shown by points along HI and represent initial starting concentrations of solutions. Above line HI there is the supercritical fluid and solid. The critical point for pure water (374.2°) does not appear to have been elevated more than two or three degrees, thus indicating that the solubility of components in the water rich liquid is very low.

Solutions more dilute than approximately 25% UO_2F_2 yield a solid phase at temperatures indicated by line JF, well below the two-liquid phase region. Analyses of samples of this solid phase obtained from each of several different solution compositions show a continuous variation in the uranium to fluoride mole ratio as indicated by Fig. 2. The analytical data are available on microfilm.[7] From these results a solid solution of $UO_2(OH)_2$ and either $UO_2(OH)F \cdot {}^1/_2H_2O$ or $UO_2F_2 \cdot H_2O$ is indicated. Because of the similarity in size of the fluoride ion and the hydroxyl radical the possibility of the existence of such solid solutions was suggested by M. A. Bredig of this Laboratory. A comparison of X-ray diffraction data obtained by H. L. Yakel, also of this Laboratory, for this solid with data for α-$UO_2(OH)_2$ shows minor differences in structure entirely consistent with the solid solution hypothesis. A photomicrograph of this solid is shown in Fig. 3.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Bis-cyclopentadienyl Compounds of Ti, Zr, V, Nb and Ta

BY G. WILKINSON AND J. M. BIRMINGHAM

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Bis-cyclopentadienyl halides of titanium, zirconium and vanadium in the IV oxidation state, and of niobium and tantalum n the V oxidation state, have been prepared by the reaction of the anhydrous metal halides with cyclopentadienylmagnesium halides or with cyclopentadienylsodium. The properties of the halides are given and the preparation of the ions $(C_5H_5)_2Ti^+$ and $(C_5H_5)_2V^+$ by reduction of the IV valent titanium and vanadium compounds in aqueous solution is described. The electronic structure of the derivatives is discussed briefly.

The existence of bis-cyclopentadienyl compounds of Cr(II), Fe(II, III), Ru(II, III), Co(II, III), Rh(III), Ir(III) and Ni(II, III) is well established[1] and preliminary notes on derivatives of Mn(II), Mo(IV, V) and W(IV, V) have been made recently.[2a,b] We now describe derivatives of titanium(III) and -(IV), of zirconium(IV), of vanadium(III) and -(IV), and of niobium and tantalum(V), some of which have been noted in a preliminary communication.[3]

I. Experimental

General Methods of Preparation.—Bis-cyclopentadienyl halides of Ti, Zr, V, Nb and Ta were made by the reaction of cyclopentadienylmagnesium chloride or bromide with the metal chloride or bromide, respectively, in benzene–ether solution. A more convenient alternative procedure, generally giving higher yields, was the reaction of cyclopentadienylsodium with the metal halide in either tetrahydrofuran or 1,2-dimethoxyethane (dimethyl "cellosolve") solution. In the Grignard method, cyclopentadienylmagnesium chloride or bromide was prepared from ether solutions of either *n*-propylmagnesium chloride or ethylmagnesium bromide, respectively. The theoretical amount of cyclopentadiene obtained by cracking dicyclopentadiene was added to the Grignard reagent (in some cases, most of the ether was first displaced by benzene), and the mixture was then warmed until gas evolution ceased (about 1 hr.); the solution was cooled in ice and was then slowly run into a solution or suspension of the metal halide in ether or benzene solution, with vigorous stirring and ice cooling. In the second method, cyclopentadienylsodium was prepared by adding the theoretical amount of cyclopentadiene to finely divided sodium in tetrahydrofuran or dimethyl "cellosolve." The mixture was stirred at room temperature until gas evolution ceased; the resulting orange solution was cooled and was run slowly into the solvent plus the metal halide, with rapid stirring and ice cooling. The halides VCl_4, $NbBr_5$ and $TaBr_5$ were prepared by the reaction of the free halogen upon the heated metals,[4] and were used without further purification; the other halides were commercially available.

The procedure employed for isolation of the bis-cyclopentadienyl compounds was very similar in all cases. After stirring the reaction mixture for 2–3 hours, the solvent was removed under reduced pressure. The residue was then repeatedly extracted with boiling chloroform through which was passed a slow stream of hydrogen chloride (for chloride preparations) or hydrogen bromide (for bromide preparations). The extract was evaporated and the residue reextracted with chloroform saturated with hydrogen chloride or bromide. The second extract was worked up differently for the several compounds. For bis-cyclopentadienyltitanium(IV) chloride and bromide, the product was crystallized from toluene. For the bis-cyclopentadienyl halides of zirconium, vanadium, niobium and tantalum, the chloroform extract, after saturation with the appropriate hydrogen halide, was cooled in a Dry Ice–acetone-bath and the crystals separated by rapid filtration. Bis-cyclopentadienylzirconium(IV) bromide was recrystallized from carbon tetrachloride containing 25% chloroform. The bis-cyclopentadienyl halides of vanadium, niobium and tantalum were recrystallized from chloroform saturated with hydrogen chloride or bromide, by cooling the solutions to −70°. An alternative procedure for the isolation of the bis-cyclopentadienylniobium and tantalum bromides was to pour the reaction mixture into an ice slush of 6 *N* hydrobromic acid. The yellow aqueous phase, which contained bis-cyclopentadienylmetal hydroxy ions was treated with bromine water. The resulting yellow precipitate was centrifuged, washed with 1 *N* hydrobromic acid until free from magnesium or sodium salts, and dissolved in boiling 48% hydrobromic acid. This solution was distilled azeotropically with benzene in a stream of hydrogen bromide; after removal of excess benzene, the product was crystallized from chloroform as before.

The quantities of the reactants used and the yields of the compounds in typical preparations are shown in Table I.

Analyses.—For determination of the metals, the bis-cyclopentadienyl compounds were destroyed by fuming with

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[1] See G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL, **76**, 1970 (1954), where references to previous works are given.

[2] (a) G. Wilkinson and F. A. Cotton, *Chemistry and Industry*, 307 (1954); (b) F. A. Cotton and G. Wilkinson, *Z. Naturforsch.*, in press.

[3] G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, THIS JOURNAL, **75**, 1011 (1953).

[4] "Handbuch der Präparativen Anorganischen Chemie," F. Enke, Stuttgart, 1953, Vol. II, p. 901.

TABLE I

TYPICAL PREPARATIONS OF BIS-CYCLOPENTADIENYL COMPOUNDS OF Ti, Zr, V, Nb AND Ta

Compound	C_5H_5MgBr or C_5H_5Na, moles		Metal halide, moles		Solvent,[a] ml.		Yield, g.	%
$C_{10}H_{10}TiBr_2$	Mg	0.4	$TiCl_4$	0.075	bz.	200	18	70
$C_{10}H_{10}TiCl_2$	Na	.2	$TiCl_4$	.075	T.H.F.	250	18	90
$C_{10}H_{10}ZrBr_2$	Mg	.25	$ZrCl_4$	.085	eth.	250	10	30
$C_{10}H_{10}VBr_2$	Mg	.25	VCl_4	.05	bz.	200	3	16
$C_{10}H_{10}VCl_2$	Na	.25	VCl_4	.11	D.M.C.	250	18	65
$C_{10}H_{10}NbBr_3$	Na	.3	$NbBr_5$	.08	T.H.F.	250	26	70
$C_{10}H_{10}TaBr_3$	Mg	.2	$TaBr_5$	.06	eth.	250	6	19
$C_{10}H_{10}TaBr_3$	Na	.2	$TaBr_5$	.06	T.H.F.	200	20	62

[a] bz = benzene, eth = diethyl ether, T.H.F. = tetrahydrofuran, D.M.C. = dimethylcellosolve.

perchloric acid. Titanium was precipitated as the hydroxide and was ignited to the oxide (ref. 5, p. 982); zirconium was determined by precipitation with cupferron (ref. 5, p. 1099); vanadium was determined volumetrically by titration with standard permanganate solution after reduction with sulfur dioxide (ref. 5, p. 1037); niobium and tantalum were precipitated by tannin and the precipitate ignited to the oxide (ref. 5, p. 346). For halogen determinations, the bis-cyclopentadienyl halides were destroyed by boiling with alkali; after filtration of the solution, the halide was precipitated as the silver salt (ref. 5, p. 269).

Carbon, hydrogen and nitrogen microanalyses were performed by Dr. S. Nagy of the Massachusetts Institute of Technology. Melting points are corrected.

Magnetic Measurements.—Measurements were made by the Gouy divided tube method and field strengths varying from 8000 to 12,000 oersteds were used to check the absence of ferromagnetic impurities. Water ($\kappa = -0.72 + 10^{-6}$ c.g.s.u.) and ferrous ammonium sulfate ($\chi_g = +32.0 \times 10^{-6}$ c.g.s.u. at 295°K.) were used as standard substances. For solids, three packings of the tube were made with the ground material; the tubes were filled in a dry-box with a nitrogen atmosphere. For paramagnetic substances, the diamagnetic corrections were calculated using Pascal's constants.

Bis-cyclopentadienyltitanium(IV) Chloride.—Crystallization from toluene gives bright-red acicular crystals, m.p. 289 ± 2°.

Anal. Calcd. for $(C_5H_5)_2TiCl_2$: C, 48.23; H, 4.05; Ti, 19.24; Cl, 28.48. Found: C, 47.9; H, 3.9; Ti, 19.50; Cl, 28.28.

The compound is moderately soluble in toluene, and chloroform, and in alcohol and other hydroxylic solvents, but is sparingly soluble in ether, benzene, carbon disulfide, carbon tetrachloride, petroleum ether and in water.

Bis-cyclopentadienyltitanium(IV) bromide[3] forms dark red crystals from toluene, melting at 314 ± 2°, and with a density of 1.920 g./cc. It is somewhat more soluble in organic solvents than the chloride, and it can be sublimed above 160° in vacuum. The compound is diamagnetic $\chi_{\text{mol}}^{298°\text{K}} = -186 \pm 3 \times 10^{-6}$ c.g.s.u.

Attempts to react bis-cyclopentadienyltitanium(IV) bromide with acetyl chloride in the Friedel–Crafts reaction failed. An attempt was also made to prepare an alcoholate by the reaction of the compound in butanol solution with a stoichiometric amount of pyridine. The color of the solution changed at once from red to pale yellow; after evaporation in vacuum, the residue was extracted with petroleum ether, in which the pyridinium hydrobromide is insoluble. While a petroleum soluble titanium compound is formed, we have been unable to isolate it in a pure state either by crystallization or sublimation, or to completely remove the halide.

Bis-cyclopentadienyltitanium(IV) fluoride was prepared by dissolving the bromide (1.5 g.) in hot 12 *N* hydrofluoric acid and heating on a steam-bath until the solution was pale yellow in color. On cooling, yellow crystals (0.7 g.) appeared; these were recrystallized from 3 *N* hydrofluoric acid solution.

Anal. Calcd. for $(C_5H_5)_2TiF_2$: C, 55.58; H, 4.66; Ti, 22.17. Found: C, 55.2; H, 4.63; Ti, 22.30.

The fluoride is much more soluble in water than are the other halides.

Bis-cyclopentadienyltitanium(IV) iodide was prepared from the bromide in reagent grade acetone by adding an excess of potassium iodide. The mixture was refluxed until the color was a deep purple (30 min.) when it was filtered and evaporated. The product crystallizes from toluene as dark purple crystals, m.p. (dec.) 319 ± 3°, yield 65%. The compound resembles the bromide in its properties.

Bis-cyclopentadienyltitanium(IV) Hydroxy Compounds.—Bis-cyclopentadienyltitanium(IV) bromide is soluble ($\sim$ 0.5 g./100 ml. at 25°) in water forming a pale yellow solution which is acid (*p*H $\sim$1.8) due to hydrolysis to the $(C_5H_5)_2TiOH^+$ ion. On increasing the concentration of hydrobromic acid, the color changes to the red of the undissociated bromide, which can actually be precipitated from the solution by saturation with hydrogen bromide. On dissolving the bromide (1 g.) in boiling water (25 ml.), evaporating under reduced pressure to 15 ml. volume, filtering, and allowing the solution to cool, large orange crystals of **bis-cyclopentadienyltitanium(IV) hydroxybromide monohydrate** were obtained.

Anal. Calcd. for $(C_5H_5)_2Ti(OH)Br \cdot H_2O$: C, 40.99; H, 4.45; Ti, 16.35; Br, 27.29. Found: C, 41.1; H, 4.6; Ti, 16.2; Br, 27.3.

This compound is moderately soluble in water, but insoluble in non-hydroxylic organic solvents. As further evidence that the $(C_5H_5)_2TiOH^+$ ion is the predominant species in the aqueous solution the **bis-cyclopentadienyltitanium(IV) hydroxypicrate** was isolated by adding a saturated solution of potassium picrate to a saturated aqueous solution of $(C_5H_5)_2TiBr_2$.

Anal. Calcd. for $(C_5H_5)_2Ti(OH)C_6H_2N_3O_7$: C, 45.41; H, 3.10; N, 9.93, Ti, 11.32. Found: C, 45.17; H, 3.28; N, 9.83; Ti, 11.28.

The reactions of the yellow aqueous solutions are similar to those of other bis-cyclopentadienyl cations. Thus insoluble precipitates are formed with large anions such as picrate, silicotungstate, triiodide, mercuriiodide, ferrocyanide and Reineckate. The dipicrate[3] was isolated by adding a saturated solution of picric acid to a saturated aqueous solution of the dibromide and recrystallizing the yellow precipitate from dilute picric acid solution. Solutions of the complex cation are stable when acid, but on neutralization to *p*H 3–4, complete disruption of the ion occurs, and titanium hydroxide and insoluble organic matter are precipitated.

The bis-cyclopentadienyltitanium(III) ion has been made as follows. An aqueous solution of $(C_5H_5)_2TiBr_2$ was converted to the perchlorate by passage through an anion-exchange resin (Dow A-2) column. A 2 millimolar solution of the ion 0.1 *M* in both sodium perchlorate and perchloric acid was studied at the dropping mercury electrode. A well-defined cathodic wave was observed at −0.44 volt *versus* the saturated calomel electrode (S.C.E.). On passing the yellow perchlorate solution through a Jones reductor, a green solution of the $(C_5H_5)_2Ti^+$ ion was produced. This solution shows a well-defined polarographic wave at the same potential as above, indicating reversibility of the system. The precipitation reactions of the green solution are typical of a bis-cyclopentadienylmetal ion. On running the eluate from the reductor into picric acid solution, the system being flushed with nitrogen, an insoluble brown picrate[3] was precipitated. The magnetic susceptibility of the solid picrate gave $\chi_{\text{mol}}^{298°\text{K}} = +2200 \pm 50 \times 10^{-6}$ c.g.s.u.; adding the estimated diamagnetic correction of -150×10^{-6} c.g.s.u., the susceptibility corresponds to a moment of 2.3 b.m., suggesting the presence of a single unpaired electron.

Bis-cyclopentadienylzirconium(IV) bromide[3] was obtained as colorless crystals m.p. (dec.) 260°. It is rather less soluble in organic solvents, more readily soluble in water and less readily hydrolyzed than its titanium analog; more detailed studies of the hydrolysis of these derivatives are in progress. The aqueous solutions of the compound give the usual precipitation reactions with large anions. Polarographic study of perchlorate solutions produced by ion exchange shows no evidence for reduction of the zirconium(IV) ion to an ion with the metal in a lower oxidation state.

Bis-cyclopentadienylvanadium(IV) chloride forms pale green crystals,[3] decomposing without melting at about 250°, and of density 1.60 g./cc. The compound is soluble in chloroform and alcohol, but is sparingly soluble in ether, carbon

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(5) N. H. Furman, Editor, "Scott's Standard Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 5th Edition, 1939, Vol. I.

disulfide, carbon tetrachloride, benzene and toluene, and is insoluble in petroleum ether. In water it dissolves readily forming a green solution which is decomposed immediately by bases, which is stable for several hours when acidified. The solution gives green precipitates with silicotungstic acid, Reinecke's salt and potassium triiodide; a dark green *picrate* has been characterized.[3] The magnetic susceptibility of the dichloride was $\chi_{\mathrm{mol}}^{296^\circ\mathrm{K}} = +1450 \pm 30 \times 10^{-6}$ c.g.s.u., indicating the presence of a single unpaired electron.

Bis-cyclopentadienylvanadium(IV) bromide was obtained as a dark green solid decomposing rapidly in the solid state, but stable in solutions of chloroform or carbon tetrachloride in which it is more soluble than the chloride analog. It behaves chemically like the chloride, however.

The bis-cyclopentadienylvanadium(III) Ion.—Polarographic study of the green aqueous solutions of bis-cyclopentadienylvanadium(IV) perchlorate, which were prepared from the chlorides by anion exchange, showed no oxidation wave; attempts to oxidize the solutions chemically by permanganate and ceric sulfate lead only to complete disruption of the compound. On the other hand, in a 0.1 *M* sodium perchlorate supporting electrolyte 0.1 *M* in perchloric acid, a well-defined cathodic wave at −0.32 volt *versus* the S.C.E. was obtained. On passing the green solution through a Jones reductor, a purple solution was obtained which gives a well-defined polarographic oxidation wave at the same potential as above. This solution, which gave a blue precipitate with silicotungstic acid and a blue-green Reineckate, was immediately oxidized by air and by 0.1 *M* hydrogen ion within two hours. The magnetic susceptibility of the ion in dilute aqueous solution (∼ 10 mg./ml.) was measured. Bis-cyclopentadienylvanadium(IV) chloride in 0.005 *M* perchloric acid was run slowly through a Jones reductor into a susceptibility tube, the whole operation being performed in a nitrogen atmosphere. The measurements were made rapidly and no change in the susceptibility was noted over a 20-minute period; the vanadium content of the solution was determined subsequently. The diamagnetism of the medium was measured directly using a 0.005 *M* perchloric acid solution which was passed alone through the reductor. Four determinations gave a value for the $(C_5H_5)_2V^+$ ion of $\chi_{\mathrm{mol}}^{296^\circ\mathrm{K}} = +3280 \pm 70 \times 10^{-6}$ c.g.s.u.; after correcting for the diamagnetism of the ion (-115×10^{-6} c.g.s.u.) the susceptibility corresponds to a moment of 2.86 ± 0.6 b.m., suggesting the presence of two unpaired electrons in the ion.

Bis-cyclopentadienylniobium(V) bromide crystallizes from chloroform at −70° as fine dark reddish brown crystals; slow evaporation of the solvent at room temperature produces acicular crystals up to 1 cm. in length, which decompose without melting at about 260°.

Anal. Calcd. for $(C_5H_5)_2NbBr_3$: C, 25.95; H, 2.16; Nb, 20.08; Br, 51.83. Found: C, 25.9; H, 2.3; Nb, 20.00; Br, 51.90.

The compound is readily soluble in polar solvents such as chloroform or alcohol, but is less soluble in benzene or toluene, and is insoluble in petroleum ether. It hydrolyzes very rapidly in air, and must be handled in a dry atmosphere; in this hydrolysis the orange-red bis-cyclopentadienylniobium(V) monohydroxy bromide is formed.

Anal. Calcd. for $(C_5H_5)_2Nb(OH)Br_2$: Nb, 23.20; Br, 40.00. Found: Nb, 23.30; Br, 40.05.

Both of these niobium compounds dissolve readily in water with partial hydrolysis, giving yellow solutions which give the usual precipitation reactions with large anions. Bromine water also gives a yellow insoluble precipitate which is presumably a hydroxy *tri*-bromide. The aqueous solutions are decomposed at once by bases, but are stable when acid; on increasing the acid concentration to 3–4 *M*, the yellow color deepens to red. The hydrolytic equilibria are being studied in more detail. Bis-cyclopentadienylniobium(V) bromide is diamagnetic, $\chi_{\mathrm{mol}}^{298^\circ\mathrm{K}} = -240 \pm 5 \times 10^{-6}$ c.g.s.u. Polarographic study of solutions of the perchlorate 0.1 *M* in both sodium perchlorate and perchloric acid, shows ill-defined cathodic waves at about −0.44 and −0.71 volt *versus* the S.C.E. On passing solutions of the compound in the V oxidation state through a Jones reductor, the color changes from yellow to purple, but the reduced solution turns cloudy and is destroyed completely within a few minutes.

Bis-cyclopentadienyltantalum(V) bromide forms rust colored crystals from chloroform saturated with hydrogen bromide, which melt with decomposition at 280°.

Anal. Calcd. for $(C_5H_5)_2TaBr_3$: C, 21.8; H, 1.8; Ta, 32.90; Br, 43.50. Found: C, 22.5; H, 2.3; Ta, 32.85; Br, 43.90.

The compound is exceedingly readily hydrolyzed by moisture, turning yellow. It is soluble in polar solvents and readily in water, giving yellow solutions, which resemble in properties those of the niobium analog. Polarographic study gives no evidence of reduction in aqueous solution.

Infrared Spectra.—Due to the low solubility of the bis-cyclopentadienyl halides of Ti, Zr, V, Nb and Ta in carbon disulfide or carbon tetrachloride, infrared absorption spectra (Figs. 1, 2) were taken in potassium halide wafers formed by compressing a finely ground mixture of the compound with the potassium salt under high pressure.[6a,b] The existence of a single C–H stretching frequency and of other bands in positions similar to those in the neutral bis-cyclopentadienyl compounds and the $(C_5H_5)_2Fe^+$ ion, provides evidence for the "sandwich" structure of the compounds. The spectra are all notably similar to each other and to the spectrum of fer-

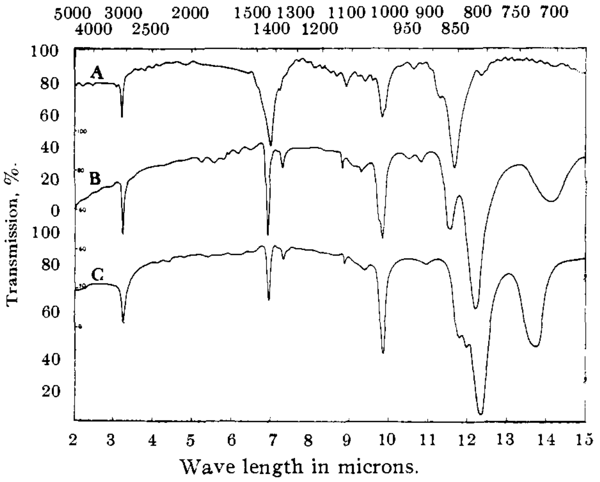

Fig. 1.—Infrared absorption spectra: A, $C_{10}H_{10}FeGaCl_4$, 4.5 mg./1.5 g. KI; B, $C_{10}H_{10}TiBr_2$, 5.1 mg./1.5 g. KF; $C_{10}H_{10}ZrBr_2$, 4.4 mg./1.5 g. KI; Perkin–Elmer double beam spectrophotometer.

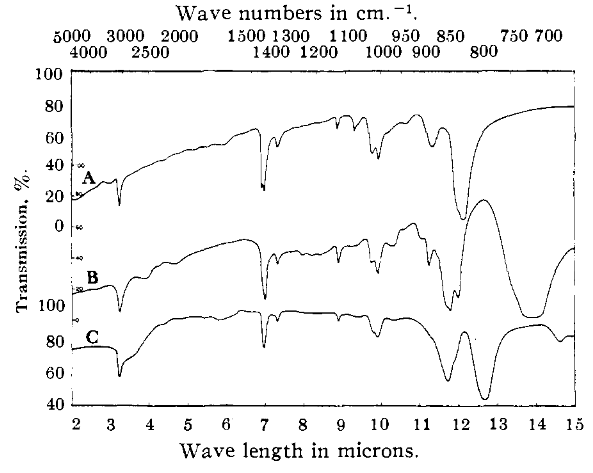

Fig. 2.—Infrared absorption spectra: A, $C_{10}H_{10}VCl_2$, 7.3 mg./1.5 g. KCl; B, $C_{10}H_{10}NbBr_3$, 8.3 mg./1.5 g. KBr; C, $C_{10}H_{10}TaBr_3$, 3.5 mg./1.5 g. KBr; Perkin–Elmer double beam spectrophotometer.

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[6] (a) U. Scheidt, *Z. Naturforsch.*, **7б**, 270 (1952); (b) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

ricinium tetrachlorogallate, which is shown for comparison. For the four titanium halides, the only notable change in the spectra is a shift to longer wave lengths of the two absorption maxima in the 850 cm.$^{-1}$ region in going from the fluoride to the iodide.

II. Discussion

Titanium has been shown[7a,b] to form metal to carbon bonds of the alkyl type; the low stability of these derivatives to air and water is in striking contrast to the stability of the cyclopentadienyltitanium derivatives.[7c] It is noteworthy that Herman and Nelson also observed[7b] that the indenyl group forms an organotitanium compound of higher stability than those of other alkyl or aryl groups. Bis-indenyl derivatives of iron(II) and cobalt(II) and -(III) have been characterized[8a,b] and these compounds unquestionably have the "sandwich" structure of their bis-cyclopentadienyl analogs, from which they may be considered to be derived by the annulation of a benzene nucleus. The increased stability of indenyltitanium compounds is thus very likely due to the different type of bonding involved. Our attempts to isolate a bis-indenyltitanium halide in a pure state from the red solutions resulting from the reaction of titanium tetrachloride with indenyllithium or indenylmagnesium bromide have, so far, been unsuccessful.

The bis-cyclopentadienyl derivatives described in this paper and their magnetic properties are of some interest with regard to the electronic structure of bis-cyclopentadienyl compounds. The existence of the stable isoelectronic diamagnetic compounds of Ti(IV), Zr(IV), Nb(V) and Ta(V) provides strong evidence for the view[9] that the bond between the metal atom and each C_5H_5 ring is essentially a two-electron bond, since in $(C_5H_5)_2TiBr_2$, for example, which can be considered as $(C_5H_5)_2Ti^{++}$, the metal has only two 3d electrons (of E_{1g} symmetry) available for overlap with each of the unpaired π electrons (in the E_{1g} orbitals of the C_5H_5 radical). It also indicates that the secondary types of bonding considered in the case of ferrocene[10] must contribute little to the bonding. In a recent extension[11] of the Dunitz and Orgel molecular orbital treatment[12] of ferrocene, the possibility of a dative bond from the Σ orbital (A_{1g} symmetry) of the rings to the d_{z^2} orbital of the metal was considered in cases such as the Ti(IV) compounds. This seems unnecessary, and, moreover, the extension leaves untouched the main deficiency of the Dunitz and Orgel view, which, like that of Jaffe's, is the inability to account for the magnetic properties of $(C_5H_5)_2M$(II) compounds.[1] Moffitt[9] has suggested that under the influence of the field of the π-electrons of the C_5H_5 rings the 3d and 4s orbitals of the metal (both of A_{1g} symmetry) can hybridize, giving an upper (ka_{1g}) and a lower (ka_{1g}) level. The magnetic properties of the bis-cyclopentadienyl derivatives of Cr(II), Mn(II) (white form), Fe(II), Co(II) and Ni(II) indicate that the ha_{1g} level is doubly occupied; for the $(C_5H_5)_2Ti^+$ ion and for $(C_5H_5)_2VCl_2$, the single unpaired electron may be either in the ha_{1g} or in the de_{2g} levels. For the $(C_5H_5)_2V^+$ ion, however, the ha_{1g} level cannot be too far below the primarily non-bonding de_{2g} orbitals, since a triplet state is observed. The additional stability associated with the attainment of maximum multiplicity must be greater than that obtained by assigning both electrons to the ha_{1g} orbital. However, this does not necessarily imply that the isoelectronic molecule $(C_5H_5)_2Ti$ is also paramagnetic. The opposing factors may well lead to a singlet ground state in this case, though it is difficult to make a more definite prediction. That this possibility is a real one may be seen by noting that whereas the ground state of the Ti atom is ^3F, $3d^24s^2$, that of the V^+ ion is ^5D, $3d^4$.[13] *Bis*-cyclopentadienyltitanium(II) has been prepared by the reaction of titanium(II) chloride with cyclopentadienylsodium in dimethyl "cellosolve," and will be reported in detail in a later paper.

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[7] (a) D. F. Herman and W. K. Nelson, *ibid.*, **75**, 3877 (1953); (b) **75**, 3882 (1953).

(7c) NOTE ADDED IN PROOF.—While we were engaged in similar experiments, L. Summers and R. H. Vloth, *ibid.*, **76**, 2278 (1954), published a preliminary description of the preparation of diphenyl bis-cyclopentadienyltitanium(IV) by the reaction of bis-cyclopentadienyltitanium(IV) chloride with phenyllithium.

[8] (a) P. L. Pauson and G. Wilkinson, *ibid.*, **76**, 2024 (1954); (b) E. O. Fischer, D. Sens and R. Jira, *Z. Naturforsch.*, **8b**, 692 (1953); E. O. Fischer, *ibid.*, **8b**, 694 (1953).

[9] W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

[10] H. H. Jaffe, *J. Chem. Phys.*, **21**, 156 (1953).

[11] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 352 (1954).

[12] J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

[13] R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, N. Y., 1932.