

Comparative Ligand Field Studies

IV. Vanadium(IV), Titanium(III), Molybdenum(V) and other Systems with one d-Electron

CHR. KLIXBÜLL JØRGENSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

The vanadium(IV) complexes can deviate so much from cubic symmetry that all the four possible bands are observed in the tartrate complex. The absorption spectra of VO en_2^{2-} , VO ox_2^{2-} , VO^{2+} and several other complexes suggest a tetragonal symmetry with stronger ligand field along one axis than along the two other axes. Thus, the oxygen atom is probably placed on the former axis and is not aquated to two hydroxyl ions. The titanium(III) complexes exhibit smaller deviations from octahedral symmetry, corresponding to shoulders on the principal band. The dark coloured binuclear complex, which is formed between Ti(III) and Ti(IV) in concentrated hydrochloric acid, is investigated. In strong HCl, molybdenum(V) occurs as MoOCl_5^{2-} , which exhibits two ligand field bands, corresponding to levels analogous to those of VO^{2+} . The behaviour of one d-electron in ligand fields and the Jahn-Teller effect is compared with the opposite tetragonality of copper(II) complexes. Other oxidation states of molybdenum, wolfram, and niobium, are shortly discussed.

Systems with only one d-electron do not exhibit levels with different values of the spin S , and thus, spin-forbidden bands do not occur as in d^2 — d^8 systems. Further, the integrals F^k of electrostatic interaction between the electrons in the partly filled shell cannot be evaluated; only one multiplet term, 2D , occurs in the gaseous ion. If the splitting between ${}^2D_{3/2}$ and ${}^2D_{5/2}$ is neglected (it amounts to 384 K in Ti^{+3} and 620 K in V^{+4}), only one absorption band is expected of an octahedral complex with the symmetry O_h . One of the historical foundations of the ligand field theory is that Ilse and Hartmann¹ interpreted the band 20 300 K of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ as the transition of the d-electron from the state γ_5 to γ_3 , thus exemplifying the parameter ${}^2\Delta$, also called (E_1 — E_2) or $10 Dq$. However, if the ligand field has a symmetry lower than O_h , more than one absorption band is predicted. Kramers' degeneracy cannot allow more than five energy levels of a single d-electron, corresponding to four absorption bands caused by transitions from the groundstate. The low symmetry of the ligand field is not necessarily caused by differences among

Table 1. Absorption bands of vanadyl complexes. Wavelength λ_n in $m\mu$, wavenumber σ_n in K ($= cm^{-1}$), and molar extinction coefficient ϵ_n of each maximum and the half-widths $\delta(-)$ and $\delta(+)$ in K towards lower and higher wavenumbers. Shoulders are given in parentheses. The ligands are abbreviated: enta⁻⁴ = ethylenediaminetetraacetate, ox⁻² = oxalate, aca⁻ = acetylacetonate, and tart⁻⁴ = tartrate (with four protons removed from D-tartaric acid).

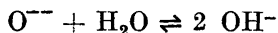
	λ_n	σ_n	ϵ_n	$\delta(-)$	$\delta(+)$
VO ⁺⁺ in 1 M HClO ₄	765	13 100	16.5	1 400	—
	(625)	16 000	7.5	—	1 400
	240	41 700	240	4 600	—
VO ⁺⁺ in 10 M HClO ₄	735	13 600	15.5	—	—
	(635)	15 800	10.5	—	1 500
VO ⁺⁺ in 12 M HCl	728	13 700	18.5	—	2 300
VO ⁺⁺ in 8 M H ₂ SO ₄	750	13 300	18	—	—
VO enta ⁻⁴	780	12 800	23	1 400	—
	582	17 200	19	—	1 400
	(336)	29 800	22	2 000	—
VO ox ₂ ⁻²	792	12 600	25	—	2 200
	605	16 500	9	—	1 700
	(340)	29 400	170	2 000	—
VO aca ₂ in C ₂ H ₅ OH	780	12 800	34	1 400	1 900
	578	17 300	13	—	1 700
VO tart ⁻⁴	910	11 000	22	1 600	1 700
	(587)	17 100	21	1 400	—
	531	18 800	25	—	1 900
VO tart H ⁻	396	25 300	45	2 000	—
	770	13 000	28	—	2 200
	565	17 700	14	—	2 000
VO citrate in 2 M NH ₃	(348)	28 800	30	—	—
	850	11 800	15	—	1 800
	533	18 800	6	—	—
VO SCN ⁺ (Ref. 24)	(416)	24 000	3	—	—
	720	13 900	58	1 700	—
	580	17 200	27	—	1 400

the six ligands of an octahedral complex; the Jahn-Teller effect produces a distortion to lower symmetry³, when the cubic groundstate is either Γ_3 , Γ_4 , or Γ_5 . The latter case of $Ti(H_2O)_6^{+++}$ was discussed by Van Vleck⁴, who found that the absolute value of the distortion was not large. The present paper demonstrates that the effect is more important for vanadium(IV) complexes.

VANADIUM(IV)

The parameter Δ is 50—80 % larger for trivalent than for divalent ions of the first transition group. Since the pairs Cr(III)—Mn(IV)⁵ and Ir(III)—Pt(IV)⁶ demonstrate a further increase of Δ from trivalent to quadrivalent ions, Δ of a vanadium(IV) hexaaquo ion would be expected to be $\sim 25\,000$ K. However, VO⁺⁺ in acidic aqueous solution exhibits a band at 13 100 K and a shoulder at 16 000 K, as seen from Fig. 1 and Table 1 and previously measured by Furman and Garner⁷ and Rossotti⁸.

The external charge + 2 of the vanadyl ion seems well established, *e. g.* by the potentiometric measurements by Ducret⁹. Since the equilibrium



is highly shifted towards the right-hand side, one might assume⁶⁵ that oxide and water cannot occur as ligands of a complex at the same time, but will exchange the hydrogen atom. Generally, the oxo-ions of the text-books seem to have seen their best time; the hydrolysis of uranium (IV)^{10,11} does not produce UO^{++} , and CrO_2^- is undoubtedly $\text{Cr}(\text{OH})_4(\text{H}_2\text{O})_2^-$ or a polymer. However, the dioxo ions of quinquivalent and hexivalent actinides seem to retain their linear form in aqueous solution¹² and one must conclude that oxygen can be so strongly bound in a complex, probably by forming also π -bonds¹³, that the proton affinity disappears.

A priori, one may consider three possibilities for the geometrical configuration of the vanadyl ion: tetrahedral (with two hydroxo- or one oxo-group), trigonal bipyramidal (with two *trans*-hydroxo groups or one perpendicular oxo group) and distorted octahedral (with two *trans*-hydroxo groups or one oxo group). The tetrahedral $\text{V}(\text{OH})_2(\text{H}_2\text{O})_2^{++}$ can be supported by many argu-

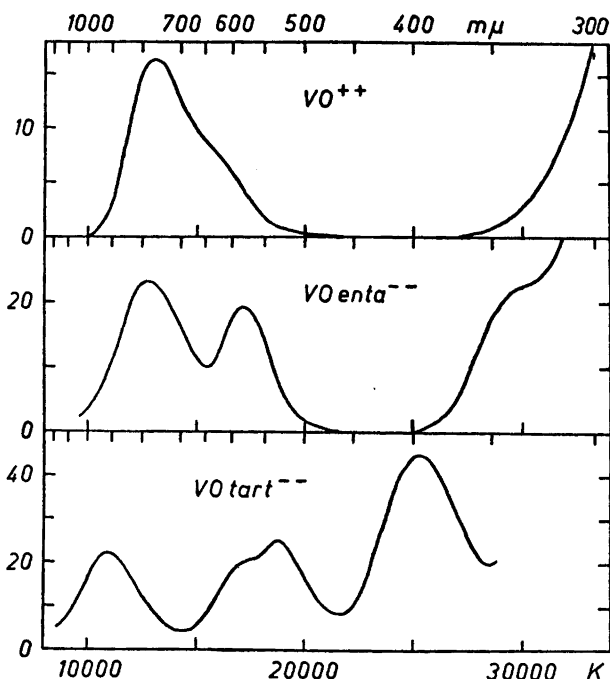


Fig. 1. Absorption spectra of vanadyl complexes.

0.1 M VO^{++} in 0.5 M to 2 M HClO_4 .

0.05 M $\text{VO}_{\text{enta}}^{--}$ from 0.1 M VO^{++} and 0.12 M Na_4enta mixed together.

0.05 M $(\text{NH}_4)_2 [\text{VO tart}] \cdot 2\text{H}_2\text{O}$ in 0.1 M NH_3 .

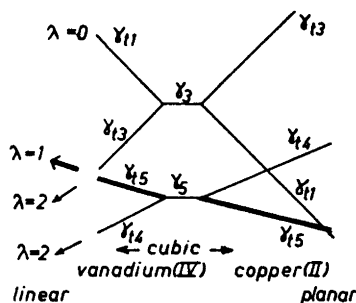
ments; Orgel¹⁴ identified the band at 9 000 K of anhydrous VCl_4 as the transition from ${}^2\Gamma_3$ to ${}^2\Gamma_5$ of a tetrahedral complex. Eventhough the intermixing of molecular orbitals¹⁵ can produce deviations from the ratio-4/9 predicted from the electrostatic model¹⁶ between the values of Δ for tetrahedral and octahedral complexes, the absorption bands of the vanadyl ion resemble much those predicted of a split excited state ${}^2\Gamma_5$. The only known values of Δ for a tetrahedral complex¹⁷, viz. those of CoCl_4^{--} and the other cobalt(II) tetrahalides¹⁴, are rather small.* The instantaneously reversible equilibrium between vanadium(IV) and vanadium(V), found by Ducret⁹, might suggest the latter to occur in acidic solution as $\text{V}(\text{OH})_4^+$. However, it is difficult to understand, why the $\text{V}(\text{H}_2\text{O})_4^{+4}$ should be so acidic for the two first protons, while the third proton^{8,18,19} has $\text{p}K$ between 5 and 6, after which the polymerisation to brown hydroxides and anions soon follows. As seen from Fig. 1 and Table 1, a change in the absorption spectrum can actually be observed by going from 2 to 10 M HClO_4 . However, the shift is so small that it might rather be ascribed to association with perchlorate ions than to a radical change of the first co-ordination sphere. Since the fourth excited level is reported below of VO en^{--} and other complexes, these cannot be tetrahedral; however, it is not totally disproven that the vanadyl ion itself has a distorted tetrahedral structure. The trigonal bipyramidic structure would produce three levels of the d-electron³, i. e. two absorption bands, and can at most be accepted for VO^{++} , but not for the complexes. Jones²⁰ discussed the possible equilibria between 5- and 6-co-ordinated vanadyl complexes. However, the X-ray structure²¹ of VO_2 shows a distorted (hemiedric) octahedral environment and $\text{VO SO}_4 \cdot 5 \text{H}_2\text{O}$ contains monomer vanadium, surrounded by six oxygen atoms²². Thus, the ionic radius of V^{+4} does not seem to be so small that the tetrahedral or trigonal bipyramidic configuration is more favoured**, except in the anhydrous VCl_4 and VBr_4 .

As seen from Table 1 and Fig. 1, most vanadyl complexes exhibit the two absorption bands more clearly separated than VO^{++} itself, as already reported by Furman and Garner²⁴ for VOSCN^+ . One of the most interesting spectra is found in the blue VO en^{--} , discovered by Schwarzenbach²⁵. It has the third band at 29 800 K, a wavenumber comparable to the expected Δ of a cubic vanadium(IV) complex. Thus, the two tetragonal components of ${}^2\Gamma_3$ in the ligand field of the distorted octahedron seem to be observed at 17 200 K and 29 800 K, a considerable distance. The second band of the complexes VO ox_2^{--} , VO aca_2 , VOSCN^+ , etc. must thus be considered as the first part of a tetragonal splitting of which the second part is hidden by the carboxylate band and other electron transfer bands in the ultraviolet. Actually, a shoulder was observed by Bürger²⁶ for $\text{VO ox}_2^{--} \sim 30\,000$ K besides the two bands at 12 600 and 16 200 K.

* Cf. the approximate values³ of Δ in MnBr_4^{--} (—2 000 K) and in FeCl_4^- (—5 000 K).

** Even vanadium(V) appears to be hexa-coordinated in the black 8-hydroxyquinolate²⁸ $(\text{C}_8\text{H}_6\text{ON})_2\text{VOOH}$, which turns red with alcohols, yellow with amines, and which forms a blue $[(\text{C}_8\text{H}_6\text{ON})_2\text{V}(\text{OH})_2]\text{Cl}$ and a green dimeric anhydride. However, perhaps the nitrogen and the oxygen of the 8-hydroxyquinoline are not both co-ordinated as in other complexes.

Fig. 2. The two opposite types of tetragonality. The behaviour of copper(II) and vanadium(IV) complexes is qualitatively described as a tetragonal distortion of the energy levels for ligand fields of exact cubic symmetry O_h . In the case of the vanadyl complexes, the energy levels can be extrapolated to those of a linear molecule with a negative value of $E\lambda$, as discussed in Ref. 29.



It is possible to determine the sign of the tetragonality by comparing the spectra of VO^{++} and the other complexes with four ligand atoms attached. Either the ligand field along two axes of a Cartesian co-ordinate is stronger than along the third axis (as is the case of copper(II) complexes ^{16,66}), or one axis has a stronger ligand field than the two others ^{27,3}. The latter seems distinctly to be the case; when $enta^{-4}$ occupies the tetragonal plane, the tetragonal splitting is decreased. As seen from Fig. 2, the behaviour is opposite to that of the copper(II) complexes. When they have low tetragonality, two or three bands are observed in the near infra-red and in the visible ^{5,28} corresponding to transitions from ${}^2\Gamma_{13}$ to ${}^2\Gamma_{11}$, ${}^2\Gamma_{14}$, and ${}^2\Gamma_{15}$. When the tetragonality is very pronounced ⁵, such as in $Cu(NH_3)_4^{++}$ or $Cu\ en_2^{++}$, only one band is observed, probably due to superposition of the three excited levels.

This result supports strongly the classical composition VO^{++} of the vanadyl ion, with the oxygen on the tetragonal axis of strong ligand field. Even though O^{--} can occur on both sides of H_2O in the spectrochemical series (*cf.* the series green Cr_2O_3 , violet $Cr(H_2O)_6^{+++}$, and red ruby), a similar strong ligand field would never be expected of two hydroxyl ions. As seen from Fig. 2, the strong bonding of the oxygen may be explained by the results for an electron in a linear ligand field ²⁹. If the influence of the ligands in the tetragonal plane vanished, ${}^2\Gamma_{14}$ and ${}^2\Gamma_{13}$ would correspond to the lowest energy level with $\lambda = 2$, ${}^2\Gamma_{15}$ to $\lambda = 1$, and ${}^2\Gamma_{11}$ of highest energy to $\lambda = 0$. Since the vanadyl ion contains only a single d-electron, it can remain in the groundstate in the level with $\lambda = 2$, while formation of both σ - and π -bonds, which increase the energy of the empty orbitals with $\lambda = 0$ and 1, respectively, does not destabilize the complex. Oxygen seem remarkably apt to π -bonding ¹³, which would explain the existence of oxo complexes with mainly linear ligand field in the beginning of the transition groups (VO^{++} , $MoOCl_5^{--}$ discussed below, UO_2^{++} etc.). The octahedral complexes in the middle of the transition groups (*e. g.* diamagnetic d^6) and the square-planar tetragonal d^9 - and diamagnetic d^8 -systems (which have high energy of the γ_{13} -orbital) are more stable with σ -bonding ligands with high values of Δ , and in the case of low oxidation states, perhaps also by π -bonding in the direction from the central ion to the ligand. Thus, the general tendency to prefer oxygen in the beginning of a transition group (even though Δ is large and electrostatic effects does not dominate, as for Mn^{++} and Ca^{++}) and nitrogen in the end may have a profound connection

with the number of d-electrons, which are destabilized because they are in anti-bonding orbitals.

The transition of VO^{++} to ${}^2\Gamma_{11}$ was expected $\sim 32\ 000$ K. However, it seems to have a somewhat higher wavenumber and is masked by the broad band at $41\ 700$ K ($\epsilon = 240$) which was also reported by Furman and Garner ⁷. The latter band is not due to hydrolysis, since it is the same in 0.1 M and 1 M HClO_4 , nor to oxidation of VO^{++} , since it is not changed by addition of a small amount of V^{+++} . The intensity does not suggest that it is allowed; but it can hardly be the ligand field band sought for, since the other complexes do not have high intensity for their transitions to ${}^2\Gamma_{11}$. Jones and Colvin ⁶⁹ have shown by potentiometric measurements that VO^{++} is not more dimeric than V^{+++} ; the band is thus not due to an oxygen bridge.

Jones ²⁰ made a valuable contribution to the vanadyl problem by showing that VO aca_2 can be made anhydrous and is soluble as a monomer in benzene; and that the solvation with one molecule of H_2O , NH_3 etc. does not change the properties of VO aca_2 to such a degree that a di-hydroxo complex could be suggested.

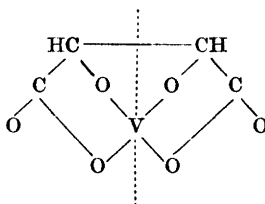
The tetragonal splitting can be made even smaller than for VO enta^{--} , and a rhombic splitting, producing in total four ligand bands, seems probable: It has previously ³⁰ been noted that tartrates and citrates in aqueous ammonia produce a purple colour with vanadium(IV). In weakly acidic solution, tartrates produce a dark blue solution, of which the spectrum resembles the other carboxylate complexes such as VO ox_2^{--} (Table 1), and a weak shoulder is observed $\sim 28\ 600$ K. The complexes of VO^{++} with organic anions exhibit a different behaviour, according to whether they contain hydroxo (alcohol) functions or not. VO ox_2^{--} and the analogous dark blue complex with succinate decompose in aqueous ammonia to brown precipitates, while the malate with a single hydroxo function forms a violet solution at not too high a concentration of NH_3 . Vanadyl tartrates, citrates, and gluconates are soluble even in concentrated NH_3 . This suggests a Fehling's solution-type complex, where the metal ion is bound to alcoxyl groups of the ligand which have released protons also from the alcohol functions.

Actually, Barbieri ⁶² prepared a solid purple salt $(\text{NH}_4)_2[\text{VOC}_4\text{H}_2\text{O}_6]$, $2\ \text{H}_2\text{O}$, which later was studied by Rosenheim and Yu-Mong ⁶³, who also prepared $\text{Ba}[\text{VOC}_4\text{H}_2\text{O}_6]$, $5\ \text{H}_2\text{O}$, demonstrating that no ammonia of constitution occurs in the anion. The anion must have two carboxylate groups and two alcoxyl groups bound to vanadium in the tetragonal plane with the vanadyl oxygen on the perpendicular axis. Ducret ⁹ reports two $\text{p}K$ values = 6.85 and 2.8 for the consecutive uptake of two protons on VO tart^{--} . Mr. Kjeld Rasmussen has kindly titrated a sample of ammonium vanadyl tartrate *, prepared ⁶³ by the author, and found the values of $\text{p}K \sim 6.1$ and ~ 2.9 . It cannot easily be decided whether the protons go on the carboxyl or alcoxyl groups; vanadyl ions seem to have a strong affinity to alcoxyl and phenoxyl groups analogous to

* However, this purple salt turns blue with an excess of tartrate, even in 1 M NH_3 , suggesting the formation of a complex with two tartrates and high absorption in the range $800\text{--}600\ \text{m}\mu$, analogous to VO tartH^- .

iron(III), as shown by the preparation of vanadyl bis(salicylates) * and bis(pyrocatechates) ⁶³.

The tetragonal splitting between the two highest levels ** of VO tart⁻ is decreased to 6 500 K, while the rhombic splitting of ² Γ_{15} amounts to 6 100 K (Table 1). This is rather remarkable, since if the complex had orthogonal axes, its symmetry would be tetragonal with two equivalent axes in the electrostatic perturbation model ³. The complex can hardly lack a plane of symmetry, intersecting the plane of the paper along the dotted line:



However, the two lines OVO in the plane do not need to be orthogonal ***. The resulting low symmetry C_2 no longer presents degenerate electronic levels, and all five possible energy levels are then separated. It must be emphasized that planar platinum(II) complexes, *trans*-Pt A_2B_2 , generally exhibit a genuine rhombic splitting ⁶⁴ which is not found in *cis*-Pt A_2B_2 in agreement with Ballhausen's and the author's predictions for complexes with orthogonal axes ³. Actually, the d^1 -systems such as vanadium(IV), and the d^9 -systems, such as copper(II), seem much more liable to exhibit effects of low symmetry than the regular d^3 -, paramagnetic d^8 -, and diamagnetic d^6 -systems, which maintain nearly the energy levels predicted for cubic symmetry O_h , even with sets of highly different ligands.

Small tetragonal splittings might also occur in vanadium(IV) complexes with six equal ligands. The dark red hexachlorides, *e. g.* $[N(CH_3)_4]_2VCl_6$ prepared by Gutmann ³¹, probably have electron transfer bands in the visible. The pink K_2VF_6 prepared by Hoppe ³² may have ² $\Gamma_{13} \sim 20\ 000$ K and ² Γ_{11} at slightly higher wavenumbers.

Vanadium(III) is also soluble in tartrate and aqueous ammonia with a dark green colour ³⁰. The solution has maxima at 612, 440 and 424 $m\mu$, the latter forming a broad band. Vanadium(III) in 12 M HCl has the bands at 675 and 448 $m\mu$, while they are situated at 588 and 396 $m\mu$ of the solution in 2 M HCl. There is no doubt that the pure hexaquo ion is still more hypsochromic, resembling the values 562 and 389 $m\mu$, found by Hartmann and Schläfer ³³ for vanadium(III) alum crystals. The spectrum of V en⁻ is rather peculiar ⁵.

* The pale purplish pink ammonium vanadyl salicylate dissolves with dark green colour in water or ethanol and can be easily re-crystallized. It decomposes with aqueous ammonia, and thus, the purple complex cannot be measured in solution.

** an alternative possibility might be ² Γ_{15} at 17 100 and 18 800 K, thus implying the distance 14 300 K between ² Γ_{13} and ² Γ_{11} .

*** Hartmann, Furlani and Bürger ^{67,68} have recently discussed the deviations from orthogonal axes. Their case, Vox_3^{-3} , exhibits surprisingly small deviations from the spectrum, predicted for an octahedral complex with the symmetry O_h .

TITANIUM(III)

Hartmann and Schläfer³⁴ observed strong variations in the absorption spectrum of titanium(III), which was ascribed to hydrolysis at low acid concentrations and formation of chloro complexes in strong hydrochloric acid. Recently, Hartmann, Schläfer, and Hansen³⁵ have investigated the spectrum of anhydrous TiCl_3 in different solvents in order to avoid some of these difficulties.

As previously discussed³⁶, the hexaquo ion is the dominating species in the reddish purple solution in 2 M HCl. The band at 492 $m\mu$ is very broad and has a shoulder at 575 $m\mu$, which was interpreted³ as distortions caused by the Jahn-Teller effect. The large half-width may be connected with the large value of Δ and the large amplitude of the ligand's vibrations in the relatively weakly bound complex², where $\delta \sim 0.15 \Delta$. However, with the picture given in Ref. 2, it is peculiar, why the bands with highest wavenumbers of the purple vanadyl tartrate and of MoOCl_5^- are so narrow.

In stronger hydrochloric acid titanium(III) turns sky-blue with a shift of the double band to about 660 and 525 $m\mu$. These spectra resemble much the spectra reported by Hartmann³⁵ of TiCl_3 in anhydrous alcohols. It may be questioned^{37,38} whether these effects are caused solely by solvation or by the partial formation of chloro complexes in the first co-ordination sphere. The hexa(alcohol) solvates seem much more unstable towards uptake of anions than hexaquo ions. In anhydrous ethanol (but not in 90 % $\text{C}_2\text{H}_5\text{OH}$), cerium(III) chloro complexes are formed at a chloride concentration ~ 0.005 M, while 10 M HCl is necessary for the same effect in aqueous hydrochloric acid³⁹.

However, if the sky-blue solutions of titanium(III) in strong HCl are slightly oxidized, they turn much darker purplish black. This oxidation may be effected by, *e. g.*, a platinum wire, catalyzing the evolution of hydrogen. Table 2 gives the molar extinction coefficients at several wavelenghts for mixtures of Ti(III) and Ti(IV) in 12 M HCl. The spectra are seen to be a linear combination of the sky-blue titanium(III) and the dark colour, which has a maximum at 482 $m\mu$ and a shoulder at 670 $m\mu$. Further, a strong absorption in the ultraviolet appears, which is absent in pure Ti(III) (which has $\epsilon = 8$ at 310 $m\mu$).

The dark-coloured complex is similar to the "interaction colours" found in the pair of oxidation states: copper(I, II)⁴⁰, tin(II, IV)⁴¹ and antimony-

Table 2. Molar extinction coefficients of titanium(III) and (IV) in 12 M HCl. For mixtures, ϵ is calculated solely with respect to the total concentration $C_{\text{Ti}+3}$ of trivalent titanium. Wavelengths in $m\mu$.

$C_{\text{Ti}+3}$	$C_{\text{Ti}+4}$	$C_{\text{Ti}+4}:C_{\text{Ti}+3}$	650	600	550	500	475	$\frac{[\text{III}, \text{IV}]}{C_{\text{Ti}+3}}$
0.1 M	0	0	4.2	5.2	6.0	5.9	5.4	—
0.100	0.02 M	0.2	6.8	8.3	9.9	10.8	10.6	0.12
0.091	0.036	0.4	9.4	11.3	13.6	15.6	15.5	0.24
0.083	0.067	0.8	12.8	15.6	19.0	22.1	22.2	0.40
0.072	0.114	1.6	19.8	23.8	28.7	34.3	34.3	0.71
0.062	0.151	2.4	22.7	27.2	33.1	39.2	39.2	0.85
0.050	0.20	4.0	24.8	29.6	35.8	42.8	42.6	0.95
0.020	0.32	16	26.5	31.5	38	45	44.5	1.00
0	0.4	—	0.1	0.1	0.1	0.15	0.25	—

(III, V) ⁴² in concentrated HCl. Thus, from the variation of ϵ in Table 2, the existence of a bi-nuclear complex containing equal amounts of Ti(III) and Ti(IV) is demonstrated. The formation constant of this complex in 12 M HCl, relative to the concentrations [III], [IV], and [III, IV], having the ϵ values of pure Ti(III), pure Ti(IV) and the limiting value of ϵ for mixtures and with the known concentrations $CTi^{+3} = [III] + [III, IV]$ and $CTi^{+4} = [IV] + [III, IV]$, can be inferred from Table 2 to

$$\frac{[III, IV]}{[III][IV]} = 12$$

Since the pure oxidation states probably occur mainly as $TiCl^{++}$ and $TiCl_6^-$ in concentrated HCl, (*cf.* Ref. 61) the composition of the mixed complex [III, IV] may perhaps be rather near to the neutral form Ti_2Cl_7 .

The interaction colours, due to titanium in both oxidation states (analogous to molybdenum blue, ferrocyanides etc.) occur probably also in the black precipitate of $Ti(OH)_3$ from $Ti(H_2O)_6^{+++}$ and alkali. The precipitate is probably oxidized by a spontaneous evolution of hydrogen, analogous to the air oxidation of white $Fe(OH)_2$ to greenish black forms. Also titanium(III, IV) solutions in strong sulphuric acid are black, while the similar phenomenon is not observed in phosphoric acid. Neither do Zr^{+4} , Th^{+4} or U^{+4} interact visibly with Ti^{+3} in strong HCl. It may be remarked that while the pale green $U(OH)_4$ on partial oxidation produces dark brown intermediates, it does not interact with U^{+3} . If the red solution * in HCl is added to aqueous ammonia, a pale orange-red precipitate of $U(OH)_3$ can be observed one second before the evolution of H_2 and the change to pale green.

Titanium (IV) complexes have a strong electron transfer band in the ultra-violet. Thus, TiO_2 is much more absorbing ⁴³ than ZrO_2 . Even while the liquid $TiCl_4$ is free of iron (the absorption band of the vapour has recently been measured ⁴⁴), its solution in 12 M HCl is pale yellow. Much more conspicuous is the reaction with thiocyanate. While a yellow solution is obtained with this reagent in water, a dark red-brown compound (probably un-ionized $Ti(SCN)_4$) can be extracted with diethyl ether. If titanium(III) is free from impurities of (IV), thiocyanate produces a clear purple colour (the maximum at $528 m\mu$ has $\epsilon_n = 12$ and $\delta = 3000 K$) which is not shifted by extraction with diethyl ether and thus probably is caused by $Ti(SCN)_3(H_2O)_3$.

The purple Ti enta⁻ has been made several times by cautious addition of Na_4 enta and NaOH to Ti(III) in 2 M HCl. Besides the broad maximum at the rather large wavelength $543 m\mu$, a band one-fourth as strong is observed $\sim 760 m\mu$, thus corresponding to large deviations from the cubic symmetry O_h .

These examples show that titanium(III) has by no means the strong tendency to form regular octahedral complexes as have d^3 -, d^8 - and diamagnetic d^6 -systems. Thus, no $Ti ox_3^{-3}$ is known; the brown ⁴⁵ $Ti ox_2^-$ has a strong absorption band $\sim 405 m\mu$. However, these bands are often electron transfer bands (perhaps also causing the strong colour of violet $TiCl_3$, which was rather expected to have $\Delta \sim 15000 K$) rather than ligand field bands.

* of chloro complexes.⁷⁰ Below a HCl-concentration 6 M, or in $HClO_4$, uranium(III) is grey.

MOLYBDENUM(V)

When molybdenum(VI) is reduced with zinc in strong HCl, a green colour is observed, which can be ascribed to MoOCl_5^{--} , of which Klason⁴⁶ and Nordenskjöld⁴⁷ prepared several salts, among those some anhydrous. Further reduction yields a red solution of Mo(III), which probably contains MoCl_6^{-3} and $\text{MoCl}_5(\text{H}_2\text{O})^{--}$. Chilesotti⁴⁸ proved by potentiometric measurements that Mo(IV) is not formed in 9 M HCl, while the reduction in more dilute acid may yield all three consecutive oxidation states +5, +4 and +3.

The behaviour seems less complicated in HCl than in other acids. In dilute sulphuric acid, molybdenum(V, VI) blue is invariably formed, and the reduction proceeds with formation of brownish black solutions. Even dilute HCl is highly different from strong HCl in respect to the colour of molybdenum(V). Hiskey, Meloche, and Springer^{49,50} studied spectrophotometrically the change of colour from pale green in 8 M HCl to strong amber yellow in 2 M HCl. Table 3 gives the absorption bands of MoOCl_5^{--} . Even though the second narrow

Table 3. Absorption bands of MoOCl_5^{--} in 9–12 M HCl. Notation as in Table 1.

λ_n	σ_n	ϵ_n	$\delta(-)$	$\delta(+)$
712	14 050	16	1 500	1 900
445	22 500	14	1 100	—
355	28 200	500	1 400	—
310.5	32 200	4 400	1 600	1 700
240	40 700	5 500	2 100	—

band has nearly the same position as the much higher, but broader, band which appears in the brown solutions by dilution with water, the present author is inclined to believe that it actually belongs to the undecomposed MoOCl_5^{--} . Thus, the intensity ratio between the two first bands is constant in the range 9 M—12 M HCl. Analogous to the levels of VO^{++} (see Fig. 2), the excited level of the band at 14 050 K is ${}^2\Gamma_{45}$, while the band at 22 600 K is ${}^2\Gamma_{13}$. The cubic contribution Δ predicted of the hypothetical MoCl_6^- is $\sim 30\,000$ K. If the spontaneous Jahn-Teller distortion is not very large, the latter ion will be nearly colourless. The second band of MoOCl_5^{--} is much narrower than the first; this may be explained by the influence of intermediate coupling, splitting ${}^2\Gamma_{45}$ in the two levels ${}^2\Gamma_{16}$ and ${}^2\Gamma_{17}$.

The third band of MoOCl_5^{--} is much higher ($\epsilon = 500$) than the first two ($\epsilon = 16$ and 14). It is probably a relatively weak electron transfer band. When molybdenum(III) in HCl is slightly oxidized, the third band of this impurity appears strongly. Thus, it can be applied as an indicator for the presence of +5, proving that the broad shoulder at 728 $m\mu$ on the red side of the sharp maximum at 673 $m\mu$ ($\epsilon = 1.7$)* is not caused by molybdenum(III). Schmidt²⁶ observed the behaviour of molybdenum(III) in strong

* The present author¹⁵ has previously identified the excited doublet levels as ${}^2\Gamma_3$ and ${}^2\Gamma_4$. However, the absence of ${}^2\Gamma_5$ is so surprising that it might be assigned to these levels in the red, implying $B \sim 450$ K as also the quartet levels do. Actually, the reflection spectrum of $(\text{NH}_4)_2[\text{MoCl}_5(\text{H}_2\text{O})]$ exhibits low bands at 1 050, 678 and a shoulder at 652 $m\mu$, while the high bands occur at 506 and 406 $m\mu$. The solution in 12 M HCl shows a band at 1 035 $m\mu$ ($\epsilon = 0.5$). Professor R. W. Asmussen and Mr. Potts Jensen have previously measured a band at 1 100 $m\mu$ of solid K_2ReCl_6 .

and dilute HCl, which resembles much that of rhodium(III) ⁶, except that the equilibria are established rapidly. Thus, the bands at 522 and 418 $m\mu$ ($\epsilon = 25$ and 35) are shifted towards 475 and 385 $m\mu$ by dilution with water.

The brown solutions of molybdenum(V) in 6 M HCl have $\epsilon \sim 20$ at 720 $m\mu$ and $\epsilon \sim 150$ at 445 $m\mu$, while the shoulder at 352 $m\mu$ is blurred out. There is some evidence that the brown hydrolysis product is more easily formed at high Mo concentrations, indicating at least two Mo atoms per complex. Sacconi and Cini ⁵¹ have found that the paramagnetism, corresponding to $S = \frac{1}{2}$ of MoOCl_5^{--} , is changed to diamagnetism of Mo(V) in dilute HCl, probably due to formation of oxygen bridges of the type ⁵² encountered in $\text{Cl}_5\text{RuORuCl}_5^{-4}$ and $\text{Cl}_5\text{ReOReCl}_5^{-4}$, of which the latter is in equilibrium ⁵³ with the monomer $\text{ReCl}_5(\text{OH})^{--}$.

WOLFRAM(V)

When tungstates(VI) are dissolved in very strong HCl, they can be reduced by amalgamated zinc at first to a blue solution, which perhaps contains the monomer WOCl_5^{--} together with some tungsten(V, VI) blue. It has a maximum (655 $m\mu$, $\epsilon \sim 7$). By further reduction, a purple solution of tungsten(IV) with $\epsilon \sim 600$ in a maximum at 19 100 K, is formed. After some time, the more robust yellow-green $\text{W}_2\text{Cl}_9^{-3}$ are formed (they are oxidized by air much more slowly than W(IV)). The spectrum of this does not exhibit two spin-allowed ligand field transitions to $^4\Gamma_5$ and $^4\Gamma_4$ such as the monomeric Mo(III) does. The first two bands (at 13 200 K, $\epsilon \sim 25$ and at 16 300 K, $\epsilon \sim 40$) are probably the spin-forbidden transitions to $^2\Gamma_3$ and $^2\Gamma_5$ with the high intensity perhaps caused by the absence of a centre of inversion in each tungsten atom. Further, a high band occurs at 22 200 K ($\epsilon \sim 1\ 200$). Laudise and Young ⁵⁴ recognize further a pale red form of tungsten(III) in addition to $\text{W}_2\text{Cl}_9^{-3}$.

NIOBIUM(IV)

Cozzi and Vivarelli ⁵⁵ investigated the absorption spectra of niobium(IV), (III) and (II) in hydrochloric acid of different concentrations. Thus, the red-orange niobium(IV) complex in 13 M HCl has a maximum at 478 $m\mu$ ($\epsilon \sim 120$), while the blue Nb(IV) solution in 8–9 M HCl has a broad band $\sim 700 m\mu$ ($\epsilon \sim 150$). It is assumed ⁵⁵ that these complexes are analogous to VO^{++} , VOCl_4^{--} and VCl_6^{--} . However, it is doubtful whether VO^{++} takes many chloride ligands up in HCl (see Table 1), since the maximum is only slightly shifted. Cf. the ion exchange measurements by Kraus, Moore and Nelson ⁶¹.

GENERAL REMARKS

Even though the d^1 -systems in some cases (VO^{++} , MoOCl_5^{--}) exhibit the opposite sign of tetragonality to that of the d^9 -systems (*e. g.* Cu^{++}), it is only in a limited range of oxidation states that the typically linear molecules occur. While titanium(III) does not deviate so much from the cubic symmetry as vanadium(IV), the higher oxidation states assume tetrahedral configuration with the necessary Jahn-Teller distortion. Thus, MnO_4^{--} has three bands of nearly equal intensity at 605, 435 and 355 $m\mu$, which must be caused by transfer of π -electrons from the oxygen atoms, analogous to the two strong bands ¹³

of MnO_4^- . With the larger ionic radii of the 4d-elements, it has become possible for molybdenum(V) to retain hexa-coordination in MoOCl_5^{--} , while ruthenium-(VII) in RuO_4^- is tetrahedral with electron transfer bands⁵⁶ at 385 and 310 $m\mu$.

It is interesting to see how much more important inherent Jahn-Teller distortion is for the development of typical tetragonal symmetry of titanium-(III), vanadium(IV), molybdenum(V) and copper(II) complexes than the tetragonality of mixed complexes, *e. g.* of chromium(III)⁵⁷, cobalt(III)⁵⁷, nickel(II)^{5,58}, rhodium(III)^{6,59} and iridium(III)^{6,59} which often is difficult to detect.

EXPERIMENTAL

The spectra were measured in the range 800–210 $m\mu$ on a Cary recording spectrophotometer, Model 11-MS-50, and above 800 $m\mu$ on a Beckman DU.

Vanadium solutions. AnalaR NH_4VO_3 was directly, or after ignition to V_2O_5 , dissolved in 2 M HClO_4 and reduced electrolytically to VO^{++} , or in 10 M HCl and reduced with amalgamated zinc to a mixture of V^{++} and V^{+++} . A 0.5 M solution of the latter kind was diluted with water to 0.1 M and used directly for vanadium(III) measurements and after spontaneous oxidation by air for vanadium(IV) measurements.

0.1 M $\text{Na}_2\text{C}_2\text{O}_4$, 0.6 M $(\text{NH}_4)_2\text{Ox}$, 1 M tartaric acid, 1 M citric acid, 12 M aqueous ammonia etc. were made from analytical or C. P. reagents, and added to vanadium and titanium solutions in measuring flasks.

Solid $(\text{NH}_4)_2[\text{VO}(\text{C}_4\text{H}_2\text{O}_6)]$, $2\text{H}_2\text{O}$ and VO aca_2 , H_2O were prepared according to Rosenheim and Yu-Mong⁶⁰.

Titanium solutions. Colourless TiCl_4 was mixed with 12 M HCl giving a 2 M solution. This solution was diluted to 0.2 M or 0.1 M TiCl_4 with different concentrations of HCl and reduced to the clearest shade of purple titanium(III) with zinc.

Molybdenum solutions. Merck's $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ was dissolved in 6 M HCl giving a 0.5 M solution. This was diluted with HCl to 0.1 M or lower concentrations and reduced with amalgamated zinc. Solid K_2MoCl_6 and $(\text{NH}_4)_2\text{MoCl}_6(\text{H}_2\text{O})^{60}$ were also used for some experiments.

Acknowledgments. I thank Professor Jannik Bjerrum for his kind interest in the investigations.

REFERENCES

1. Ilse, F. E. and Hartmann, H. *Z. physik. Chem.* **197** (1951) 239.
2. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **11** (1957) 53.
3. Ballhausen, C. J. and Jørgensen, C. Klixbüll, *Kgl. Danske Videnskab Selskab Mat.-fys. Medd.* **29** (1955) No. 14.
4. Van Vleck, J. H. *J. Chem. Phys.* **7** (1939) 61, 72.
5. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **9** (1955) 1362.
6. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **10** (1956) 500, 518.
7. Furman, S. C. and Garner, C. S. *J. Am. Chem. Soc.* **72** (1950) 1785.
8. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **9** (1955) 1177.
9. Ducret, L. P. *Thesis*. Université de Paris 1951.
10. Kraus, K. A. and Nelson, F. AEC D-1888, and *J. Am. Chem. Soc.* **72** (1950) 3901.
11. Hietanen, S. *Rec. trav. chim.* **75** (1956) 711 and *Acta Chem. Scand.* **10** (1956) 1531.
12. Seaborg, G. T. and Katz, J. J. *The Actinide Elements. Natl. Nuclear Energy Ser. Div. IV, Vol. 14* A.
13. Wolfberg, M. and Helmholtz, L. *J. Chem. Phys.* **20** (1952) 837.
14. Orgel, L. E. *J. Chem. Phys.* **23** (1955) 1004.
15. Jørgensen, C. Klixbüll, *Reports of the Xth Solvay Conference, Bruxelles, May 1956*.
16. Ballhausen, C. J. *Kgl. Danske Videnskab. Selskab Mat. fys. Medd.* **29** (1954) No. 4.
17. Ballhausen, C. J. and Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **9** (1955) 397.
18. Jones, G. and Ray, W. A. *J. Am. Chem. Soc.* **66** (1944) 1571.
19. Ducret, L. *Bull. soc. chim. France* **1948** 658.

20. Jones, M. M. *J. Am. Chem. Soc.* **76** (1954) 5995.
21. Anderson, G. *Acta Chem. Scand.* **10** (1956) 623.
22. Lundgren, G. *Rec. trav. chim.* **75** (1956) 585.
23. Blair, A. J. and Pantony, D. A. *Anal. Chim. Acta* **13** (1955) 1.
24. Furman, S. C. and Garner, C. S. *J. Am. Chem. Soc.* **73** (1951) 4528.
25. Schwarzenbach, G. and Sanders, J. *Helv. Chim. Acta* **36** (1953) 1089.
26. Hartmann, H. and Schläfer, H. L. *Angew. Chem.* **66** (1954) 768.
27. Bethe, H. *Ann. Physik* [5] **3** (1929) 133.
28. Belford, R. L. *Bonding and Spectra of Metal Chelates. Thesis.* University of California 1955 (UCRL-3051).
29. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **11** (1957) 166.
30. Jørgensen, C. Klixbüll, *Naturviden (Ungdommens naturvidenskabelige forening)* **6** (1952) 61.
31. Gutmann, V. *Monatsh.* **85** (1954) 286.
32. Hoppe, R. *Rec. trav. chim.* **75** (1956) 569.
33. Hartmann, H. and Schläfer, H. L. *Z. Naturforsch.* **6a** (1951) 754.
34. Hartmann, H. and Schläfer, H. L. *Z. physik. Chem.* **197** (1951) 116.
35. Hartmann, H. Schläfer, H. L. and Hansen, K. H. *Z. anorg. Chem.* **284** (1956) 153.
36. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **9** (1955) 405.
37. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **8** (1954) 175.
38. Jørgensen, C. Klixbüll and Bjerrum, J. *Nature* **175** (1955) 426.
39. Jørgensen, C. Klixbüll, *Kgl. Danske Videnskab. Selskab Mat. fys. Medd.* **30** (1956) No. 22.
40. Mc Connell, H. and Davidsen, N. *J. Am. Chem. Soc.* **72** (1950) 3168, 5557.
41. Browne, C. I., Craig, N. and Davidson, N. *J. Am. Chem. Soc.* **73** (1951) 1946.
42. Whitney, J. E. and Davidson, N. *J. Am. Chem. Soc.* **71** (1949) 3809.
43. Treiber, E., Stenius, A. S., Lang, W. and Berndt, W. *Acta Chem. Scand.* **8** (1954) 1865.
44. Mason, D. M. and Vango, S. P. *J. Phys. Chem.* **60** (1956) 622.
45. Pecsok, R. L. *J. Am. Chem. Soc.* **73** (1951) 1304.
46. Klason, P. *Ber.* **34** (1901) 149.
47. Nordenskjöld, I. *Ber.* **34** (1901) 1572.
48. Chilesotti, A. *Z. Elektrochem.* **12** (1906) 173.
49. Hiskey, C. F., Springer, V. F. and Meloche, V. W. *J. Am. Chem. Soc.* **61** (1939) 3125.
50. Hiskey, C. F. and Meloche, V. W. *J. Am. Chem. Soc.* **62** (1940) 1565.
51. Sacconi, L. and Cini, R. *J. Am. Chem. Soc.* **76** (1954) 4239.
52. Nyholm, R. S. *Reports of the Xth Solvay Conference, Bruxelles, May 1956.*
53. Jezowska-Trzebiatowska, B. and Wajda, S. *Bull. acad. polon. sci. Classe III* **2** (1954) 249 (cf. *Chem. Abstracts* 1954 13518).
54. Laudise, R. A. and Young, R. C. *J. Am. Chem. Soc.* **77** (1955) 5288.
55. Cozzi, D. and Vivarelli, S. *Z. anorg. Chem.* **279** (1955) 165.
56. Connick, R. E. and Herley, C. R. *J. Am. Chem. Soc.* **74** (1954) 5012.
57. Schäffer, C. E. *Acta Chem. Scand.* **11** (1957). *To be published.*
58. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **10** (1956) 887.
59. Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **11** (1957) 151.
60. Lohmann, K. H. and Young, R. C. *Inorganic Syntheses* **4** (1953) 97.
61. Kraus, K. A., Moore, G. E. and Nelson, F. *J. Am. Chem. Soc.* **78** (1956) 2692.
62. Barbieri, G. A. *Atti accad. nazl. Lincei* [2] **23** (1914) 47.
63. Rosenheim, A. and Yu-Mong, Hsien *Z. anorg. Chem.* **148** (1925) 25.
64. Babaeva, A. *Izvest. Sektora Platiny i Drug. Blagorod Metal. Inst. Obschchei i Neorg. Khim. Akad. Nauk. SSSR* **25** (1950) 56.
65. Bjerrum, J. *Metal Ammine Formation. Thesis,* Copenhagen 1941, p. 70.
66. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **8** (1954) 1275.
67. Hartmann, H., Furlani, C. and Bürger, A. *Z. physik. Chem.* **9** (1956) 62.
68. Hartmann, H. and Furlani, C. *Z. physik. Chem.* **9** (1956) 162.
69. Jones, G. and Colvin, J. H. *J. Am. Chem. Soc.* **66** (1944) 1563 and 1573.
70. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **10** (1956) 1503.

Received October 12, 1956.