\cdot}2NMe_3$, prepared by other methods, was described and found to have a pentacoordinate geometry around the metal.[9]

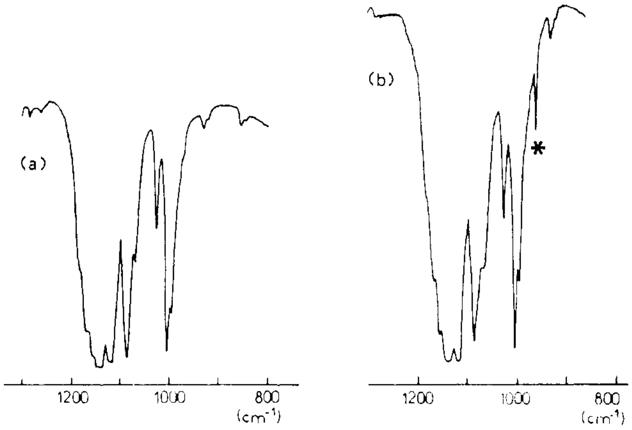

Figure 1. (a) Infrared spectrum of $VOCl_2{\cdot}2OPPh_3$ in the 800–1200-cm^{-1} region. (b) Spectrum in the same region of $V[^{18}O]Cl_2{\cdot}2[^{18}O]PPh_3$. The starred peak is due to $\nu(V{=}^{18}O)$.

(d) O Donors. Light to dark brown solutions were obtained for the three ligands examined with the formation of crystalline precipitates. These adducts have already been characterized.[4] Elemental analysis showed coordination of two ligands for THF and benzophenone and one for dioxane. For the last compound, however, a bridge structure was postulated. These adducts hydrolyze easily in moist air to give vanadyl species, but no well-defined compound could be isolated. We have included them in our study for the sake of comparison of their EPR parameters, as will be shown below.

2. EPR Spectra. (a) O- and N-Donor Ligands. Typical EPR spectra of $VCl_4{\cdot}2L$ adducts obtained with O- and N-donor ligands are shown in Figure 2. An isotropic solution spectrum is observed at room temperature exhibiting the expected eight hyperfine lines arising from the interaction of the unpaired 3d^1 electron ($S = {}^1/_2$) of a V^{4+} ion with the nuclear spin of vanadium ($I = {}^7/_2$). The frozen-solution spectrum is attributable to a V^{4+} ion in a nearly axially distorted octahedral ligand field and displays both parallel and perpendicular features of the hyperfine structure. The isotropic and anisotropic parallel EPR parameters can be easily measured from the spectra of the fluid and frozen solutions, respectively. The perpendicular components can also be easily measured in the cases where shf interaction with the ligand nucleus is absent such as in part 1 of Figure 2 (and Table I), where the $m_I = -{}^7/_2$ and $m_I = {}^7/_2$ lines are clearly resolved. These values are consistent with the relations $\langle g\rangle = {}^1/_3(g_\parallel + 2g_\perp)$ and $\langle A\rangle = {}^1/_3(A_\parallel + 2A_\perp)$. The $g_\perp$ and $A_\perp$ values in the other cases were calculated by using these relations.

Hyperfine interaction with the N nucleus of the N-donor ligands was not observed, presumably due to the small magnitude of this hyperfine constant. This was estimated to be about 2.8 G,[10] too

---

[4] Bridgland, B. E.; Fowles, G. W. A.; Walton, R. A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 383.

[5] Guilard, R.; Fontessa, M.; Fournari, P.; Lecomte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1976**, 162.

[6] Caira, M. A.; Gellatly, B. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1198.

[7] Kilty, P. A.; Nicholls, D. *J. Chem. Soc.* **1965**, 4015.

[8] Zah-Letho, J.; Samuel, E.; Drumzee, Y.; Jeannin, Y. *Inorg. Chim. Acta* **1987**, *126*, 35.

[9] Drake, J. E.; Verkis, J.; Wood, J. S. *J. Chem. Soc. A* **1968**, 1000.

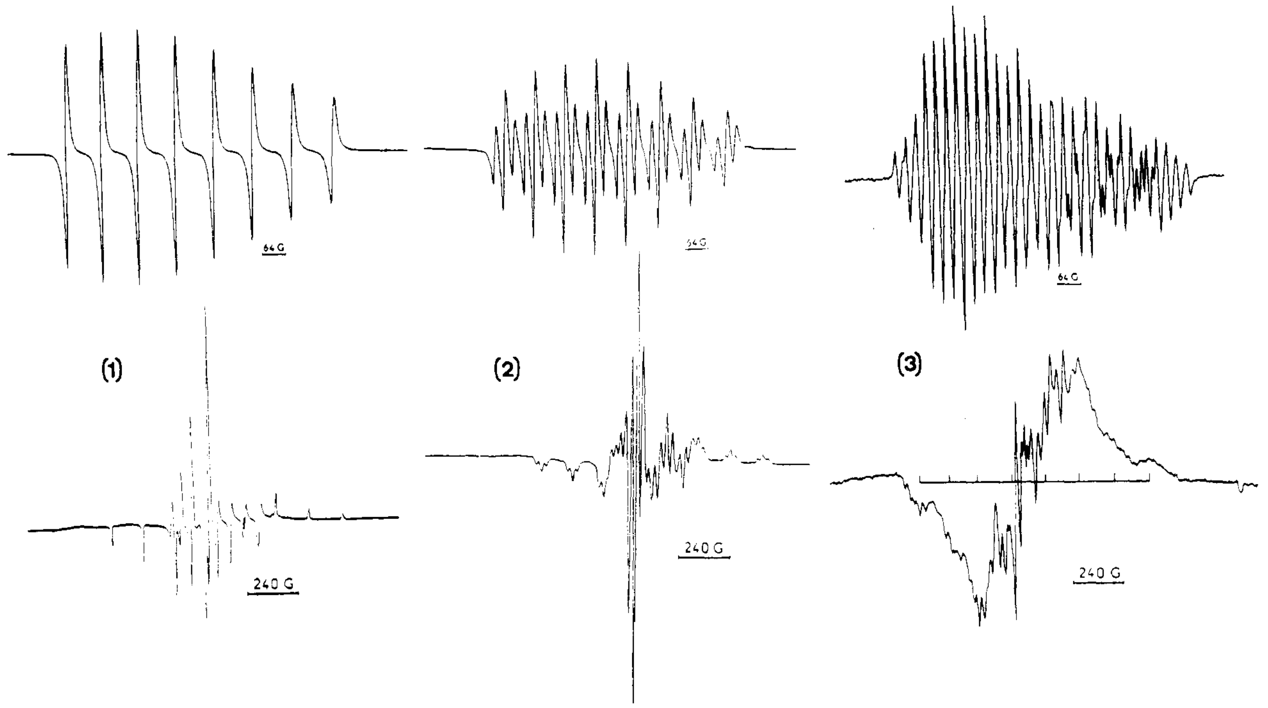

Figure 2. EPR spectra of $VCl_4{\cdot}2L$ adducts in liquid (upper) and frozen (lower) solution: (1) L = THF; (2) L = PEt_3; (3) L = $AsMe_3$. The "sticks" in the lower part of (3) locate what are assumed to be the $A_\parallel$ components.

Table I. EPR Parameters in Liquid and Frozen Toluene Solutions of $VCl_4{\cdot}2L$ Addition Compounds[a]

L	$\langle g \rangle$	$g_\parallel$	$g_\perp$	$\langle A \rangle$(V)	$A_\parallel$(V)	$A_\perp$(V)	$\langle a \rangle$(P)	$a_\parallel$(P)	$a_\perp$(P)
PMe_3	1.982	1.963	1.992	91.2	165.0	54.3	28.0	27.5	28.3
PEt_3	1.983	1.965	1.992	91.0	161.2	55.6	26.7	26.8	26.6
$PMePh_2$	1.983	1.969	1.989	92.0	163.3	56.0	26.3	25.5	26.7
$PEtPh_2$	1.984	1.971	1.990	91.3	164.0	55.0	25.4	25.0	25.5
PPh_3	1.985	1.966	1.994	93.0	165.0	57.0	25.0	26.0	24.0
P(*i*-Pr)$_3$	1.981	1.972	1.986	93.0	164.4	57.0	26.0	24.5	26.7
P(*t*-Bu)$_3$	1.973	1.939	1.990	97.2	178.0	57.0	23.0	21.6	24.0
PCy_3	1.983	1.973	1.988	90.6	166.0	53.0	22.6	24.0	22.0
$PPh(OEt)_2$	1.979	1.969	1.984	90.4	164.3	53.4	31.1	31.2	31.1
P(*t*-Bu)$_2$Cl	1.972	1.939	1.989	112.3	196.0	70.0			
$P(OEt)_3$	1.969	1.937	1.984	113.5	195.8	69.9			
PEt_3 + $P(OEt)_3$[b]	1.975	1.956	1.984	100.5	176	63	35.1	32.9	36.2
$AsMe_3$	1.983	1.981	1.984	93.0	172.0	49.1	29.5[c]	29.4[c]	30.5[c]
py	1.975	1.959	1.981	101.2	177.0	61.4			
3-Etpy	1.973	1.958	1.980	101.4	176.0	60.0			
4-(*t*-Bu)py	1.977	1.973	1.984	102.0	166.2	54.0			
NMe_3	1.974	1.948	1.991	103.1	183.1	61.3			
THF	1.970	1.948	1.987	111.5	189.5	68.0			
Diox	1.970	1.945	1.987	111.5	191.2	68.5			
PhCOPh	1.946	1.917	1.945	113.1	191.5	75.0			

[a] Hyperfine constants are in gauss. 1 G = 10^{-4} T. Where P shf interaction is not resolved, $A_\perp$(V) values are those measured; otherwise they are calculated. $a_\perp$(P) values are calculated. [b] 1/1 mixture of the two phosphines; the signal is a set of doublets. [c] Values are for As.

small to be resolved with the observed EPR line width. All the results are reported in Table I.

(b) P-Donor Ligands. EPR spectra of $VCl_4{\cdot}2L$ adducts, where L is a P donor, exhibit a more complex hyperfine structure (Figure 2). The room-temperature spectrum is made up of eight triplets. These triplets are also clearly resolved in the parallel components of the frozen-solution spectrum. These spectra are due to the hyperfine interaction of one unpaired electron ($S = {}^1/_2$) with the nuclear spin of vanadium and the superhyperfine interaction with two phosphorus atoms ($I = {}^1/_2$) splitting each hyperfine line into three lines with relative intensities 1:2:1. The superhyperfine structure clearly indicates axially symmetric $VCl_4{\cdot}2L$ adducts where both L ligands are presumably in trans positions. Isotropic and parallel EPR parameters can be easily measured on the spectrum and the perpendicular components deduced as previously described (Table I). It should be noticed that the superhyperfine coupling with the phosphorus atoms is no longer resolved in the case of phosphite and chlorophosphine ligands. This will be discussed below.

(c) As-Donor Ligands. The trimethylarsine adduct gave a well-resolved spectrum at room temperature. The frozen-solution spectrum is not so well defined, but the $A_\parallel$ and $a_\parallel$(As) values could be extracted nevertheless (Figure 2).

Discussion

A survey of the literature on the chemistry of VCl_4 shows that addition compounds with nucleophiles (Nu) could be isolated only in a few cases.[11] They were found to have the composition 1/1 or 1/2 (V/Nu), depending on the conditions of preparation and on the nature of the ligand. To our knowledge, no systematic

---

(10) Assour, J. M. *J. Chem. Phys.* **1965**, *43*, 2477.

(11) Nicholls, D. *Coord. Chem. Rev.* **1966**, *1*, 379.

(12) Clark, R. J. H.; Lewis, J.; Nyholm, R. S.; Pauling, P.; Robertson, G. B. *Nature (London)* **1961**, *192*, 222.

(13) Clark, R. J. H.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1960**, 2460.

Table II. Vanadium b_{2g} Orbital Spin Densities (α^2), Phosphorus (3s) Spin Densities $(\alpha^L)^2$, and Optical Absorption Maxima (ν_1, ν_2, ν_3; in cm^{-1}) for $VCl_4{\cdot}2L$ Complexes[a]

L in $VCl_4{\cdot}2L$	α^2	$(\alpha^L{}_{ns})^2$	ν_1	ν_2	ν_3
PMe_3	0.66	0.0077	21 276	15 258	12 987
PEt_3	0.63	0.0073	20 200	16 050	12 900
$PMePh_2$	0.64	0.0072	20 000	14 815	12 121
$PEtPh_2$	0.65	0.0069			
PPh_3	0.64	0.0068	17 544	13 423	11 494
$P(i\text{-}Pr)_3$	0.65	0.0071			
$P(t\text{-}Bu)_3$	0.70	0.0063			
PCy_3	0.68	0.0062	20 000	17 241	14 286
$PPh(OEt)_2$	0.69	0.0085			
$P(OEt)_3$	0.71		20 400	13 590	11 360
$AsMe_3$	0.72	0.0086	22 222	18 868	13 513
py	0.71				
3-Etpy	0.75				
4-(*t*-Bu)py	0.88			14 286	11 765
NMe_3[a]	0.73		19 802	16 528	12 987
THF	0.76				
Diox	0.75		20 000		12 903
PhCOPh	0.68		23 223		

[a] Major product.

investigation of this class of compounds was undertaken.

This study attempts to describe the results of some reactions of VCl_4 with a selected number of bases bearing different donor atoms and consequently having different nucleophilic character, under uniform and mild conditions of preparation. Some systematic understanding of the geometry of the compounds formed in solution can then be obtained, essentially from analysis of their EPR spectra.

1. g Tensor. The overall shape of the frozen-solution EPR spectra clearly shows that all adducts exhibit an axial symmetry, with $g_\parallel > g_\perp$. The measured g values ($g_\parallel < g_{iso} < g_e$) suggest that the unpaired electron should be in a d_{xy} orbital. The g values are close to those reported in the literature for $[VO(H_2O)_6]^{2+}$ and $[VO(TPP)]^{2+}$, where a d_{xy} configuration was established.[14] Such a ground state could correspond to a hexacoordinate complex with an axial distortion along the 4-fold z axis leading to a D_{4h} molecular symmetry. The distortion corresponds to stronger donor ligands along the z axis, resulting in a destabilization of the d orbitals lying outside the xy plane.

Three absorption bands were usually observed in the visible range. These were tentatively assigned to d–d transitions from the $^2B_{2g}$ ground state.

2. V Hyperfine Tensor. All ESR spectra exhibit the eight hyperfine lines arising from the coupling of one unpaired electron with the nuclear spin of the vanadium. The A tensor can be analyzed in terms of a symmetry very close to axial with $A_y = A_z = A_\perp$. Its components, corresponding to a d_{xy} configuration, can be expressed as

$$A_\parallel = A(\text{iso}) + P[-{}^4\!/\!_7\alpha^2 + (g_\parallel - g_e) + {}^3\!/\!_7(g_\perp - g_e)]$$

$$A_\perp = A(\text{iso}) + P[{}^2\!/\!_7\alpha^2 + {}^{11}\!/\!_{14}(g_\perp - g_e)]$$

$$\langle A\rangle = A(\text{iso}) + P[g(\text{iso}) - g_e]$$

$P = g_n\beta_n g_e\beta_e(1/\langle r^3\rangle)$ is intrinsically positive and depends on the effective charge on the metal nucleus, which in the case of the V^{4+} ion is equal to 172 G.[15a] α^2 is the fractional spin density in the $b_{2g}(d_{xy})$ molecular orbital, and A(iso) is the Fermi contact term. The signs for the coupling constants are established from the condition that P must be positive.[15b] However, the relative signs of $\langle A\rangle$ (and also $A_\parallel$ and $A\perp$) can be determined from the bandwidths of the isotropic and anisotropic lines.[15c] Thus, the line width increases on going upfield, so that all the three constants are of the same sign and are probably negative, since A is due to spin polarization and is probably negative.[15d] The values given in Table II are the results obtained from solving these expressions. They show the influence of phosphine basicities on the extent of unpaired electron delocalization toward the chloride ligands in the xy plane.

3. Ligand Hyperfine Interaction. Table I shows that, in the case of most P donors and in the case of $AsMe_3$, well-resolved superhyperfine interaction of the unpaired electron with the donor nucleus, in both liquid and frozen solutions, is observed, easily attributable (in the case of P donors at least) to two ligand molecules coordinated to the metal. The axial symmetry of the A(V) tensor leads us therefore to assign to the complexes formed with these monodentate ligands a hexacoordinate structure with tetragonal distortion in a D_{4h} molecular symmetry, with the unpaired electron residing in a $b_{2g}(d_{xy})$ orbital. These, to our knowledge, are the first examples in VCl_4 chemistry of phosphine and arsine coordination revealed by EPR.

The case with the bidentate DMPE ligand deserves special attention. The room-temperature spectrum exhibits a complex pattern quite different from the set of eight well-resolved triplets observed for the tertiary phosphine adducts, and the frozen-solution spectrum suggests an approximately axial symmetry. However, the number of phosphorus atoms coordinated to vanadium could not be easily deduced from these spectra, in view of the complexity of the parallel components in the frozen-solution spectrum. However, it is clear that this number exceeds 2. It appears therefore that more than one bidentate phosphine ligand is bound to the metal atom. In the chemistry of the early transition metals a few well-established examples are known[12] of bidentate ligands giving an eight-coordinate structure. Clark et al. prepared in 1961 a series of diarsine adducts[13] including the $VCl_4{\cdot}2$diars compound. This adduct was found to be isostructural with the Ti analogue, whose structure, determined by X-ray diffraction, revealed a dodecahedron with eight vertices occupied by four equivalent chlorine and four equivalent arsenic atoms. It is not unlikely in our case that we are dealing with coordination higher than 6, but further investigations are needed to clarify this interesting situation.

The adduct of $AsMe_3$ with VCl_4 exhibits at room temperature a complex spectrum (^{75}As: $I = {}^3\!/\!_2$, 100%) that indicates coordination of two arsine ligands to vanadium along the same lines as for the phosphine compounds; analysis of the spectrum on the basis of this assumption gives the values indicated in Table I. This was confirmed by computer simulation of the high-field portion of the isotropic spectrum (without taking into account second-order effects); an exact replica of the experimental spectrum was obtained.

Superhyperfine splitting with the P nucleus was observed only with some of the phosphines examined. The coupling constants are small because of the absence of delocalization on the P nucleus and are fairly isotropic. The dipolar coupling must be small because of the high spin density on the metal and also the delocalization toward the Cl ligands. This is a function of $1/r^3$, where r is the M–P bond length. The general well-known expressions are [13c]

$$a_\parallel(\text{dip}) = 2g\beta_e\beta_n g_n/r^3$$

$$a_\perp(\text{dip}) = -g\beta_e\beta_n g_n/r^3$$

where $g_n\beta_n$ refers to the ligand nucleus. Assuming $r \simeq 2.0$ Å for the V–P distance (by analogy with V–N $\simeq$ 2 Å[8,9]), the results show that this coupling is indeed very small and is close to the experimental error (about 1 G). Therefore, spin polarization of the PR_3 σ electrons seems to be responsible for the small isotropic coupling, which is thus negative. The isotropic phosphorus coupling constants yield the 3s spin densities $(\alpha^L)^2$, which are given in Table II; these were calculated by using the formula $a(\text{iso}) = K(\alpha_{3s})^2$, where $K = 8\pi/3g_n\beta_n|\psi_{o(3s)})|^2 = 3640$ G for phosphorus for example,[15b] which shows very small delocalization on σ phosphorus orbitals.

---

(14) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111.

(15) (a) McGarvey, B. R. *J. Phys. Chem.* **1967**, *71*, 51. (b) Raynor, J. B.; Goodman, G. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*. (c) Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: New York, 1967; p 20. (d) Freeman, A. J.; Watson, R. E. In *Magnetism*; Rado G. T., Suhl, H.; Academic: New York, 1965; Vol. 11A, p 167.

Conclusion

From the axial **g** tensor and the experimental preparation conditions, there is enough evidence, mostly from the hyperfine interaction with two P- or As-donor ligands, to show that the compounds under investigation are VCl_4 adducts of octahedral geometry with the donor ligands in axial trans positions.

In an earlier study Olivê and Olivê reported from EPR investigations the formation of 1/2 adducts between $VOCl_2$ and PR_3 (R = alkyl or alkoxy groups) by the observation of hyperfine interaction with the two P nuclei of the ligands. The geometry was supposed to be tetrahedral, and the isotropic g and A values were found to be almost identical for the few compounds examined. Thus, no dependence on the nature of the phosphine ligand was observed.[16,17] It was not said whether the two phosphine ligands were cis or trans in the basal plane of the molecular tetrahedron.

The same authors reported the formation of a paramagnetic arsine compound thought to be $VOCl_2$·2(arsine).[17,18] The reported isotropic spectrum (a septet pattern) is very similar to the one we obtained above. Hyperfine interaction with As nuclei was also observed in the thiolato-bridged oxovanadium(IV) compound $VO(S_2AsMe_2)_2$.[19]

All the EPR parameters related to these vanadyl compounds are close to the values observed in our VCl_4 adducts, reflecting the well-known poor sensitivity of the magnetic parameters in V(IV) compounds toward ligand effects. The reason is that the unpaired electron resides in a d_{xy} orbital of metallic character and, in both types of compounds (VCl_4 and vanadyl adducts), no overlap with axial ligand orbitals takes place. This constrasts with the case for Co compounds, for instance, where interaction with the axial donor ligands occurs via the dz^2 metal oribtal, which, due to direct overlap, has a strong influence on the magnitude of the unpaired electron interaction with the axial ligand.[20,21]

The g values fall within a narrow range and denote the symmetry of the molecule and the nature of the orbital in which the unpaired electron is confined. On the other hand, the hyperfine interaction constants afford information of interest about the metal–ligand interaction. If we refer to the values of $\langle A_V \rangle$, we can easily notice that they are significantly sensitive to (1) the nature of the donor atom and, (2) within the phosphine ligands, the nature of the substituent on P. $\langle A_V \rangle$ values are found to lie within three ranges: 91–97 G for PR_3 (R = alkyl or aryl), 100–113 G for $P(OR)_3$ (R = Me, Et) or PR_2Cl and for O-donor ligands, and 100–103 G for N-donor ligands. It is tempting to correlate this variation with the nucleophilic character of the donor atom. Furthermore, an important observation in the case of phosphines is the existence of superhyperfine interaction with the phosphorus nucleus. Resolution disappears when phosphorus bears acceptor groups such as Cl or OR. This is accompanied by an appreciable increase of $\langle A_V \rangle$. As was shown earlier, this parameter can be taken as a measure of the extent of unpaired electron delocalization on vanadium ($P \propto 1/r^3$) so that a high value reflects a poorer transfer to the chlorine ligands and as a consequence a lower covalency (or higher ionic character) of the V–Cl bond. Also, the superhyperfine interaction with phosphorus nuclei is operative via a spin polarization mechanism since σ transfer is rather negligible (no π back-bonding). Examination of Table I shows that there is some interdependence between the two parameters. Thus, the lower $\langle A \rangle$ values (about 90 G) are associated with the existence of hyperfine interaction with the ligand nuclei (P, As), and values higher than 100 G are associated with phosphines having electron-withdrawing groups (Cl, OR) and also with N-donor ligands (lower nucleophilicity than phosphines). In the last two cases, hyperfine interaction with the ligand nucleus vanishes. Higher values (about 110 G) are found with O donors, where nucleophilicity is lowest. It seems therefore that strong nucleophiles tend to delocalize unpaired electron density toward the Cl ligands whereas weak nucleophiles leave a higher electron population on the V nucleus. An interesting intermediary situation is when the adduct is formed from VCl_4 with a 1/1 mixture of the ligands PEt_3 + $P(OEt)_3$ (last entry in the first part of Table I). The EPR spectrum is composed of a set of doublets instead of the triplets with $EpEt_3$, which obviously indicates superhyperfine interaction with only one phosphorus nucleus, very probably belonging to the PEt_3 ligand. On the basis of these considerations, the compound formed is assumed to be the mixed-ligand adduct VCl_4·PEt_3·$P(OEt)_3$; the $\langle A \rangle$ value (100.5 G) lies roughly between that of the bis(triethylphosphine) (91.0 G) and the bis(triethyl phosphite) (113.5 G) adducts.

The second conclusion is that there is little, if any, observable effect among the alkylphosphines themselves on $\langle A \rangle$ with respect to their nucleophilic characters or their cone angles.[22] Thus, PMe_3 with a cone angle of 118° has an A value close to that of PCy_3 with a cone angle of 170° and somewhat lower than $P(t\text{-}Bu)_3$ (cone angle 182°). This A value is not very different from that of PPh_3, known to be a rather poor nucleophile, so that correlation of phosphine basicities can be still a subject of unending debate, as was also reported lately on results based on UV photoelectron studies, where it was concluded that the lone pair ionization energies tend to show that the trend in PMe_3 (8.62 eV) versus PPh_3 (7.80 eV) is opposite that predicted from electronegativity considerations.[23]

It should be added that a general dependence of EPR line width on ligand bulkiness was effectively observed with these compounds along the same lines as was reported earlier.[17]

Further studies on the chemistry of these compounds are under way, with a special effort toward X-ray structural determinations when possible.

Registry No. VCl_4·$2PMe_3$, 114551-84-7; VCl_4·$2PEt_3$, 73079-35-3; VCl_4·$2PMePh_2$, 114551-85-8; VCl_4·$2PEtPh_2$, 114551-86-9; VCl_4·$2PPh_3$, 114611-84-6; VCl_4·$2P(i\text{-}Pr)_3$, 114551-87-0; VCl_4·$2P(t\text{-}Bu)_3$, 114551-88-1; VCl_4·$2P(Cy)_3$, 114551-89-2; VCl_4·$2P(Ph)(OEt)_2$, 114551-90-5; VCl_4·$2P(t\text{-}Bu)_2Cl$, 114551-91-6; VCl_4·$2P(OEt)_3$, 114611-85-7; VCl_4·$P(OEt)_3$·PEt_3, 114551-92-7; VCl_4·$2AsMe_3$, 114551-93-8; VCl_4·2py, 114611-86-8; VCl_4·2(3-Etpy), 107459-91-6; VCl_4·2(4-(t-Bu)py), 114551-94-9; VCl_4·$2NMe_3$, 114611-87-9; VCl_4·2THF, 114611-88-0; VCl_4·2Diox, 114551-95-0; VCl_4·2PhCOPh, 114551-96-1; $VOCl_2$·$2OPPh_3$, 68510-48-5; $VOCl_2$·2(3-Etpy)·H_2O, 107444-32-6.

---

(16) Olivê, G. H.; Olivê, S. *Angew. Chem.* **1970**, *24*, 955.

(17) Olivê, G. H.; Olivê, S. *J. Am. Chem. Soc.* **1971**, *93*, 4154.

(18) Olivê, G. H.; Olivê, S. *J. Chem. Soc. D* **1969**, 596.

(19) McCormick, J.; Featherstone, J. L.; Stoklosa, H. J.; Wasson, J. R. *Inorg. Chem.* **1973**, *12*, 592.

(20) Wayland, E. B.; Abdel-Mageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 4809.

(21) (a) Raynor, J. B.; Nye, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 504. (b) Labauze, G.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1980**, 590, 2388.

(22) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(23) Puddephatt, R. J.; Bancroft, G. M.; Chan, T. *Inorg. Chim. Acta* **1983**, *73*, 83.