lution at around 70–80 °C, the following reaction takes place:

$$\mathrm{RuX_2(\beta\text{-}dk)L_2 + py \xrightarrow{80\ ^\circ C} RuX_2(\beta\text{-}dk)L(py) + L}$$

This reaction is quite interesting because this suggests the stereochemistry as proposed in Figure 3 and shows the presence of loosely bound phosphine or arsine in these molecules. It is interesting to note that molecules of the type MX_3L_3 also have loosely bound PPh_3 or $AsPh_3$ ligands and dissociate in solution:

$$\mathrm{MX_3L_3 \rightarrow MX_3L_2 + L}$$

The reason for this lability is trans influence and/or steric effect of the bulky PPh_3 (or $AsPh_3$) groups. The role of such loosely bound ligands in a complex will be to distort the molecules from the idealized geometry—a fact confirmed by the EPR results in Tables II and III. Such molecules are likely to be highly reactive because they are in the so-called[29] entatic state (a term which refers to similar situation for metal ions in an enzyme).

For molecules with three distinct components we found two solutions a and b, where the results are not very much different from each other. The highest lying orbital is d_{xy}, and the ground state may be either (a) d_{yz} or (b) d_{xz}. It is not possible to decide between the two possibilities. However, it was possible to distinguish between the facial and meridional isomers of $RuCl_3(AsPh_3)_3$. The facial isomers have C_{3v} symmetry. On the basis of the trigonal model,[28] the hole is in the $t_2{}^0(d_{z^2})$ orbital, leaving d_{xz}, d_{yz} lowest. The electronic configuration is $(e)^4(a_1)^1$ which implies a ^2A ground term. The meridional isomers show rhombic distortion ($g_x \neq g_y \neq g_z$). There is a significant difference between the relative d-orbital energies of the facial and meridional isomers (Table IV). The large difference in the value of k in these two isomers cannot be given any simple interpretation.

Conclusion

In this paper we have presented experimental results of a large number of Ru(III) complexes containing triphenylphosphine or triphenylarsine as one of the ligands. The results show a large axial distortion and a ^2B (or an ^2A) ground term for these complexes. The low-symmetry ligand field component is larger than the spin–orbit coupling constant ($\Delta > \lambda$). There may be two contributing factors for the large axial distortion: (1) a geometric factor and (2) anisotropy in the covalent bonding.[2] The anisotropy in covalent bonding probably plays an important role in distorting the molecules. Unfortunately it was not possible to estimate covalency because of the possible influence of CI and CT states.

The present ligand field model for interpreting the magnetic data was not quite successful in estimating the orbital reduction factor. From the EPR and magnetic susceptibility data it was felt that inclusion of configurational and charge-transfer mixing into the theory is worthy of further attention.

Registry No. *fac*-$RuCl_3(AsPh_3)_3$, 72747-39-8; *mer*-$RuCl_3(AsPh_3)_3$, 61769-11-7; $RuCl_3(AsPh_3)_2(OAsPh_3)$, 61730-99-2; *mer*-$RuBr_3(AsPh_3)_3$, 72747-40-1; $RuBr_3(AsPh_3)_2CH_3OH$, 15692-69-0; $RuBr_3(PPh_3)_2CH_3OH$, 15692-71-4; $RuCl_2(acac)(AsPh_3)_2$, 72747-41-2; $RuCl_2(dbm)(AsPh_3)_2$, 72747-42-3; $RuCl_2(ba)(AsPh_3)_2$, 72747-43-4; $RuCl_2(acac)(PPh_3)_2$, 72747-33-2; $RuCl_2(ba)(PPh_3)_2$, 72748-18-6; $RuBr_2(acac)(AsPh_3)_2$, 72747-34-3; $RuBr_2(ba)(AsPh_3)_2$, 72747-35-4; $RuBr_2(acac)(PPh_3)_2$, 72747-36-5; $RuBr_2(dbm)(PPh_3)_2$, 72747-37-6; $RuBr_2(ba)(PPh_3)_2$, 72747-38-7; $RuCl_2(dbm)(PPh_3)(py)$, 72692-65-0; $RuCl_2(dbm)(AsPh_3)(py)$, 72708-36-2; $RuBr_3(AsPh_3)_3$, 63632-06-4.

---

[29] B. L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. U.S.A.*, **59**, 498 (1968); *Chem. Br.*, **4**, 397 (1968).

Contribution from the Laboratoire de Chimie Organique
Industrielle ENSCP LA 161, 75005 Paris, France,
and the Laboratoire de Spectrochimie du Solide LA 302,
Université P. et M. Curie, 75005 Paris, France

Phosphane Adducts with Vanadium, Niobium, and Tantalum Tetrachlorides: Synthesis and Study by Electron Spin Resonance

Gérard Labauze, Edmond Samuel,* and Jacques Livage

Received October 26, 1979

A large number of transition-metal halides are known to give molecular adducts of well-defined stoichiometry with a variety of phosphorus-donor ligands such as phosphanes or phosphites. These compounds are of great interest as precursors in the synthesis of highly reactive low-valent metal complexes whose role in homogeneous catalysis and activation of chemically inert molecules is not to be emphasized. Surprisingly, phosphane adducts of the vanadium group did not appear to receive hitherto much attention.[1–3] It is noteworthy that ESR methods are particularly well adapted for their study because of their simple electronic configuration (d^1) and the high isotopic ratio of the metal having a nuclear magnetic moment.

Earlier we reported[4] that $NbCl_4$ coordinates with two molecules of PR_3 (R = *n*-butyl, isobutyl) to form $NbCl_4{\cdot}2PR_3$ adducts of octahedral geometry, well characterized from their room- and low-temperature ESR spectra. We report here[5] on the formation of adducts of the general formula $MCl_4{\cdot}2Pr_3$ (M = V, Nb, Ta; R = ethyl) and show that significant information can be obtained from ESR and UV–visible spectra about their molecular geometry and ligand–metal interaction, allowing comparison to be made in a homogeneous series of compounds going down the periodic table. Furthermore, our results report on what to our knowledge is the first example of metal–ligand interaction detectable by ESR in a third-row transition-metal compound.

Experimental Section

All manipulations were performed under argon. Commercial VCl_4 (Alfa Inorganics) was used without further purification. $NbCl_4$ and $TaCl_4$ were prepared by the reduction of the respective pentahalides with aluminum foil according to literature methods. ESR spectra were recorded on a JEOL ME 3X X-band spectrometer with Bruker B-A6 accessory for field calibration. UV-visible spectra were recorded on a Cary 14 spectrometer in toluene solutions.

Results and Discussion

Vanadium and niobium tetrachlorides react with stoichiometric amounts (1:2) of triethylphosphine in toluene, and tantalum tetrachloride reacts with excess phosphine (as solvent, the reaction does not appear to take place in toluene) to yield colored solutions whose study by ESR reveals the nature of the species formed. The solution spectra at room temperature (Figure 1) are well resolved and exhibit hyperfine splitting due to interaction of the unpaired electron with the metal nuclei (^{51}V, ^{93}Nb, and ^{181}Ta) as well as superhyperfine splitting (for V and Nb only) due to interaction with two ^{31}P nuclei of the phosphane ligands. At −130 °C the frozen solution spectra display features due to parallel and perpendicular components indicative of axially symmetric molecular geometry and patterns which suggest the formation of 1:2 adducts in all three compounds. Phosphorus superhyperfine splitting is neatly resolved on both the high- and the low-field parallel components of the vanadium compound and only on the low-field part in the niobium and tantalum compounds. The ESR

---

*To whom correspondence should be adressed at the Laboratoire de Chimie Organique Industrielle ENSCP, Paris.

0020-1669/80/1319-1384$01.00/0

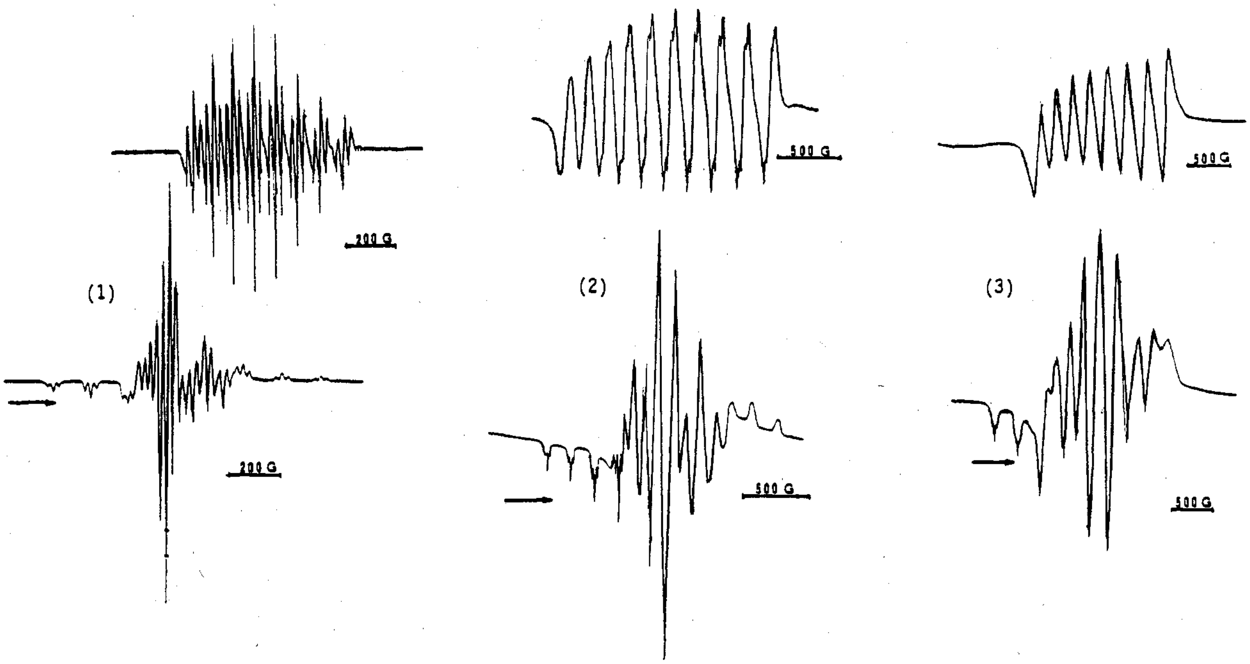


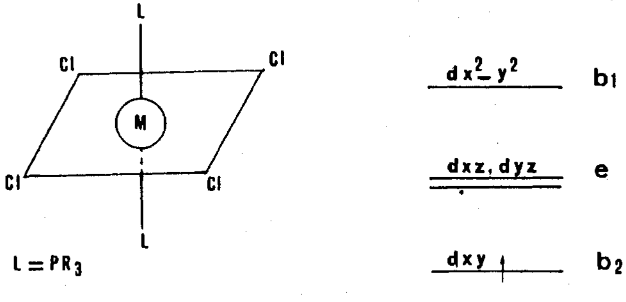
Figure 1. ESR spectra of (1) $VCl_4 \cdot 2PR_3$ in toluene, (2) $NbCl_4 \cdot 2PR_3$ in toluene, and (3) $TaCl_4 . 2PR_3$ in PR_3 ($R = C_2H_5$) in fluid (upper spectra) and frozen (lower spectra) solutions.

Table I. ESR Parameters of $MCl_4 \cdot 2PR_3$ Compounds

	V	Nb	Ta
$g_\parallel$	1.972	1.959	1.831
$g_\perp$	1.985	1.912	1.695
g_{iso}	1.981	1.927	1.740
$A_\parallel$,[a] G	163	218.5	285
$A_\perp$, G	55	103	174
A_{iso}, G	91	141.5	211
$a_\parallel$,[b] G	25.6	23.6	25
$a_\perp$,[c] G	27	26.3	
a_{iso},[c] G	26.5	25.4	

[a] Hyperfine interaction constants relative to metal. [b] Hyperfine interaction constants relative to ^{31}P. [c] a_{iso} and $a_\perp$ could not be measured for tantalum.

Scheme I



parameters are gathered in Table I.

From these spectra it can be deduced that in all cases the molecular symmetry is approximately D_{4h} with the unpaired electron residing in a b_{2g} (d_{xy}) orbital (Scheme I). The other possibility that it occupies the degenerate e_g orbital is excluded since relaxation time would be too short for resolution to be observable at room temperature.

Table II. UV-Visible Absorption Bands of $MCl_4 \cdot 2PR_3$ (M = V, Nb) in Toluene

compd	$\Delta E(b_1 \leftarrow b_2)$, nm	$\delta E(e \leftarrow b_2)$, nm	δ/Δ
$VCl_4 \cdot 2PR_3$	16 050	12 900	0.80
$NbCl_4 \cdot 2PR_3$	15 000	8 440	0.56

The g values of an unpaired electron in a b_{2g} orbital are given by

$$g_\parallel = g_e - \frac{8\lambda}{\Delta E(b_1\text{–}b_2)} + \frac{8\lambda}{\Delta E(b_2\text{–}b_{1L})}$$

$$g_\perp = g_e - \frac{2\lambda}{\delta E(e\text{–}b_2)}$$

where $g_e = 2.0023$ and b_{1L} is the bonding "b_1" orbital mainly of ligand character; λ is the spin–orbit coupling parameter of the metal ion in the complex. From Table I the following remarks can be made: (1) The g values decrease when going from vanadium to tantalum. This can be mainly attributed to the increase with the atomic number of the spin–orbit coupling parameter[6] (250 cm^{-1} for V^{4+}, 750 cm^{-1} for Nb^{4+}, and 1400 cm^{-1} for Ta^{4+}). (2) In the vanadium complex, $g_\parallel < g_\perp$ whereas in the niobium and tantalum compounds $g_\parallel > g_\perp$. The latter situation has already been observed for Nb^{4+} compounds and is due to a $g_\parallel$ shift arising from the fact that the b_{1L} level is close to b_2. This effect can also be enhanced by the axial distortion along the C_4 axis. If we write

$$g_e - g_\perp = 8\lambda/\delta$$

then the smaller the tetragonal distortion (for a given value of λ) the larger the difference $g_e - g_\perp$. The $g_\perp$ value increases with $\delta E(e\text{–}b_2)$ and may exceed $g_\parallel$ if δ/Δ is large enough. Such a behavior has been observed in many compounds containing V^{4+} in a more or less distorted symmetry. This interpretation is in agreement with the electronic absorption spectra which

---

(1) Fairbrother, F. "The Chemistry of Niobium and Tantalum"; Elsevier: Amsterdam, 1967.
(2) Kepert, D. L. "The Early Transition Metals"; Academic Press: New York, 1972.
(3) Clark, R. J. H. "The chemistry of Titanium and Vanadium"; Elsevier: Amsterdam, 1968.
(4) Samuel, E.; Labauze, G.; Livage, J. *Nouv. J. Chim.* **1977**, *1*, 93.
(5) Preliminary results were reported at the Xth International Conference on Electron Spin Resonance of Transition Metal Ions, Nottingham, 1979.
(6) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*.

give a measure of $\delta E(\mathrm{e{-}b_2})$ and $\Delta E(\mathrm{b_1{-}b_2})$. The results obtained for vanadium and niobium compounds are given in Table II. (3) The A values increase progressively from V to Ta. This variation does not seem to be related to the dipolar part of the hyperfine coupling, the anisotropic components ($A_{\parallel} - A_{\mathrm{iso}}$) and ($A_{\perp} - A_{\mathrm{iso}}$) being almost constant throughout the series, but seems to be rather due to the Fermi contact term which increases when going down the periodic table.[7] It is also possible to determine the correct signs of the A parameters using the analysis of Fortman.[8] The unpaired electron is in an orbital perpendicular to the symmetry axis and the nuclear magnetic moment is positive for the three elements ^{51}V, ^{91}Nb, and ^{181}Ta; it follows that the anisotropic splitting component A_{p} is negative.[9] The isotropic splitting A_{iso} is negative also since the nuclear magnetic moment is positive and also because the 4s contribution to the hyperfine splitting is small due to nonmixing with the 4s and the d_{xy} orbitals. With the experimental A values (see Table I) and the relationship $A_{\mathrm{iso}} = {}^1/_3(A_{\parallel} + 2A_{\perp})$, $A_{\parallel}$, $A_{\perp}$, and A_{iso} are all of the same sign, and from the above results they are all negative for the three compounds ($A_{\parallel} = 2A_{\mathrm{p}} + A_{\mathrm{iso}}$ and $A_{\perp} = A_{\mathrm{iso}} - A_{\mathrm{p}}$). (4) The line width of the solution ESR spectra increases considerably from vanadium to tantalum (20, 60, and 70 G for V, Nb, and Ta, respectively). This could be due to a nonresolved quadrupole coupling which is particularly large in tantalum, the quadrupole moment being 10 times larger than that for vanadium and niobium. An additional factor is the increase in the molecular volume when going down the series, the molecular tumbling correlation time being dependent on the molecular size of the complex. Another interesting observation is that the line width variation with M_{I} within the same spectrum does not follow the same behavior in the three complexes. For vanadium the broader line lies on the high-field side of the spectrum, whereas the reverse effect is observed for niobium and tantalum.

According to Kivelson,[10,11] the line width $1/T^2$ in the case of rapid tumbling is related to the nuclear spin parameter number by the relation

$$1/T^2 = \frac{\tau_{\mathrm{c}}(g_{\mathrm{b}}\beta H + bM_{\mathrm{I}})^2}{\hbar^2} \qquad (1)$$

where τ_{c} is the correlation time of the molecular tumbling, $g_{\mathrm{b}} = {}^1/_3(g_{\parallel} - g_{\perp})$ and $b = {}^1/_3(A_{\parallel} - A_{\perp})$. The smaller line width should occur for that value of M_{I} which minimizes the expression within the parentheses in eq 1. The main difference between the three compounds arises from the fact that for vanadium g_{b} is negative while it is positive for niobium and tantalum. This may account for the difference observed in the variation of line width with M_{I}.

A well-resolved superhyperfine structure is observed on the ESR spectra of the vanadium compound, showing that the 3d electron is interacting with two equivalent phosphorus nuclei. This hyperfine splitting is less neatly resolved in the case of niobium, and for tantalum it is only visible on the frozen solution spectrum. This of course is due to line width variation which increases down the series.

The superhyperfine coupling parameters (a) for the three compounds keep a virtually constant value throughout the series and are almost isotropic, showing that they mainly involve "s" orbital electron density. They are also rather low, showing weak interaction of the unpaired electron with phosphorus.

An electron transfer from the d_{xy} metal orbital toward the "σ" phosphorus orbital cannot account for the observed superhyperfine coupling. It would be forbidden anyway by symmetry considerations, the "σ" orbitals being orthogonal to the $\mathrm{b_{2g}}$ molecular orbitals. A spin polarization of the "σ" doublet by the unpaired 3d electron would give a more satisfactory model for the superhyperfine coupling mechanism.

The reactions of these tetrahalides with other phosphines of varying basicity and correlation of this basicity with the ESR parameters will be described in a forthcoming publication.

Registry No. $\mathrm{VCl_4}$, 7632-51-1; $\mathrm{NbCl_4}$, 13569-70-5; $\mathrm{TaCl_4}$, 13569-72-7; $\mathrm{VCl_4{\cdot}2PEt_3}$, 73079-35-3; $\mathrm{NbCl_4{\cdot}2PEt_3}$, 73135-97-4; $\mathrm{TaCl_4{\cdot}2PEt_3}$, 73079-36-4.

---

[7] Freeman, A. J.; Watson, R. E. In "Magnetism"; Academic Press: New York, 1965; Vol. IIA.

[8] Fortman, J. J.; Hayes, R. G. *J. Chem. Phys.* **1965**, *43*, 15.

[9] $A_{\mathrm{p}} = {}^2/_7 g_{\mathrm{e}} g_{\mathrm{N}} \beta_{\mathrm{e}} \beta_{\mathrm{N}} \langle 1/r^3 \rangle$.

[10] Wilson, R.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 154, 4440.

[11] Atkins, P. W.; Kivelson D. *J. Chem. Phys.* **1966**, *44*, 169.

Contribution from the Laboratoire d'Electrochimie et de Chimie
Physique du Corps Solide, E.R.A. au CNRS No. 468, and
the Laboratoire de Chimie Organique Physique,
E.R.A. au CNRS No. 265, Université Louis Pasteur,
67000 Strasbourg, France

Redox Behavior of a Dinuclear Copper Cryptate: A Dielectronic Receptor Site

J. P. Gisselbrecht,[1a] M. Gross,*[1a] A. H. Alberts,[1b]
and J. M. Lehn[1b]

Received April 24, 1979

Several recent papers[2–5] have been devoted to the analysis of the redox behavior of dinuclear copper(II) complexes, in the hope to clarify or to replicate the oxido-reductive function of copper proteins. Depending upon the ligand, the reduction into the corresponding Cu(I) complexes occurs via two successive and distinct monoelectronic steps[2a,4,5] or in a unique dielectronic step involving two monoelectronic transfers of identical standard potential.[2b,3] This last system[2b,3] is the only example known up to now in which a dinuclear Cu(II) complex is reversibly reduced to the corresponding dinuclear Cu(I) species by two monoelectronic steps which are simultaneous on the macroscopic time scale of the electrochemical measurements (i.e., identical values of $E_{1/2}$). However, with one exception,[5] all the above complexes involve oxygen-bridged Cu(II) cations. Thus, the two Cu(II) are not structurally independent, and it is therefore not surprising that the two $E_{1/2}$ potentials, corresponding to their successive reductions to the dinuclear species (Cu(II), Cu(I)) and (Cu(I), Cu(II)), differ by values ranging from 0[2b,3] to several tens or hundreds of millivolts[2a,4,5] depending on the ligand. Furthermore these complexes[2–5] exhibit standard redox potentials E_0 at least 600 mV more negative than the standard redox potentials characterizing the copper proteins.[6]

The synthesis and the properties of a new macrocyclic ligand and of its Cu(II) dinuclear complex,[7] as well as its structure,[8] have been recently reported. Complexation of Cu(II) by this macrotricyclic ligand (1,7,13,19-tetraaza-4,16-dioxa-

---

[1] (a) Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide. (b) Laboratoire de Chimie Organique Physique.

[2] (a) A. W. Addison, *Inorg. Nucl. Chem. Lett.*, **12**, 899 (1976); (b) D. E. Fenton, R. R. Schroeder, and R. L. Lindtvedt, *J. Am. Chem. Soc.*, **100**, 1931 (1978).

[3] D. E. Fenton and R. L. Lindtvedt, *J. Am. Chem. Soc.*, **100**, 6367 (1978).

[4] R. R. Gagne, C. A. Koval, and T. J. Smith, *J. Am. Chem. Soc.*, **99**, 8367 (1977).

[5] G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, **4**, 257 (1975).

[6] J. A. Fee, *Struct. Bonding (Berlin)*, **23**, 1 (1975).

[7] A. H. Alberts, R. Annunziata, and J. M. Lehn, *J. Am. Chem. Soc.*, **99**, 8502 (1977).

[8] R. Louis, Y. Agnus, and R. Weiss, *J. Am. Chem. Soc.*, **100**, 3604 (1978).

0020-1669/80/1319-1386$01.00/0