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Eight-Coordinate Complexes of Niobium, Tantalum, and Uranium Tetrahalides

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In order to assign the d-d spectral transitions in dodecahedral complexes, further eight-coordinate complexes of niobium tetrahalides of the type $NbX_4(diars)_2$ (where X is Cl, Br, or I) with diarsine-like ligands (where diars is *o*-phenylenebis(dimethylarsine)) have been prepared from the tetrahalides in acetonitrile solution. The d-d bands have been assigned by studying variations in their energies for different halides and for different ligands. The complexes $NbX_4(C_2H_5diars)_2$ (where X is Cl or Br and C_2H_5diars is *o*-phenylenebis(diethylarsine)) dissolve unchanged in toluene but partially dissociate in acetonitrile and completely dissociate in pyridine. Under the same conditions tantalum tetrachloride forms only monoadducts of the type $TaCl_4(diars)$, although $TaCl_4(diars)_2$ can be obtained in an impure form from a sealed-tube reaction. The uranium complex $UCl_4(diars)_2$ was also prepared and characterized.

The ligand *o*-phenylenebis(dimethylarsine) (or diarsine) is remarkably effective in forming eight-coordinate complexes of the type $MX_4(diars)_2$ (where X = Cl and M = Ti, Zr, Hf, V, Nb; X = Br and M = Ti, Zr, Hf, Nb; X = I and M = Nb).¹⁻³ The chloro and bromo complexes are isomorphous, and the structure of $TiCl_4(diars)_2$ shows dodecahedral stereochemistry. The two bidentate ligands form a tetrahedron elongated along the fourfold inversion axis, while the four halogen atoms occupy positions between the two bidentate ligands. The properties of the d^1 niobium complexes were of particular interest, although only diffuse reflectance spectra could be obtained, and the magnetic properties were complicated by the presence of an antiferromagnetic impurity.² In this paper the preparation and spectral and magnetic properties of magnetically pure eight-coordinate d^1 niobium complexes with diarsine and some related ligands are described. Tantalum and uranium analogs are also reported.

Experimental Section

Ligands.—*o*-Phenylenebis(dimethylarsine) (or diarsine), 1,2-bis(dimethylarsine)-4-methylbenzene (or 4-methyldiarsine), *o*-phenylenebis(diethylarsine) (or ethyldiarsine), and *o*-dimethylaminodimethylarsinobenzene were prepared as described elsewhere.⁴ *o*-Phenylenebis(diphenylarsine) (or phenyldiarsine) was prepared according to the literature.⁵ *Anal.* Calcd for $C_{20}H_{24}As_2$: C, 67.5; H, 4.5. Found: C, 67.9; H, 4.3.

Niobium Tetrachloride.—Niobium pentachloride was reduced with niobium according to the literature,⁶ except that the temperature gradient used was from 360 (niobium end) to 250°, rather than 400 to 250°. The slightly lower temperature reduced the amount of disproportionation of the niobium tetrachloride. A large excess of niobium metal was used, but the reaction was stopped while liquid niobium pentachloride was still present at the cool end of the tube.

Niobium Tetrabromide.—Niobium pentabromide was prepared by reaction of the elements and reduced with niobium by the method used for the preparation of the tetrachloride, using a temperature gradient from 350 to 410°.

Tantalum Tetrachloride.—Tantalum tetrachloride was prepared from the pentachloride either by reduction with aluminum foil in a 350–200° temperature gradient⁷ to give a black crystalline material (*Anal.* Calcd for $TaCl_4$: Cl, 43.9. Found: Cl, 42.0) or with aluminum powder⁸ to give a dark green powder isomorphous with niobium tetrachloride (*Anal.* Found: Cl, 43.4).

Complexes.—All operations were conducted under dry, oxygen-free conditions on a standard vacuum system. The degassed solvents were dried over sodium (for dioxane) or phosphorus pentoxide followed by calcium hydride or lithium aluminum hydride (for all other solvents). Yields were not measured but were close to 100%.

Tetrachlorobis(*o*-phenylenebis(dimethylarsine))niobium(IV).—A hot solution of niobium tetrachloride (0.70 g, 3.0 mmol) in acetonitrile was slowly added, with stirring, to a solution of diarsine (2.1 g, 7.5 mmol) in acetonitrile. The precipitate, which was formed immediately, was filtered off, washed well with acetonitrile, and pumped dry. *Anal.* Calcd for $NbCl_4(C_{10}H_{16}As_2)_2$: C, 29.8; H, 4.0; Cl, 17.6; Nb, 11.5. Found: C, 30.6; H, 4.0; Cl, 17.3; Nb, 12.0. The complex was insoluble in acetonitrile, dioxane, and nonpolar solvents but could be recrystallized from pyridine to give small blue-green octahedra.

Tetrachlorobis(1,2-bis(dimethylarsine)-4-methylbenzene)niobium(IV).—This compound was prepared in the same way as the above diarsine complex, using 0.50 g (2.1 mmol) of niobium tetrachloride and 0.9 ml (4.3 mmol) of 4-methyldiarsine. *Anal.* Calcd for $NbCl_4(C_{11}H_{18}As_2)_2$: C, 31.8; H, 4.4; Cl, 17.0; Nb, 11.2. Found: C, 31.9; H, 4.7; Cl, 16.5; Nb, 11.9. This complex had a conductance of $5 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ for a $1.0 \times 10^{-3} M$ solution in pyridine, compared with a value of approximately $70 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ for a 1:1 electrolyte.

Tetrachlorobis(*o*-phenylenebis(diethylarsine))niobium(IV).—A solution of niobium tetrachloride (0.50 g, 2.1 mmol) in acetonitrile (100 ml) was filtered into a solution of ethyldiarsine (10 ml, 5.0 mmol) in the same solvent (100 ml), and the solution was heated to its boiling point. The product, which crystallized out on cooling as pale green platelike crystals, was filtered off, washed with acetonitrile, and pumped dry. *Anal.* Calcd for $NbCl_4(C_{14}H_{24}As_2)_2$: C, 36.6; H, 5.3; Cl, 15.4; Nb, 10.0. Found: C, 36.8; H, 5.2; Cl, 15.5; Nb, 10.6. This complex was more reactive with air than the above complexes, and it rapidly decomposed to a purple substance when ground in the drybox.

In an attempt to prepare the monoadduct of niobium tetrachloride with ethyldiarsine, the ligand was treated with an excess of niobium tetrachloride (greater than 1 mol/mol of ligand) in acetonitrile. However, only the complexes $NbCl_4(C_2H_5diars)_2$

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(1) R. J. H. Clark, J. Lewis, and S. Nyholm, *J. Chem. Soc.*, 2460 (1962).(2) R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *ibid.*, 2865 (1965).(3) R. J. H. Clark, W. Errington, J. Lewis, and R. S. Nyholm, *ibid.*, A, 989 (1966).(4) W. P. Crisp, R. L. Deutscher, and D. L. Kepert, *ibid.*, A, in press.(5) J. Chatt and F. A. Hart, *ibid.*, 1378 (1960).(6) R. E. McCarley and B. A. Torp, *Inorg. Chem.*, 2, 540 (1963).(7) H. Schafer and L. Grau, *Z. Anorg. Allg. Chem.*, 275, 198 (1954).(8) L. M. Petrova and B. G. Korshunov, *Melody Poluch. Khim. Reaktivov Prep.*, No. 16, 161 (1967); *Chem. Abstr.*, 69, 40789 (1968).

and $\text{NbCl}_4(\text{CH}_3\text{CN})_2$, as identified by their visible and infrared spectra, were isolated from the reaction mixture.

Tetrabromobis(*o*-phenylenebis(diethylarsine))niobium(IV).—A hot solution of the complex $\text{NbBr}_4(\text{CH}_3\text{CN})_2$ (1.0 g, 2.0 mmol) in acetonitrile (150 ml) was added to a solution of ethyldiarsine (1.1 ml, 4.6 mmol) in the same solvent (50 ml). The product, which was less soluble than the chloro complex, was filtered off, washed with acetonitrile, and pumped dry. *Anal.* Calcd for $\text{NbBr}_4(\text{C}_{14}\text{H}_{24}\text{As}_2)_2$: C, 30.7; H, 4.5; Br, 29.2; Nb, 8.5. Found: C, 30.9; H, 4.9; Br, 28.8; Nb, 8.8.

Tetraiodobis(*o*-phenylenebis(diethylarsine))niobium(IV).—Ethyldiarsine (0.6 ml, 2.5 mmol) was added to a slurry of the acetonitrile adduct of niobium tetraiodide (0.8 g, 1.2 mmol) in acetonitrile (200 ml). The mixture was stirred for 2 hr at 70°. The product, which was only very slightly soluble in acetonitrile, was filtered off, washed with acetonitrile, and pumped dry. *Anal.* Calcd for $\text{NbI}_4(\text{C}_{14}\text{H}_{24}\text{As}_2)_2$: C, 26.2; H, 4.5; I, 39.4; Nb, 7.3. Found: C, 26.1; H, 3.9; I, 40.0; Nb, 8.0.

Reaction of Niobium Tetrachloride with Other Bidentate Ligands.—Niobium tetrachloride (0.2 g, 0.9 mmol) was added to a slurry of *o*-phenylenebis(diphenylarsine) (2 g, 4 mmol) in acetonitrile (100 ml), and the mixture was refluxed for 5 min. The solution was evaporated down to a small volume and filtered from the unreacted ligand. The filtrate was evaporated to dryness and the infrared spectrum of the complex identified it as $\text{NbCl}_4(\text{CH}_3\text{CN})_2$. It may be noted that triphenylarsine did not react with niobium tetrachloride in acetonitrile.⁹

When niobium tetrachloride was treated with *o*-dimethylaminodimethylarsinobenzene or *o*-phenylenebis(dimethylamine)¹⁰ in acetonitrile solution, or in sealed tubes, only dark brown tars, which were not investigated further, were produced.

Tetrachloro(*o*-phenylenebis(dimethylarsine))tantalum(IV).—Tantalum tetrachloride (1.2 g, 3.7 mmol) was dissolved with a minimum of heating in acetonitrile (200 ml) and the solution was filtered into a solution of diarsine (1.6 ml, 8.0 mmol) in the same solvent. The product, which precipitated immediately, was filtered off, washed, and pumped dry. *Anal.* Calcd for $\text{TaCl}_4(\text{C}_{10}\text{H}_{16}\text{As}_2)_2$: C, 19.8; H, 2.7; Cl, 23.3; Ta, 29.8. Found: C, 19.1; H, 2.6; Cl, 24.1; Ta, 30.5.

Tetrachloro(*o*-phenylenebis(diethylarsine))tantalum(IV).—This was prepared in the same way as the diarsine complex, using 2.6 g (8 mmol) of tantalum tetrachloride and 2 ml (8 mmol) of ethyldiarsine. *Anal.* Calcd for $\text{TaCl}_4(\text{C}_{14}\text{H}_{24}\text{As}_2)_2$: C, 25.3; H, 3.6; Cl, 21.4; Ta, 27.2. Found: C, 27.4; H, 4.5; Cl, 21.2; Ta, 28.8.

Tetrachlorobis(*o*-phenylenebis(dimethylarsine))tantalum(IV).—Tantalum tetrachloride (0.8 g, 2.5 mmol) and diarsine (1.3 ml, 6.5 mmol) were heated in a sealed tube at 200° for 14 hr; the mixture was washed with toluene and pumped dry. The reaction product also contained a few dark brown crystals, but with care, these crystals could be kept in the reaction vessel while the fine yellow-green powder was washed onto the sintered-glass disk of the apparatus used. The product analyzed approximately as $\text{TaCl}_4 \cdot 1.5\text{diars}$. *Anal.* Calcd for $\text{TaCl}_4 \cdot 1.5(\text{C}_{10}\text{H}_{16}\text{As}_2)_2$: C, 24.0; H, 3.4; Cl, 18.8; Ta, 24.1. Found: C, 24.3; H, 3.3; Cl, 17.6; Ta, 24.4. Some bands in the infrared spectrum were split into components typical for both eight-coordinate and lower coordinate diarsine complexes. The absorptions most sensitive to coordination number are the $\text{As}-\text{CH}_3$ rocking frequencies at 885 and 847 cm^{-1} and the $\text{As}-\text{CH}_3$ stretching frequencies at 581 and 571 cm^{-1} in the free ligand,¹¹ which are shifted to 913, 876, 619, and 600 cm^{-1} in $\text{TaCl}_4\text{diars}$ and $\text{TaCl}_5\text{diars}$,¹² but in this mixture additional bands of intermediate energy appear at 904, 867, 612, and 595 cm^{-1} , which are typical of diarsine bonded to an eight-coordinate

TABLE I

INTERPLANAR SPACINGS, d (Å) ^a			
$\text{NbCl}_4(\text{diars})_2$	$\text{TaCl}_4(\text{diars})_2$	$\text{NbCl}_4(\text{diars})_2$	$\text{TaCl}_4(\text{diars})_2$
4.066 vs	4.087 vs	1.314 m	1.317 w
	3.860 w	1.258 m	1.260 w
	3.539 w	1.233 m	1.234 w
3.304 vs	3.326 vs	1.198 w	1.201 w
2.589 s	2.614 s	1.16 m	1.168 w
2.354 w	2.376 w	1.127 w	
2.063 w		1.119 m	1.120 m
2.051 s	2.054 m	1.092 m	1.091 m
1.768 m	1.787 m	1.06 w	1.059 w
1.695 m	1.697 m	1.01 m	1.010 m
1.567 m	1.576 m	0.983 m	0.986 w
1.438 m	1.442 m	0.974 m	0.975 w
1.407 w	1.407 w	0.935 m	0.938 w
1.346 m		0.879 m	0.879 w
1.335 m	1.338 w	0.852 w	0.854 w

^a Abbreviations: vs, very strong; s, strong; m, medium; w, weak.

metal atom.¹³ X-Ray powder diffraction photographs confirmed that the main component of the powder was isomorphous with $\text{NbCl}_4(\text{diars})_2$ (Table I). The second component of this mixture cannot be identified with certainty, but it may be a mixture of $\text{TaCl}_4\text{diars}$ and $\text{TaCl}_5\text{diars}$,¹² the latter arising from the disproportionation of tantalum(IV).

The reaction of $\text{TaCl}_4\text{diars}$ with excess diarsine in a sealed tube at 120° for 5 weeks gave a product which still contained a large amount of starting material, as shown by the visible spectrum.

Tetrachlorobis(*o*-phenylenebis(dimethylarsine))uranium(IV).—Uranium tetrachloride (0.9 g, 2.4 mmol) in dioxane (150 ml) was filtered into a solution of diarsine (1 ml, 5.0 mmol) in dioxane (50 ml). The product, which slowly precipitated, was filtered off, washed with dioxane, and pumped dry. *Anal.* Calcd for $\text{UCl}_4(\text{C}_{10}\text{H}_{16}\text{As}_2)_2$: C, 25.2; H, 3.4; Cl, 14.9; U, 25.0. Found: C, 24.7; H, 3.4; Cl, 14.2; U, 26.1. The compound appeared to be insoluble in acetonitrile and dioxane. The complex is not isomorphous with $\text{NbCl}_4(\text{diars})_2$, but the two X-ray powder diffraction photographs are very similar. The $\text{As}-\text{CH}_3$ rocking and stretching frequencies observed at 904, 865, 612, and 595 cm^{-1} are typical for diarsine attached to an eight-coordinate metal atom.

Magnetic Measurements.—Susceptibilities were measured by the Faraday method. Samples for room-temperature measurements were held in a glass bucket with an airtight rubber stopper, while temperature-dependent measurements were made in an atmosphere of oxygen-free nitrogen using a Delrin bucket.¹⁴ The sample holders were loaded in the drybox and silver shot was used as calibrant.¹⁵ Standard diamagnetic corrections were applied.¹⁶

X-Ray Measurements.—X-Ray powder photographs were taken with a Philips Debye-Scherrer camera, 114.8 cm in diameter, using Ni-filtered $\text{Cu K}\alpha$ radiation.

Spectral Measurements.—Ultraviolet and visible spectra were recorded on a Unicam SP 700 spectrophotometer calibrated against 4% holmium oxide in 1.4 *M* perchloric acid.¹⁷ Solution spectra were measured using sealed-off 2-mm quartz cells containing solutions prepared on the vacuum line. Diffuse reflectance spectra were measured on the same instrument fitted with a Unicam SP 735 diffuse reflectance attachment in an airtight cell which was prepared in a drybox. Magnesium oxide was used as reference.

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TABLE II
 ABSORPTION MAXIMA (kK) IN THE DIFFUSE REFLECTANCE (DR) AND SOLUTION SPECTRA IN THE VISIBLE
 AND ULTRAVIOLET REGIONS FOR EIGHT-COORDINATE NIOBIUM AND TANTALUM COMPLEXES^a

		$d_{xy}-d_x^2$	$d_{xy}-d_{xz}, d_{yz}$	$d_{xy}-d_x^2-y^2$?	Charge transfer				
NbCl ₄ (diars) ₂	DR	10.45	13.35 (15.5)	(17.8)	(22)	20.28	(26.5)	31.3	(38)	(45)
	Pyridine ^b						(25.0)			
NbCl ₄ (C ₂ H ₅ diars) ₂	DR	(9.80)	13.05 (15.7)	(17.5)	(23)		(28)	(31)	37.2	44.8
	Toluene	(9.75)	12.80 (14.7)	17.47	(23)					
	Acetonitrile ^c	(9.6)	12.6	<i>d</i>				24.08		
	Pyridine ^b					20.20	(24.0)			
NbBr ₄ (C ₂ H ₅ diars) ₂	DR	9.70	13.05	16.00	18.75			(33)	(37)	44.2
	Toluene	(9.8)	12.72	15.95						
NbI ₄ (C ₂ H ₅ diars) ₂	DR ^e	9.80	(13.1)	15.35	18.2		(28.5)	(32)	(38.0)	44.7
	Toluene ^e	10.1	(12.7)	<i>f</i>			18.40			
NbCl ₄ (4-CH ₃ diars) ₂	DR	10.50	13.45 (15)	(17.8)	(23)		(28)	32.6	36.9	44.1
TaCl ₄ (diars) ₂	DR	9.90	14.25 (15.8)	19.20			24.85	34.7	36.9	43.9
NbCl ₄ (diars) ₂	DR ^g	10.7	13.8 (15.3)	17.3	(22.7)					
NbBr ₄ (diars) ₂	DR ^g	10.6	13.8	16.7	(21.2)					
NbI ₄ (diars) ₂	DR ^g	10.25	(13.1)	15.2	(19.7)					
UCl ₄ (diars) ₂	DR ^h						(28)	(32)	36.8	44.3
TaCl ₄ (diars) ⁱ	DR	(10.4)		17.6			23.5	33.6	37.6	44.0
TaCl ₄ (C ₂ H ₅ diars) ^j	DR	(11.4)		(16.7)			22.8	(31)	36.7	45.1

^a Shoulders are enclosed in parentheses. ^b The complex is dissociated in this solvent. ^c The complex is partially dissociated in this solvent. ^d A d-d band of the dissociated species at 18.45 kK obscures this band of the undissociated species. ^e Additional charge-transfer bands at 22.55, 24.45, and (26.4) kK. ^f This band obscured by the charge-transfer band of the dissociated species. ^g Taken from ref 2. ^h For transitions of the uranium(IV) ion, see Table V. ⁱ Additional shoulders at 13 and 17 kK for the spectrum in acetonitrile. ^j Acetonitrile solution shows a strong band at 24.6 kK. The compound was insufficiently soluble to detect d-d bands.

Results

The pale green NbX₄L₂ compounds (where X is Cl and L is diarsine, 4-methyldiarsine, or ethyldiarsine and where X is Br and L is ethyldiarsine) were prepared by precipitation from acetonitrile solutions of the tetrahalides, while the yellow-green NbI₄(C₂H₅diars)₂ was prepared from a slurry of the tetraiodide in acetonitrile. The ligand *o*-phenylenebis(diphenylarsine) did not react with niobium tetrachloride in acetonitrile. The formation of a bis adduct of niobium tetrachloride with ethyldiarsine is in contrast to the behavior of the tetrachlorides of titanium and vanadium, for which only the monoadducts could be isolated with this ligand.^{4,18} This difference in behavior may be reflecting the greater radius of niobium(IV) in comparison with the other metal ions.

All the complexes have similar visible spectra in the region assigned to d-d transitions and are thus assumed to have a dodecahedral structure, since NbCl₄(diars)₂ is isomorphous with the known dodecahedral complex TiCl₄(diars)₂.¹ The three NbX₄(C₂H₅diars)₂ complexes all have different X-ray powder diffraction patterns.

When tantalum tetrachloride was treated with excess diarsine (mole ratio greater than 1:2) or ethyldiarsine in acetonitrile, only the monoadducts precipitated. This relatively large difference in the chemistry of the electropositive niobium and tantalum brought about with ligands of low electronegativity can be compared to the differences in zirconium and hafnium brought about by the same ligand.^{1,3} The elusive TaCl₄(diars)₂ could only be obtained in an impure state by the reaction of tantalum tetrachloride and diarsine in a sealed tube.

Discussion

Visible and Ultraviolet Spectra.—The absorption

(18) R. J. H. Clark, *J. Chem. Soc.*, 5699 (1965).

maxima in the visible and ultraviolet spectra of the niobium and tantalum compounds are shown in Table II. The higher energy bands are assigned to arsenic-to-metal charge-transfer transitions (see Table II) due to comparison with the spectra of other diarsine complexes,⁴ in particular the complexes of niobium pentahalides,¹² and also due to their greater intensities.

The first charge-transfer band in the diffuse reflectance spectrum of the niobium-ethyldiarsine complex is at higher energy than the corresponding band of the diarsine complex, whereas for the hexacoordinate titanium tetrachloride complexes, the reverse is found.⁴ This result may be explained by assuming that the niobium-arsenic distance is greater for the ethyldiarsine complex than for the diarsine complex. A similar conclusion is reached by a study of the d-d transitions of the complexes (see below). It is also relevant to note that ethyldiarsine is unable to form a bis adduct with titanium tetrachloride.^{4,18}

Representative spectra in the lower energy region are shown in Figures 1-3. All consist of three main bands (molar extinction coefficients of 6, 26, and 10 for NbCl₄(C₂H₅diars)₂ in toluene) which are assigned to the three d-d transitions expected for a dodecahedral complex.¹⁹ The complexes also show weak shoulders or bands near the base of the first charge-transfer band, and the tetrachloro complexes also show a weak shoulder on the most intense (middle) d-d band, both of which have molar extinction coefficients of less than 2 (for the ethyldiarsine complex).

The exact shape parameters of NbCl₄(diars)₂ are not known, but for the isomorphous TiCl₄(diars)₂, $\theta_A = 36.4^\circ$ and $\theta_B = 72.5^\circ$,^{1,20} where θ_A and θ_B are the angles

(19) R. V. Parish and P. G. Perkins, *ibid.*, A, 345 (1967). In Table II of this paper, the coefficient for a_2 in the dodecahedral crystal field functions H_{22} , H_{44} should be $2/7$ and not $1/7$.

(20) P. Pauling and G. B. Robertson, personal communication, University College, London, 1965.

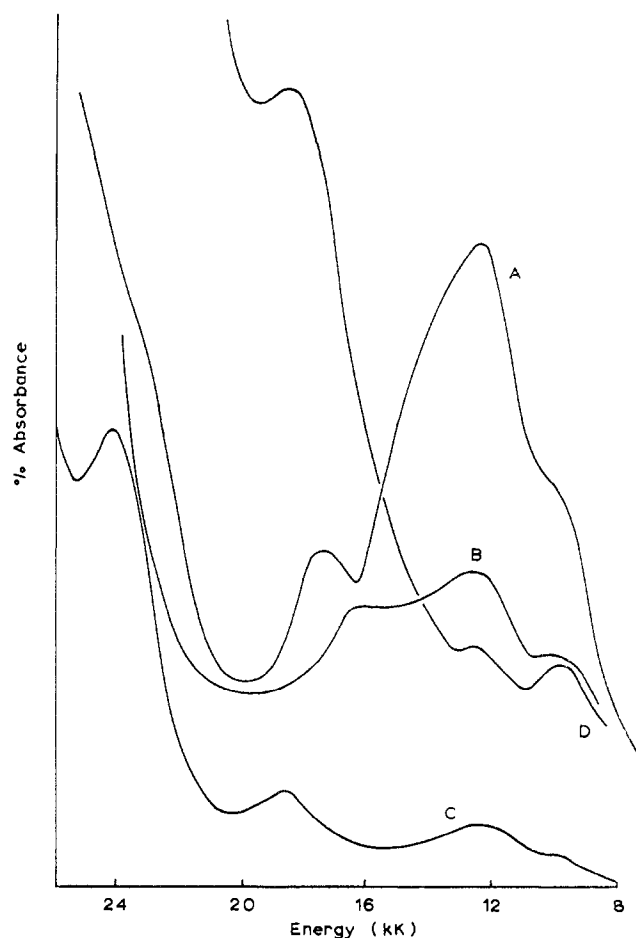


Figure 1.—Solution spectra of ethyldiarsine complexes of niobium tetrahalides: (A) $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$ in toluene; (B) $\text{NbBr}_4(\text{C}_2\text{H}_5\text{diars})_2$ in toluene; (C) $\text{NbI}_4(\text{C}_2\text{H}_5\text{diars})_2$ in toluene; (D) $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$ in acetonitrile.

the M-A bonds and the M-B bonds make with the fourfold inversion axis of a dodecahedron. If the coordinate axes are placed so that the z axis lies along the fourfold inversion axis of the molecule, the splitting patterns calculated place the d_{xy} orbital at considerably lower energy than the other four approximately degenerate d orbitals.¹⁹ However an increase in θ_B of $3\text{--}4^\circ$, which would escape detection by the X-ray powder photographs, leads to approximately equally spaced orbitals $d_{xy} < d_{z^2} < d_{xz}$, $d_{yz} < d_{x^2-y^2}$. These splitting patterns would be further modified due to the presence of two different ligands. The similarity of the spectra indicates that the relative order of the d orbitals does not vary in these complexes, which also means that they probably all have similar structures.

As the $d_{x^2-y^2}$ orbital points more directly at the B positions of the dodecahedron than do the other orbitals, changes in the halogen atoms should affect this orbital to the greatest extent. It is experimentally found (Table II) that it is the highest energy band which is most affected by changing the halogen atom in the series NbX_4L_2 (where X is Cl, Br, or I, and L is diarsine or ethyldiarsine) as predicted from the above order. The effect of changing the halogen atom on the other two bands is small.



Figure 2.—Diffuse reflectance spectra of ethyldiarsine complexes of niobium tetrahalides: (A) $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$; (B) $\text{NbBr}_4(\text{C}_2\text{H}_5\text{diars})_2$; (C) $\text{NbI}_4(\text{C}_2\text{H}_5\text{diars})_2$.

The effect of changing the arsenic ligands is not so obvious. The absorption maxima in the lower energy diffuse reflectance spectrum of $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$ are at lower energies than the maxima for $\text{NbCl}_4(\text{diars})_2$, whereas the ethyldiarsine complex would be expected to have a stronger crystal field effect. However, as discussed above the steric interactions are larger for ethyldiarsine than for diarsine. This would increase the metal-ligand bond lengths and reduce the crystal field produced by the ethyldiarsine ligands. The lowest energy absorption maximum is changed by the largest amount in going from $\text{NbCl}_4(\text{diars})_2$ or $\text{NbCl}_4(4\text{-CH}_3\text{diars})_2$ to $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$, which suggests that this is due to a transition to the d_{z^2} orbitals since these would be most affected by the arsine ligand.

If it is assumed that the middle, most intense band in the low-energy spectra is due to the transition to the d_{xz} and d_{yz} orbitals, then the weak shoulder found on this band for the chloro complexes could be due to a splitting of the two orbitals by a slight distortion from D_{2d} symmetry (possibly toward D_{4d} symmetry²¹) possibly by a Jahn-Teller effect.²² This distortion would be less unfavorable, considering ligand-ligand repulsions, for the tetrachloride than for the tetrabromide or tetraiodide complexes. These tentative assignments are included in Table II. The weak shoulder or band at

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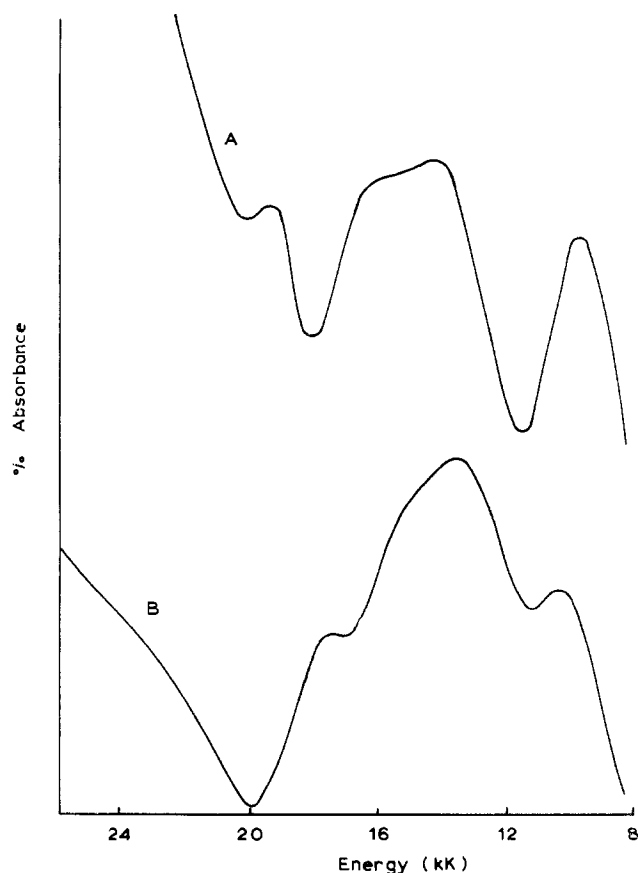


Figure 3.—Diffuse reflectance spectra of (A) $\text{TaCl}_4(\text{diars})_2$ and (B) $\text{NbCl}_4(4\text{-CH}_3\text{diars})_2$.

20 kK near the foot of the first charge-transfer band is not assigned.

The three bands show a greater separation for the tantalum complex, and the shoulder on the central band is much more pronounced, whereas for the vanadium complex only a single rather broad band at 13.25 kK is observed.¹

Solution Spectra.—The solution spectra of the ethyldiarsine complex of niobium tetrachloride and tetrabromide in toluene are almost unchanged from the diffuse reflectance spectra, indicating that ligand dissociation does not occur, unlike the case for the diarsine complexes of titanium tetrahalides.^{1,4} It is also good evidence against stereochemical nonrigidity for these complexes in solution.^{21,23} The solution spectrum of $\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$ in acetonitrile is different from the spectrum in toluene (Figure 1), and it appears that the spectrum is due to the superposition of the spectra of undissociated and partly dissociated species. The spectrum is also different from that of $\text{NbCl}_4(\text{CH}_3\text{CN})_2$.²⁴ The solution spectrum of $\text{NbI}_4(\text{C}_2\text{H}_5\text{diars})_2$ (Figure 1) is different from the diffuse reflectance spectrum (Figure 2) presumably due to partial dissociation in this solvent. These changes are not due to partial hydrolysis or oxidation, as admission of air to the measuring cell produced different spectra. The three niobium tetra-

chloride complexes dissolved in pyridine to form deep red nonconducting solutions due to bands at approximately 20 kK ($\epsilon \sim 1000$) in the spectra which are assigned to charge-transfer transitions.

Magnetic Studies.—The room-temperature effective magnetic moments of the eight-coordinate niobium tetrachloro and tetrabromo complexes are in the range 1.60–1.67 BM (Table III) and are not unexpected

TABLE III
ROOM-TEMPERATURE EFFECTIVE MAGNETIC MOMENTS

Complex	μ_{eff} , BM
$\text{NbCl}_4(\text{diars})_2$	1.60
$\text{NbCl}_4(4\text{-CH}_3\text{diars})_2$	1.63
$\text{NbCl}_4(\text{C}_2\text{H}_5\text{diars})_2$	1.63
$\text{NbBr}_4(\text{C}_2\text{H}_5\text{diars})_2$	1.67
$\text{NbI}_4(\text{C}_2\text{H}_5\text{diars})_2$	1.80
$\text{TaCl}_4(\text{diars})$	0.40 ($10^6\chi_M' = 65$ cgsu)
$\text{TaCl}_4(\text{C}_2\text{H}_5\text{diars})$	($10^6\chi_M' = -4$ cgsu)

for a single d electron in an orbitally nondegenerate ground state.²⁵ The magnetic moment of $\text{NbI}_4(\text{C}_2\text{H}_5\text{diars})_2$ is not easily explained as it is above the spin-only value for one unpaired electron (although the complex could have a high temperature-independent paramagnetism). The magnetic susceptibility, measured on two different samples, at different field strengths, and on a sample exposed to moist air for 10 min, varied by less than 2%. The complexes of niobium tetrahalides with diarsine, prepared by sealed-tube reactions, contained ferromagnetic impurities.

The magnetic susceptibility of $\text{NbCl}_4(\text{diars})_2$ as a function of temperature (Table IV) follows the Curie-

TABLE IV
THE UNCORRECTED MOLAR MAGNETIC SUSCEPTIBILITY OF
 $\text{NbCl}_4(\text{diars})_2$ AS A FUNCTION OF TEMPERATURE

Temp, °K	$10^6\chi_M$, cgsu	Temp, °K	$10^6\chi_M$, cgsu	Temp, °K	$10^6\chi_M$, cgsu
309.4	621	234.8	927	146.3	1686
291.2	696	204.1	1126	112.7	2252
261.3	817	177.5	1363	79.9	3387

Weiss law with $\theta = 10^\circ$ and shows no temperature-independent paramagnetism. As the single d electron of the complex occupies an orbitally nondegenerate energy level, the magnetic susceptibility would be expected to follow the Curie law ($\theta = 0^\circ$).²⁵

The magnetic moments of the six-coordinate tantalum complexes are much lower, the ethyldiarsine complex being diamagnetic. However, low magnetic moments for tantalum(IV) complexes can be predicted because of the large spin-orbit coupling constant.²⁵ Within the limits of experimental error and inaccuracies in the ligand diamagnetic corrections, the susceptibility of $\text{TaCl}_4(\text{C}_2\text{H}_5\text{diars})$ could be positive. Other six-coordinate adducts of tantalum tetrahalides have magnetic moments in the range 0.4–1 BM.^{24,26,27}

UCl₄(diars)₂.—When uranium tetrachloride was

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treated with diarsine in dioxane, the pale blue-gray complex $\text{UCl}_4(\text{diars})_2$ precipitated. This complex appears to be the first eight-coordinate diarsine complex of a nontransition element and the first complex of an actinide element with coordinated diarsine. Uranium tetrachloride did not react with ethylenebis(diphenylarsine) in tetrahydrofuran.²⁸

As well as the expected broad charge-transfer bands at energies above 25 kK (Table II), the complex shows a series of sharp bands in its diffuse reflectance spectrum at energies between 4 and 22 kK (Table V²⁹). Tentative assignments of the spectrum, based on a comparison with the spectra of hexahalo complexes of uranium(IV) and energy level calculations for octahedral uranium(IV),³⁰ are included.

The room-temperature effective magnetic moment of the complex is 2.74 BM. Many other eight-coordinate complexes of uranium(IV) have magnetic moments of approximately 3 BM,^{28,31} but the expected value is very sensitive to the stereochemistry of the complex, and the magnetic moment does not appear to have been calculated for dodecahedral or square-antiprismatic

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TABLE V

ABSORPTION MAXIMA (kK) IN THE DIFFUSE REFLECTANCE SPECTRUM OF $\text{UCl}_4(\text{diars})_2$ BETWEEN 4 AND 22 kK^a

21.93	} ³ P ₂	10.86	} ³ H ₆
(21.66)		8.84	
19.72	} ¹ I ₆	8.31	} ³ F ₃ , ³ F ₄
18.82		(7.94)	
16.92	} ³ P ₁	(6.61)	} ³ H ₅
15.79		6.38	
(15.75)	} ¹ D ₂ , ¹ G ₄ , ³ P ₀	4.40	} ³ F ₂
14.97			
14.69			
14.34			
(13.94)			

^a The tentative assignments are transitions from the ³H₄ state. Shoulders are enclosed in parentheses. The complex also shows sharp absorptions at (5.87), 5.74, 5.42, and approximately 4.0 kK. Absorptions are found at similar energies in the diffuse reflectance spectra of all diarsine complexes, and they have been assigned to vibrational overtone and combination bands of the diarsine ligands.²⁹

complexes. The magnetic moment of an f² ion in a cubic ligand field is predicted to be 2.83 BM.³²

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Superexchange Interaction in Anhydrous Copper(II) Formate

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The magnetic susceptibilities of two modifications of anhydrous copper(II) formate were determined in a temperature range of 4.2–300°K. The energy of exchange interaction between copper ions within a two-dimensional lattice was evaluated as $J/k = -42^\circ\text{K}$ (J , exchange integral) for the blue modification and 9.9°K for the royal blue modification. An antiferromagnetic transition accompanied by parasitic ferromagnetism was found at about 20°K in the blue modification. A contact shift was observed in the broad-line pmr spectrum of either form of copper(II) formate. Carbon atoms in the formate groups of these compounds carry a negative spin density. Two types of exchange mechanism are involved in the superexchange interaction through formate groups. A path through π orbitals predominates in the blue form, whereas in the royal blue form, contribution from a σ path masks the antiferromagnetic interaction associated with the π path.

Introduction

The magnetic susceptibility of copper(II) formate tetrahydrate has been determined in a wide temperature range.^{1–3} The results indicate the presence of a strong superexchange interaction due to anti-anti bonding arrangements (see Figure 1) of Cu–O–C–O–Cu links in a two-dimensional lattice.⁴ Martin and Waterman¹

have prepared three modifications of anhydrous copper(II) formate (blue, royal blue, and turquoise blue modifications) and determined their magnetic susceptibilities between 80 and 300°K. The blue modification is presumed to have crystal structure resembling that of the tetrahydrate.^{1,5} The Weiss constant amounts to about -175°K . On the other hand, a small positive Weiss constant has been found for the royal blue form. The X-ray crystal analysis of the royal blue form has indicated that anti-syn bridging arrangements (see Figure

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