264. 2,2′-*Bipyridyl and* o-*Phenanthroline Complexes of Titanium*(IV) *and Vanadium*(IV).

By R. J. H. CLARK.

Complexes of the type MCl_4,L (M = titanium(IV) or vanadium(IV); L = 2,2′-bipyridyl or *o*-phenanthroline) have been prepared and their properties investigated. They are very readily hydrolysed; while the vanadium complexes form stable products of empirical formula $VOCl_2,L$, the titanium analogues appear to yield products of indefinite composition. The infrared and visible spectra of the complexes have been recorded between 200 and 30,000 cm.$^{-1}$. The metal–chlorine stretching vibrations are at ~370 cm.$^{-1}$, the vanadium–oxygen stretching vibrations at 890 cm.$^{-1}$, and the *d–d* electronic transitions of vanadium(IV) are located and assigned. The magnetic moments of the vanadium(IV) complexes are close to the spin-only value of 1·73 B.M.; in particular, those of the pseudo-octahedral complexes VCl_4,L have been determined between 300° and 80°K, in order to ascertain the distortion from octahedral of the ligand field about the vanadium(IV) ions.

TITANIUM TETRACHLORIDE forms a wide variety of adducts with ethers, furans, alcohols, ketones, esters, nitriles, amides, etc. These compounds are usually either 1 : 1 or 1 : 2 adducts; the latter are six-co-ordinate monomers, but the former may be either five-co-ordinate monomers or six-co-ordinate dimers, *e.g.*, as in the compound $[TiCl_4,POCl_3]_2$.[2]

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[1] Gmelin, " Handbuch der Anorganischen Chemie—Titan," Verlag Chemie, Leipzig, 1951.

[2] Bränden and Lindquist, *Acta Chem. Scand.*, 1960, **14**, 726.

Eight-co-ordination for titanium(IV) and vanadium(IV) has now also been established for bidentate arsine complexes of titanium and vanadium tetrahalides.[3]

The stability of adducts of titanium tetrachloride with nitrogen-donor ligands appears to be less than that of adducts with oxygen-donor ligands. This may be because the lower electronegativity of a nitrogen atom than of an oxygen atom renders the former more susceptible to the polarizing power of the titanium(IV) atom. Thus, while alcohols form simple adducts with titanium tetrachloride, primary or secondary amines eliminate hydrogen chloride after initial co-ordination of the amine.[4] With tertiary amines, it is even possible for partial reduction of titanium(IV) to titanium(III) to occur, *e.g.*, to produce the compound [5] $(Me_3N)_2TiCl_3$. Vanadium tetrachloride behaves similarly with an excess of tertiary amine,[6] and with ammonia to produce the compound $VCl(NH_2)_3$.

The reactions of vanadium tetrachloride with electron-donor ligands are similar to those of titanium tetrachloride but are less well investigated. Few simple addition compounds, *e.g.*, of the type $VCl_4,2CH_3\cdot CN$, have been reported.[7] Instead, elimination reactions appear to be more prevalent, *e.g.*, with methanol, the vanadyl complex $VOCl_2,3MeOH$ is produced. Vanadyl complexes, *i.e.*, those containing discrete vanadium–oxygen double bonds, occur much more commonly than the analogous titanyl complexes.[8] Indeed, many of the compounds referred to in Gmelin [1] as titanyl compounds do not contain discrete titanium–oxygen double bonds but consist of chain polymers. Titanyl sulphate is an example in point, in which an *X*-ray investigation has demonstrated the existence of metal–oxygen–metal chains.[9]

The reactions of the bidentate ligands 2,2′-bipyridyl (bipy) and *o*-phenanthroline (phen) with titanium and vanadium tetrachlorides do not appear yet to have been reported, although it is well known that these ligands co-ordinate with a large number of transition and non-transition elements in several valency states to form complexes of relatively high stability. In Group IVB, germanium tetrachloride is reported to form the monomeric adducts [10] $GeCl_4$,bipy and $GeCl_4$,phen and stannic chloride [11] to form $SnCl_4$,bipy. Titanium and vanadium tetrachlorides react with the appropriate ligands in an inert solvent to give immediate precipitates of complexes which are non-electrolytes of general formula MCl_4,L. Hydrolysis of the vanadium complexes yields products of formula $VOCl_2$,L, but hydrolysis of the titanium analogues does not yield specific products.

The complexes of the type VCl_4,L are of particular spectroscopic and magnetic interest. Under the action of an octahedral ligand field the ^2D ground term of vanadium(IV) is split into a lower lying $^2T_{2g}$ term and an upper ^2E_g term. The non-equivalence of the six ligands introduces at least a tetragonal component to the ligand field, which has the effect of splitting the $^2T_{2g}$ term into the terms $^2B_{2g}$ (usually lower lying) [12] and ^2E_g, and the ^2E_g term into $^2A_{1g}$ and $^2B_{1g}$ (in the nomenclature for D_{4h} symmetry).[13] The actual symmetry of the ligand field is lower than D_{4h} (C_{2v} in fact) and this will result in a slight splitting of the ^2E_g term derived from the $^2T_{2g}$ term. Two transitions are thus expected in the visible region $^2A_{1g} \leftarrow {}^2B_{2g}$ and $^2B_{1g} \leftarrow {}^2B_{2g}$, from the positions of which the asymmetric component to the ligand field about the excited vanadium(IV) ion may be estimated. The separation between the levels derived from the $^2T_{2g}$ ground term may be estimated

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[3] Clark, Lewis, Nyholm, Robertson, and Pauling, *Nature*, 1961, **192**, 222; Clark, Lewis, and Nyholm, *J.*, 1962, 2460.

[4] Cowdell and Fowles, *J.*, 1960, 2522.

[5] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[6] Fowles and Pleass, *J.*, 1957, 1674; Fowles and Nichols, *J.*, 1958, 1687.

[7] Funk, Mohaupt, and Paul, *Z. anorg. Chem.*, 1959, **302**, 199.

[8] Ballhausen and Gray, *Inorg. Chem.*, 1962, **1**, 111.

[9] Lundgren, *Arkiv Kemi*, 1957, **10**, 397.

[10] Lebedev and Tronev, *Russ. J. Inorg. Chem.*, 1960, **5**, 837.

[11] Allison and Mann, *J.*, 1949, 2915.

[12] Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.

[13] Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.

from a measurement of the magnetic moment of the complex between 300° and 80°K.[14] The data are compared with those obtained previously for other d^1 systems.[12]

The magnetic and spectroscopic properties of complexes of the type $VOCl_2$,L are also of considerable interest, for the presence of discrete metal–oxygen double bonds probably implies a large tetragonal component to the ligand field, leading to a characteristic absorption spectrum [8] and a magnetic moment close to the spin-only value of 1·73 B.M. The vanadium–oxygen stretching frequency has been located, as well as the metal–chlorine stretching frequencies.

RESULTS AND DISCUSSION

Infrared Spectra.—The infrared spectra of the complexes have been recorded between 4000 and 200 cm.$^{-1}$ and are consistent with the presence of co-ordinated bipyridyl and co-ordinated phenanthroline.[15] In particular, the strong band at 756 cm.$^{-1}$ in free bipyridyl, associated with the out-of-plane deformation vibration of the two equivalent sets of four adjacent hydrogen atoms in this molecule,[16] is split on co-ordination, as are many other bands. Similarly, the out-of-plane hydrogen deformation vibrations of free phenanthroline at 734 and 841 cm.$^{-1}$ are modified on co-ordination.

TABLE 1.

Infrared spectra of complexes (cm.$^{-1}$).

Bipyridyl		756;			
$TiCl_4$,bipy		764, 726;		384, 366;	(307)
VCl_4,bipy		765, 726;		366, 356;	(301)
$VOCl_2$,bipy	890;	765, 729;		371	
Phenanthroline		855, 841;	734;		
$TiCl_4$,phen		868, 848;	734, 718;	379, 356;	(303)
VCl_4,phen		871, 850;	737, 720;	380, 361;	(298)
$VOCl_2$,phen	890;	872, 845;	737, 720;	366;	
Assignment	V=O;	out-of-plane H deformation vibrations		M–Cl	

The vanadium–oxygen stretching frequencies in the vanadyl complexes are located at 890 cm.$^{-1}$ (see Table 1). The bands are sharp and very strong and in the region expected for metal–double bond–oxygen stretching frequencies,[17] *e.g.*, this band occurs at 995 cm.$^{-1}$ for vanadyl bisacetylacetone, which is known to be a tetragonal pyramid with a unique vanadium–oxygen double bond,[18] and at 1035 cm.$^{-1}$ for the monomeric vanadyl trichloride.[17]

The metal–chlorine stretching vibrations are strong and located in the vicinity of 370 cm.$^{-1}$. For compounds of the type MCl_4,L, group C_{2v}, the four M–Cl stretching vibrations are classified as $2A_1 + B_1 + B_2$ and are thus all infrared-active. Similarly, in the complexes of the type $VOCl_2$,L, group C_s, the two M–Cl vibrations transform as $A' + A''$ and are thus both infrared-active. For the former class of compounds, two strong bands are readily observable in the 390—360 cm.$^{-1}$ region and are presumed to be two of the asymmetric M–Cl vibrations. Thus they lie ~80 cm.$^{-1}$ above the asymmetric M–Cl vibration (T_2) of complexes containing tetrahedral MCl_4^{2-} anions.[19] The compound VCl_4,bipy shows a further weak shoulder at 384 cm.$^{-1}$, and all four compounds have a weak band in the region 310—300 cm.$^{-1}$ which may be one of the symmetric M–Cl stretching vibrations, these being expected to be weaker than the asymmetric bands. The M–Cl vibrations in the compounds $VOCl_2$,bipy and $VOCl_2$,phen are sharp and occur at 371 and 366 cm.$^{-1}$, respectively. A weak band in the 300 cm.$^{-1}$ region also occurs for this class of compound.

[14] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198, 204.
[15] Schilt and Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.
[16] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 77.
[17] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.
[18] Dodge, Templeton, and Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.
[19] Clark and Dunn, *J.*, 1963, 1198.

Bipyridyl itself has a weak band at 429 cm.$^{-1}$ and a stronger one at 403 cm.$^{-1}$; phenanthroline has bands at 431w, 408m, 259m, and 241s cm.$^{-1}$; these bands are modified somewhat on co-ordination, but can be identified and do not interfere with the M–Cl assignments.

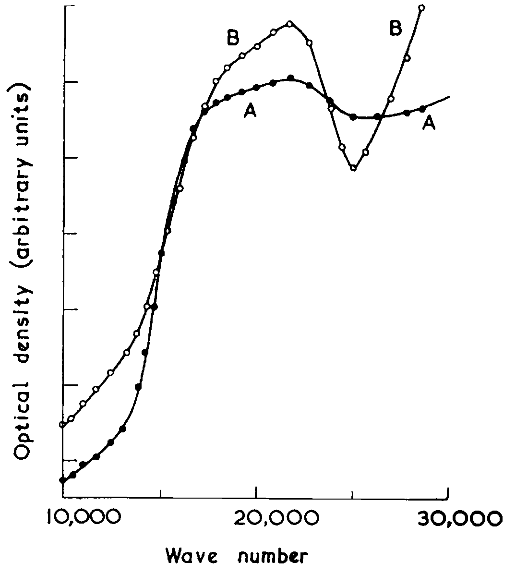

FIG. 1.

FIG. 1. Diffuse reflectance spectra of (A) VCl_4,bipyridyl and (B) VCl_4,phenanthroline.

Spectra of (FIG. 2) $VOCl_2$,bipyridyl and (FIG. 3) $VOCl_2$,phenanthroline (A) by diffuse reflectance and (B) in ethanol solution.

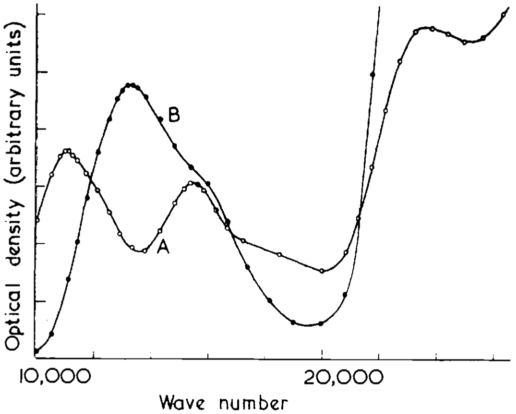

FIG. 2.

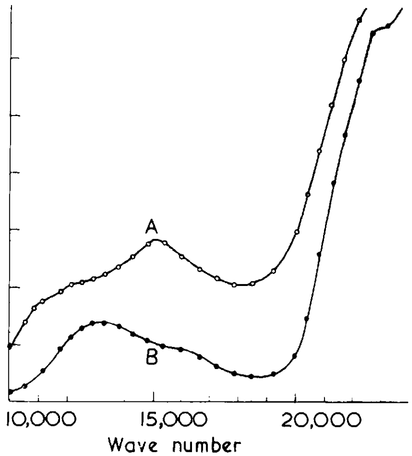

FIG. 3.

Visible Spectra (MCl_4,L).—The compounds $TiCl_4$,L are very pale yellow, and, having no *d*-electrons, are of little interest to ligand-field theory. The analogous vanadium compounds are brown and it is probable that this colour is associated with an electronic transition of the single *d*-electron within the *d*-orbitals. Unfortunately, the compounds are only very slightly soluble in polar solvents (insoluble in non-polar ones) and they decompose in solution before absorption spectra can be recorded. Diffuse reflectance spectra of the solids can, however, be obtained and these are shown in Fig. 1. Both compounds have a broad asymmetric peak in the region 17,000—22,000 cm.$^{-1}$ which is presumed to arise from an electronic transition from the ground term ($^2B_{2g}$) of vanadium(IV)

TABLE 2.

	$^2A_{1g}$	$^2B_{1g}$	δ'
VCl_4,bipy	17,400	21,300	3900
VCl_4,phen	18,000	21,700	3700

to the terms $^2A_{1g}$ and $^2B_{1g}$ derived from the upper ^2E_g term in O_h symmetry. The spectra of the two compounds are remarkably similar. This is, we feel, strong evidence for the above assignment of the bands because in both compounds the vanadium(IV) ion is surrounded by a ligand field of four chloride ions and two nitrogen atoms. It seems unlikely that the change-transfer spectra of the two compounds would be so similar, *e.g.*, the ions Fe(bipyridyl)$_3^{2+}$ and Fe(phenanthroline)$_3^{2+}$ have quite different charge-transfer spectra.[20] The approximate band positions are indicated in Table 2, together with an estimate of the separation of the $^2A_{1g}$ and $^2B_{1g}$ terms (δ') (it is not known which of these two terms is the higher).

The positions of the bands are close to those expected for a vanadium(IV) ion in such a ligand field on the basis of the known positions of chloride, bipyridyl, and phenanthroline in the spectrochemical series and Jørgensen's rule of average environment.[21]

TABLE 3.

	1	2	3
$VOCl_2$,bipy	11,060	15,500	23,500
$VOCl_2$,phen	11,000; 12,000	15,150	23,200
$VO(H_2O)_5^{2+}$	13,000	16,000	

Visible Spectra ($VOCl_2$,L).—The diffuse reflectance spectra of the compounds $VOCl_2$,bipy and $VOCl_2$,phen have been recorded (Figs. 2 and 3). These may be interpreted [8] as spectra of vanadyl complexes (Table 3). Band (1) is interpreted as the $^2E \leftarrow {}^2B_2$ transition for C_{4v} symmetry; it appears to be single for the bipyridyl complex, but is split by ~1000 cm.$^{-1}$ for the phenanthroline complex. Band (2) is the $^2B_1 \leftarrow {}^2B_2$ transition which gives a direct estimate of the value of $10Dq$. The corresponding bands for the $VO(H_2O)_5^{2+}$ molecule ion [8] are given also in Table 3. It is seen from a comparison of the positions of band (1) that the tetragonal component to the ligand field is less in the compounds $VOCl_2$,L than in the $VO(H_2O)_5^{2+}$ ion. The infrared spectra are consistent with this result, for the V=O stretching frequency for the compounds $VOCl_2$,L (890 cm.$^{-1}$) is lower than that found for $VOSO_4,5H_2O$ (~1000 cm.$^{-1}$),[17] and it is the V=O bond which is primarily responsible for the tetragonal component to the ligand field.

It seems probable that the band observed at ~23,500 cm.$^{-1}$ [band (3)] is the $^2A_1 \leftarrow {}^2B_2$ transition; this band, which appears as a shoulder on the side of charge-transfer bands, is found [22] at 29,800 cm.$^{-1}$ for VO(enta)$^{2-}$, at 29,400 cm.$^{-1}$ for VO(oxalate)$_2^{2-}$, and at 25,300 cm.$^{-1}$ for VO(tartrate)$_2^{2-}$.

The compounds are insoluble in non-polar solvents, but are slightly soluble in polar solvents, such as acetone and dioxan and more so in ethanol, acetonitrile, pyridine, and formamide. The absorption spectra of these solutions (*e.g.*, in ethanol, also shown in Figs. 3 and 4) are, however, different from the diffuse reflectance spectra of the original solids. If the latter are five-co-ordinate monomers, it seems probable that the solvent is co-ordinating in the sixth position of the octahedron with concomitant changes in absorption spectrum; if they are six-co-ordinate dimers, with chlorine bridges, it seems equally probable that these bridges are broken on dissolution and six co-ordination is retained by co-ordination of a molecule of the solvent. The absorption peaks of the compound $VOCl_2$,bipy in ethanol occur at 13,300 cm.^{1} ($\varepsilon = 39$), 16,000 cm.$^{-1}$ ($\varepsilon = 25$, shoulder), and 26,800 cm.$^{-1}$ (ε ~500) while those of the compound $VOCl_2$,phen occur at 13,200 cm.$^{-1}$ ($\varepsilon = 35$), 16,000 cm.$^{-1}$ ($\varepsilon = 22$), and 23,000 cm.$^{-1}$ (shoulder). The effects of solvents upon these bands are more appropriately dealt with in a later communication.

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[20] Schläfer, *Z. phys. Chem.* (*Frankfurt*), 1956, **8**, 373.

[21] Jørgensen, 10^e Conseil de l'Institut International de Chimie Solvay, 1956, p. 355.

[22] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

TABLE 4.

Magnetic susceptibility measurements.

VCl_4,bipyridyl		VCl_4,bipyridyl		VCl_4,phenanthroline		VCl_4,phenanthroline	
Temp. (K)	χ(V)	Temp. (K)	χ(V)	Temp. (K)	χ(V)	Temp. (K)	χ(V)
290·4°	1320	151·6°	2215	295·7°	1284	150·5°	2232
266·2	1406	129·7	2574	268·2	1394	130·8	2501
242·8	1516	112·5	2905	244·2	1504	114·0	2843
219·0	1637	97·6	3320	220·0	1636	97·1	3247
195·5	1799	79·5	4006	197·4	1789	81·1	3855
172·0	1995			174·5	1987		

Magnetism (VCl_4,L).—The magnetic moment of the compound VCl_4,bipy at 300°K is 1·77 B.M. and that of VCl_4,phen is 1·76 B.M. These values fall to about 1·60 B.M. at 80°K (Figs. 4 and 5; Table 4). The data over the temperature range have been fitted to the following parameters: [12,14] k, the orbital delocalization factor; v, the distortion of the ligand field from octahedral; λ', the value to which the spin–orbit coupling constant of the free vanadium(IV) ion ($\lambda = 250$ cm.$^{-1}$) [23] is reduced on complex formation; δ, the implied separation between the ^2E_g and $^2B_{2g}$ terms derived from the term ($^2T_{2g}$) which lies lowest for a d^1 system in an octahedral ligand field (Table 5). These magnetic results imply that the bidentate ligand brings about, through its dissimilarity to chloride in perturbing power, a fairly large separation (~1000 cm.$^{-1}$) between the levels derived from $^2T_{2g}$ for octahedral symmetry. The reduction of the spin–orbit coupling constant (~35%) from its free-ion value is similar to that found and discussed previously by Dunn,[24] and is regarded as being due primarily to a σ-electron transfer from the d^2sp^3-bonding orbitals. The reduction in k from unity, which may arise from charge transfer in the opposite direction, *i.e.*, from the d-orbitals of the metal on to the ligands,[14] is only ~10% and scarcely

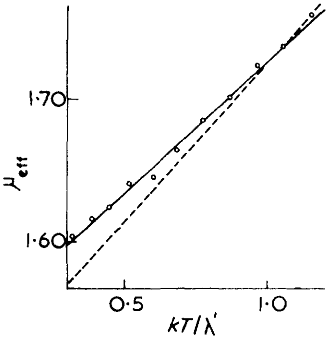

FIG. 4.

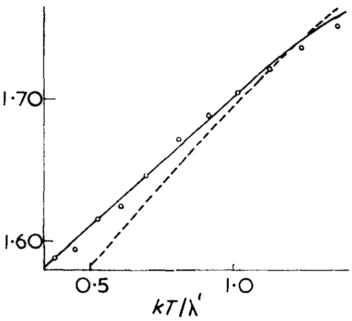

FIG. 5.

FIG. 4. Plot of $\mu_{eff.}$ against kT/λ', with $k = 0·95$, for VCl_4,bipyridyl. Points are experimental; the full line is calculated for $v = 6·3$ (best fit), and the broken line for $v = 5·0$, thus indicating the sensitivity of the method.

FIG. 5. Plot of $\mu_{eff.}$ against kT/λ', with $k = 0·85$, for VCl_4,phenanthroline. Points are experimental; the full line is calculated for $v = 5·0$ (best fit), and the broken line for $v = 4·0$.

TABLE 5.

	v	λ'/λ	k	δ (cm.$^{-1}$)
VCl_4,bipy	6·3	0·7	0·95	1100
VCl_4,phen	5·0	0·6	0·85	750

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[23] Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[24] Dunn, *J.*, 1959, 623.

significant. This is to be expected for a M(IV) complex, in which any charge transfer must surely be towards the metal if the Pauling electroneutrality principle is valid.

The analogous titanium complexes are diamagnetic as expected for d^0 systems:

$$\mathrm{TiCl_4,bipy} \quad 10^6\chi_g = -0{\cdot}375;$$

$$\mathrm{TiCl_4,phen} \quad 10^6\chi_g = -0{\cdot}370.$$

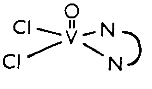
Magnetism ($VOCl_2$,L).—The compounds $VOCl_2$,bipy and $VOCl_2$,phen have magnetic moments of 1·74 and 1·73 B.M., respectively, at 295°K. The values are similar to those found previously for other vanadyl complexes,[8] *e.g.*, vanadyl sulphate pentahydrate μ = 1·73 B.M., vanadyl bisacetylacetone μ = 1·73 B.M., and are to be expected when the orbital contribution to the magnetic moment is completely quenched by the strong tetragonal component to the ligand field.

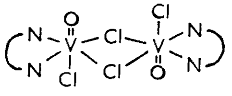
Other Physical Measurements.—*X*-Ray powder photographs of the complexes MCl_4,L have been recorded. The complexes $TiCl_4$,bipy and VCl_4,bipy are isomorphous, and the analogous phenanthroline complexes have closely similar, but not identical, powder patterns.

Two of the complexes MCl_4,L had just sufficient solubility for conductivity results to be obtained. The compound $TiCl_4$,bipy had a conductivity of 0·1 cm.^{2} ohm^{-1} mole^{-1} in $\sim 10^{-3}$ M-solution in nitromethane, while the compound VCl_4,phen had the same conductivity in 9×10^{-3}M-solution in nitrobenzene. The compounds are non-electrolytes, and thus are six-co-ordinate monomers as expected.

General Discussion.—2,2′-Bipyridyl and *o*-phenanthroline react with titanium and vanadium tetrachlorides to give 1 : 1 adducts in which the ligand field about the metal ion is fairly strongly distorted from octahedral in both the ground and the excited state. The distortion in both states is somewhat larger than is found for similar titanium(III) complexes.[12] The analysis of the magnetic data may also be applied to results recently obtained [25] for the compounds vanadium tetrafluoride and potassium hexafluorovanadate, yielding: $k = 0{\cdot}85,\ 0{\cdot}95$; $\lambda' = 0{\cdot}8\lambda$; $v = 1{\cdot}0,\ 1{\cdot}9$; $\delta = 200,\ 380$ cm.$^{-1}$, respectively. The magnetic moment of vanadium tetrafluoride falls to 1·18 B.M. at 80°K; this result could imply that the metal is effectively octahedrally co-ordinated in the solid state with a distortion of only 200 cm.$^{-1}$, as implied above. Alternatively, vanadium tetrafluoride could be tetrahedral, with antiferromagnetic interactions responsible for the lowering of the magnetic moment from the free-ion value of 1·73 B.M. Certainly this molecule cannot consist of magnetically dilute tetrahedra, for it should then exhibit a magnetic moment of 1·73 B.M. at all temperatures consequent upon its single *d*-electron being associated with the non-magnetic ^2E term. The analysis for the hexafluoride yielding a ground-state distortion of 380 cm.$^{-1}$ may be valid, but it is still possible that antiferromagnetic interactions may be partly responsible for the lowering of the magnetic moment with temperature.

From the evidence available it is not possible to decide whether the complexes $VOCl_2$,L are monomeric or dimeric. Molecular-weight measurements would be invalidated by the spectrally obvious change of composition on dissolution of the complexes. Oxygen bridging is ruled out by the existence of the vanadium–oxygen double-bond stretching frequency, but chlorine-bridging cannot be thus eliminated, *e.g.*, the possibilities are:





In either case, the ligand field would be strongly distorted from octahedral, leading to a magnetic moment which tends towards the spin-only value at all temperatures. Thus

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[25] Cavell and Clark, *J.*, 1962, 2692.

magnetic data over a temperature range could not be expected to differentiate between these two structures.

A study of corresponding complexes of zirconium, hafnium, niobium, and tantalum is being undertaken.

EXPERIMENTAL

Spectra.—Absorption spectra were recorded with a Unicam S.P. 500 spectrophotometer and 1 cm. silica cells. Diffuse reflectance spectra were recorded by use of a standard attachment to the above spectrophotometer, and magnesium carbonate as a reference reflector. Infrared spectra were recorded on Grubb-Parsons double-beam grating spectrophotometers, type GS2A for the region 4000—400 cm.$^{-1}$, and type DM2 serial no. 27 for the region 450—200 cm.$^{-1}$. The compounds were made into mulls with both hexachlorobutadiene and Nujol (sodium chloride plates being used) for the former region, and with Nujol and Polythene plates for the latter region.

Magnetic Susceptibilities.—The magnetic susceptibilities of the complexes at room temperature were determined by the Gouy method with glass tubes sealed from the air. The measurements of the relative susceptibilities at different temperatures were made on equipment described previously.[26]

Conductivity.—The equivalent conductivities of the complexes were determined by breaking a tared ampoule of the solid, under nitrogen, into a glass apparatus containing anhydrous and deoxygenated solvent. The electrodes were incorporated in the apparatus.

Powder Photographs.—*X*-Ray powder photographs were taken with a Philips Debye-Scherrer camera of 114·8 mm. diameter and copper-K_α radiation with a nickel filter. The complexes were sealed in Lindemann glass capillaries.

Preparation of Compounds.—British Oxygen Company's " white spot " nitrogen was deoxygenated [27] by being passed through an activated copper column at 280° and dehydrated by being passed through a magnesium perchlorate column. All operations were carried out in an all-glass vacuum system, using this purified nitrogen.

Compounds of the type MCl_4,L were prepared by distilling the appropriate tetrahalide under anhydrous nitrogen into the reaction flask containing the anhydrous ligand dissolved in redistilled benzene or carbon tetrachloride. The precipitates, which were formed immediately, were filtered under nitrogen and dried in a vacuum. When dry, the complexes were sealed in glass manifolds under a vacuum.

Compounds of the type $VOCl_2$,L were prepared by treating those of the type VCl_4,L with a moist solvent. Immediate hydrolysis ensued, and the resulting green stable complexes were dried under a vacuum and sealed in glass manifolds.

Analyses.—Metals were determined by ignition to the oxides. Chloride was determined potentiometrically. Carbon, hydrogen, and nitrogen analyses were carried out by the microanalytical service of this Department. Results were as follows:

Tetrachloro-2,2'-bipyridyltitanium(IV) (Found: C, 34·6; H, 2·6; Cl, 40·7; N, 8·0; Ti, 13·8. $C_{10}H_8Cl_4N_2Ti$ requires C, 34·7; H, 2·3; Cl, 41·0; N, 8·1; Ti, 13·8%).

Tetrachloro-o-*phenanthrolinetitanium*(IV) (Found: C, 38·1; H, 2·2; Cl, 38·7; N, 7·5; Ti, 13·0. $C_{12}H_8Cl_4N_2Ti$ requires C, 38·9; H, 2·2; Cl, 38·3; N, 7·6; Ti, 13·0%).

Tetrachloro-2,2'-bipyridylvanadium(IV) (Found: C, 34·2; H, 3·2; Cl, 40·2; N, 7·8; V, 14·4. $C_{10}H_8Cl_4N_2V$ requires C, 34·4; H, 2·3; Cl, 40·6; N, 8·0; V, 14·6%).

Tetrachloro-o-*phenanthrolinevanadium*(IV) (Found: C, 39·7; H, 3·4; N, 7·5; V, 13·5. $C_{12}H_8Cl_4N_2V$ requires C, 38·6; H, 2·2; N, 7·5; V, 13·7%).

Oxodichloro-2,2'-bipyridylvanadium(IV) (Found: C, 40·6; H, 3·0; Cl, 24·0; N, 9·4; V, 17·1. $C_{10}H_8Cl_2N_2OV$ requires C, 40·8; H, 2·7; Cl, 24·1; N, 9·5; V, 17·3%).

Oxodichloro-o-*phenanthrolinevanadium*(IV) (Found: C, 44·7; H, 2·9; Cl, 22·6; N, 8·8; V, 15·7. $C_{12}H_8Cl_2N_2OV$ requires C, 45·3; H, 2·5; Cl, 22·3; N, 8·8; V, 16·0%).

The author thanks Drs. T. M. Dunn and B. N. Figgis and Professor R. S. Nyholm for helpful discussions.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET,
LONDON, W.C.1.

[*Received, August* 16*th*, 1962.]

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