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Eight Coordinate Tetrakis-Chelate Complexes of Niobium(IV) and Tantalum(IV)

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Eight coordinate complexes of the type $Nb^{IV}(chelate)_4$ *have been obtained by the reaction of niobium tetrachloride with tropolone, 8-hydroxyquinoline, and a number or β-diketones, in the presence of base. In the presence of dioxane, the acetylacetonate complex forms* $Nb^{IV}(acac)_4(dioxane)$ *which is probably nine coordinate. Chlorine-containing products of the type* $Nb^{IV}Cl_2(chelate)_2$ *and* $Nb^{IV}Cl(chelate)_3$ *were obtained in the absence of base. Similar reactions were studied with tantalum tetrachloride, but these were complicated by oxygen-abstraction reactions forming, for example,* $[Ta^{V}Cl_3(chelate)]_2O$. *The tetrakis chelate complexes are the first eight coordinate* d^1 *complexes of this type to be reported, and the magnetic and ultra violet and visible spectral properties are discussed.*

Introduction

A large number of eight coordinate tetrakis-chelate complexes of the type $M^{IV}(chelate)_4$ (where M is Zr, Hf, Th, Ce, or U, and in a few cases, Ti) are known.[1] However, very few of the corresponding complexes of metal ions containing a partially filled *d* subshell have been prepared. The complexes reported of this type are $W(oxine)_4$ (where Hoxine is 8-hydroxyquinoline)[2], $K_4[Mo(C_2O_4)_4]8H_2O$,[3] some tetrakisdialkyldithiocarbamates of vanadium(IV) and niobium(IV),[4] and the tetrakismonothiodibenzoyl methanate complexes of ruthenium(IV) and osmium(IV).[5] The only structurally characterised tetrakis-chelate complexes of metal ions containing partially filled *d* orbitals are $K_3[Cr(O_2)_4]$[6], $Ca[Cu(CH_3COO)_4]$,[7] and $(Ph_4As)_2[Co(CF_3COO)_4]$.[8]

The preparation and magnetic and spectral properties of a number of eight cordinate chelate complexes of niobium(IV) and tantalum(IV) are described in this Paper.

Experimental Section

Niobium tetrachloride and tantalum tetrachloride were prepared as described in a preceding paper.[9] All operations were conducted under dry, oxygen-free conditions on a standard vacuum system. Oxygen was removed from «oxygen-free» nitrogen by passage over heated (150°) activated copper (BTS-Katalysator) and dried with concentrated sulphuric acid, a liquid air-cooled trap, and molecular sieves. Solvents were purified by standard methods,[10] fractionally distilled, dried by refluxing over phosphorus pentoxide for several hours, and transferred to the vacuum line. The solvent was then degassed by alternately applying a vacuum and admitting nitrogen. Final drying was achieved by refluxing for several hours with calcium hydride (for triethylamine, acetonitrile, and benzene), lithium aluminium hydride (for tetrahydrofuran and n-hexane), or sodium (for dioxane and toluene). The solvent was then fractionally distilled into the reaction vessel.

All ligands are commercially available. Acetylacetone was fractionally distilled, dibenzoylmethane was recrystallised from petroleum ether, and all other ligands were purified by vacuum subimation.

Magnetic, X-ray and spectral measurements were performed as described in a preceding paper.[9] E.S.R. spectra were measured on powder at room temperature using a Varian V-4502-12 spectrometer. Chlorine and metal analyses were performed by standard techniques. Other elements were determined by the Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

Tetrakisacetylacetonatoniobium(IV). Niobium tetrachloride (1.1 g) in acetonitrile (70 ml) was added to a slurry of the stoichiometric amount of acetylacetonatothallium(I) (prepared from thallium ethoxide and recrystallized from benzene) in acetonitrile (50 ml) and the mixture refluxed for five minutes. The acetonitrile was pumped off and the residue extracted with tetrahydrofuran. The tetrahydrofuran solution was concentrated by evaporation *in vacuo,* and the product precipitated with n-hexane, filtered off, washed once with tetrahydrofuran and twice with n-hexane, and pumped dry.

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Anal. Calcd for $C_{20}H_{28}NbO_4$; C, 49.1; H, 5.8; Nb, 19.0. Found: C, 47.8; H, 5.5; Nb, 20.8.

Tetrathenoyltrifluoroacetonatoniobium(IV). (i) Thenoyltrifluoroacetone (2.3 g) in acetonitrile (50 ml) was added to a solution of niobium tetrachloride (0.67 g) and triethylamine (3 ml) in acetonitrile (100 ml). The solution was refluxed for five minutes and evaporated to dryness. The residue was extracted with benzene and on concentration of the extract, the product precipitated. It was filtered off, washed with benzene and pumped dry.
Anal. Calcd for $C_{32}H_{16}F_{12}NbO_8S_4$: C, 39.3; H, 1.7; F, 23.3; Nb, 9.5; S, 13.1. Found: C, 39.3; H, 2.3; F, 23.4; Nb, 9.6; S, 13.0.

(ii) A solution of thenoyltrifluoroacetone (2.5 g) in dioxane (30 ml) was added to a solution of niobium tetrachloride (0.70 g) in dioxane (100 ml). Triethylamine (3 ml) was added, and the solution refluxed for one minute, cooled, and filtered. The product, which precipitated on concentration of the filtrate, was filtered off, washed well with dioxane, and pumped dry.
Anal. Found: C, 40.7; H, 2.2. The two different preparations had identical infra red spectra.

Tetrabenzoyltrifluoroacetonatoniobium(IV). Triethylamine (4 ml) and then a solution of benzoyltrifluoroacetone in toluene were added to a slurry of niobium tetrachloride (0.75 g) in toluene (100 ml). The mixture was refluxed for five minutes and filtered. The filtrate was concentrated and the product precipitated by the addition of n-hexane, filtered off, washed well with n-hexane and pumped dry.
Anal. Calcd for $C_{40}H_{24}F_{12}NbO_8$: C, 50.4; H, 2.5; Nb, 9.7. Found: C, 49.1; H, 2.9; Nb, 10.0.

Tetradibenzoylmethanatoniobium(IV). Triethylamine (2 ml) was added to a solution of niobium tetrachloride (0.6 g) in acetonitrile (70 ml) and this solution was filtered into a solution of dibenzoylmethane (2.4 g) in acetonitrile (50 ml). The mixture was refluxed for two minutes and the product which crystallized out on cooling was filtered off, washed well with acetonitrile, and pumped dry.
Anal. Calcd for $C_{60}H_{44}NbO_8$: C, 73.2; H, 4.5; Nb, 9.4. Found: C, 72.5; H, 4.6; Nb, 10.1.

Tetrakis-8-hydroxyquinolatoniobium(IV). Niobium tetrachloride (0.6 g) in acetonitrile (150 ml) was filtered into a solution of 8-hydroxyquinoline (1.5 g) in the same solvent, and triethylamine (3 ml) was added. The mixture was refluxed for three minutes and the precipitate filtered off, washed well with acetonitrile, and pumped dry.
Anal. Calcd for $C_{36}H_{24}N_4NbO_4$: C, 64.6; H, 3.6; Nb, 13.9. Found: C, 62.6; H, 3.6; Nb, 15.0.

Tetratropolonatoniobium(IV). A solution of niobium tetrachloride (0.9 g) and triethylamine (3 ml) in acetonitrile (100 ml) was filtered into a solution of tropolone (4.1 g) in the same solvent. The solution was refluxed for five minutes and the product, which precipitated during this time, was filtered off, washed well with acetonitrile, and pumped dry.
Anal. Calcd for $C_{28}H_{20}NbO_8$: C, 58.3; H, 3.4; Nb, 16.1. Found: C, 55.5; H, 3.4; Nb, 16.1. Unfortunately the carbon analysis, which was the best for four different preparations, was 5% below the theoretical. However, the good metal analyses obtained and the absence of infra red absorptions between 4,000 and 500 cm^{-1} not ascribable to the ligand show that the low solubility and magnetic moment are not due to gross contamination with oxoniobium(IV) species.

Tetrakisacetylacetonato(dioxane)niobium(IV). A solution of niobium tetrachloride (0.4 g) in dioxane (80 ml) was added to a slurry of acetylacetonatothallium(I) in the same solvent (50 ml), and the mixture was refluxed for five minutes and filtered. The solid which separated on concentration of the filtrate was filtered off, washed well with dioxane and pumped dry.
Anal. Calcd for $C_{24}H_{36}NbO_{10}$: C, 49.9; H, 6.3; Nb, 16.1. Found: C, 49.4; H, 6.1; Nb, 16.4. The following peaks in the infra red spectrum of the complex were attributed to dioxane: 1253(s), 1113(s), 1094(m, sh), 1076(m), 897(m), 871(s), 820(sh), 799(s), and 620(m) cm^{-1} (where s means strong, m medium, and sh shoulder).

Tetrakisbenzoylacetonatoniobium(IV). This was prepared by the second method used for preparing tetrakisthenoyltrifluoroacetonato niobium(IV), using 0.7 g niobium tetrachloride, 2 ml of triethylamine, and 2.0 g of benzoylacetone.
Anal. Calcd for $C_{44}H_{44}NbO_{10}$: C, 64.0; H, 5.4; Nb, 11.3 Found: C, 62.5; H, 5.2; Nb, 12.0.

Dichlorobisdibenzoylmethanatoniobium(IV). Niobium tetrachloride (0.8 g) was dissolved in acetonitrile (100 ml), the solution added to a solution of dibenzoylmethane (2.9 g) in the same solvent (50 ml), and the mixture was refluxed for five minutes. The product which precipitated out was filtered, washed well with acetonitrile, and pumped dry.
Anal. Calcd for $C_{30}H_{22}Cl_2NbO_4$: C, 59.1; H, 3.6; Cl, 11.6; Nb, 15.3. Found: C, 59.2; H, 4.0; Cl, 11.5; Nb, 15.4.

Chlorotristropolonatoniobium(IV). A solution of niobium tetrachloride (0.27 g) in acetonitrile (70 ml) was filtered into a solution of tropolone (0.6 g) in the same solvent (50 ml). The solution was refluxed for five minutes and then evacuated several times and the process was repeated. During this time a fine crystallin precipitate was formed and this was filtered off from the warm solution, washed well with acetonitrile and pumped dry.
Anal. Calcd for $C_{21}H_{15}ClNbO_6$: C, 51.3; H, 3.1; Cl, 7.2; Nb, 18.9. Found: C, 50.3; H, 3.8; Cl, 7.3; Nb, 19.3.

Tetradibenzoylmethanatotantalum(IV). This was prepared in the same way as the niobium analogue, using 0.7 g tantalum tetrachloride, 2 ml triethylamine and 2 g dibenzoylmethane. Solutions of tantalum tetrachloride in acetonitrile were prepared using a minimum of heat to prevent further reaction. A large amount of yellow compound was also produced, but this could be removed by washing with acetonitrile.
Anal. Calcd for $C_{60}H_{44}O_8Ta$: C, 57.1; H, 4.5; Ta, 16.9. Found: C, 66.4; H, 3.9; Ta, 18.1. The compound is not isomorphous with the corresponding niobium or thorium complexes, and is less soluble in non-

polar solvents than the niobium complex, but it has a similar infra red spectrum and is consequently assigned an eight coordinate structure.

In attempts to prepare other complexes of tantalum, the methods used in preparing the corresponding niobium compounds were followed. The reaction of tantalum tetrachloride with acetylacetonatothallium(I) in acetonitrile gave a yellow tar with an infra red spectrum similar to that for $NbOCl_2(acac)$,[11] showing strong bands at 788 and 857 cm^{-1} which are attributed to tantalum-oxygen bonds. The black, crystalline compound obtained by the reaction of tantalum tetrachloride with 8-hydroxyquinoline and triethylamine was contaminated with a yellow solid which could not be completely removed by washing. When chloroform was used to extract the product, further decomposition occurred. It appears that oxygen abstraction is occurring in these reactions between tantalum tetrachloride and oxygen containing molecules.

Tetrachlorodibenzoylmethanatotantalum(V). Tantalum tetrachloride (1.2 g) was dissolved in acetonitrile (200 ml) with only slight heating and the solution was filtered into a solution of dibenzoylmethane (1.6 g) in the same solvent (50 ml). The solution was evacuated for about ten minutes and the low yield of red precipitate filtered off, washed well with acetonitrile and pumped dry.

Anal. Calcd for $C_{15}H_{11}Cl_4TaO_2$: C, 33.0; H, 2.2; Cl, 26.0. Found: C, 34.2; H, 2.7; Cl, 25.1.

The compound was diamagnetic ($10^6\chi_M'=-5$ cgsu) and its infra red spectrum was very similar to other dibenzoylmethanate complexes. The main product of the reaction was obtained as a yellow-green tar on evaporation of the filtrate. This product showed a strong broad band in its infra red spectrum centred at 855 cm^{-1} which is attributable to a tantalum oxo-complex.

Oxobis(trichlorodibenzoylmethanatotantalum(V)). The procedure used in preparing the above red compound was followed, except that the solution was refluxed for five minutes to give a mustard-coloured precipitate. This was filtered off, washed well with acetonitrile and pumped dry.

Anal. Calcd for $C_{30}H_{22}Cl_6Ta_2O_5$: C, 34.7; H, 2.3; Cl, 20.5; Ta, 34.8. Found: C, 34.3; H, 3.5; Cl, 21.3; Ta, 34.8. A large amount of yellow tar was obtained by evaporation of the filtrate.

Oxotrichlorobis(dioxane)tantalum(V). Tantalum tetrachloride (2 g) was dissolved in dioxane (200 ml) by heating for a few minutes. A small amount of dark brown solid was formed; this was filtered off, washed with dioxane and pumped dry.

Anal. Found: C, 15.1; H, 2.9; Cl, 26.5. The filtrate was evaporated down to a small volume and a pale red-brown compound was precipitated by the addition of n-hexane. This was filtered off, washed with dioxane and n-hexane and pumped dry.

Anal. Calcd for $C_8H_{16}Cl_3TaO_5$: C, 20.0; H, 3.4; Cl, 22.2; Ta, 37.8. Found: C, 19.4; H, 3.4; Cl, 22.6; Ta, 37.8. The filtrate deposited a red-brown oil on standing.

Tetrachlorobis(dioxane)niobium(IV). Niobium tetrachloride (1 g) was dissolved in dioxane (150 ml), the solution was filtered, and the product which was obtained on concentration of the filtrate was filtered off, washed with dioxane, and pumped dry.

Anal. Calcd for $C_8H_{16}Cl_4NbO_4$: C, 23.4; H, 3.9; Cl, 34.5; Nb, 22.6. Found: C, 23.2; H, 3.7; Cl, 34.3; Nb, 23.1.

Results

Tetrakis-chelate complexes of niobium(IV) were prepared with 8-hydroxyquinoline (Hoxine), and the β-diketones acetylacetone (Hacac), dibenzoylmethane (HDBM), benzoyltrifluoroacetone (HBTA) and thenoyltrifluoroacetone (HTTA). Tetrakisacetylacetonatoniobium(IV) was prepared by reacting niobium tetrachloride with acetylacetonatothallium(I), while the other complexes were obtained using the free ligand in the presence of triethylamine. Chlorine-containing products were obtained if triethylamine was not used, of which only $NbCl_2(DBM)_2$ was characterized.

The acetylacetonate and 8-hydroxyquinolate complexes are dark purple and the other complexes dark green. All complexes are stable *in vacuo*; $Nb(TTA)_4$, $Nb(BTA)_4$, and $Nb(oxine)_4$ can be sublimed without appreciable decomposition, but the other complexes decompose without sublimation. The complex $Nb(acac)_4$ decomposes rapidly in air, $Nb(oxine)_4$ and $Nb(DBM)_4$ are more stable, whereas $Nb(TTA)_4$ and $NbBTA)_4$ showed only slight decomposition after several months. All compounds decompose rapidly in moist solvents. They are moderately soluble in dry nonpolar solvents such as benzene and toluene. The infra red spectra are normal for the cordinated bidentate ligand, showing no bands between 1600 and 1800 cm^{-1}.[12] The complex $Nb(TTA)_4$ is not isomorphous with $M(TTA)_4$ (where M is Zr, Hf, Th, Ce, U, and Pu),[13] $Nb(acac)_4$ is not isomorphous with $Zr(acac)_4$,[14] and $Nb(DBM)_4$ is not isomorphous with $Th(DBM)_4$.[15]

The reaction of niobium tetrachloride with tropolone (HT) and triethylamine gave black NbT_4. In the absence of triethylamine red $NbClT_3$ was obtained.

Table I. Room temperature magnetic moments.

	μ_{eff}(B.M.)
$Nb(acac)_4$	1.47
$Nb(TTA)_4$	1.61
$Nb(BTA)_4$	1.43
$Nb(DBM)_4$	1.66
$Nb(oxine)_4$	1.60
$Nb(bzac)_4$. dioxane	1.44
$Nb(acac)_4(dioxane)$	1.73
NbT_4	0.74
$NbClT_3$	0.40
$NbCl_2(DBM)_2$	1.58
$NbCl_4(dioxane)_2$	1.47
$Ta(DBM)_4$	0.53
$TaCl_4(DBM)$	diamagnetic $10^6\chi'_M=-5$ cgsu
$[TaCl_3(DBM)]_2O$	$10^6\chi'_M= 23$ cgsu

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Table II. Absorption Maxima (kK) in the Diffuse Reflectance (D.R.) and Solution Spectra in the Visible and Ultra Violet Regions for β-Diketonate Complexes. (Log$_{10}$ of Molar Estinction Coefficient in Parentheses, where measured).

		π_3 to π_5?	Aromatic Ring	π_3 to π_4	d to π_4	π_3 to d
Nb(acac)$_4$	D.R.	45.6		33.9	23.9	16.6
	Toluene				24.37(3.08)	19.45(2.95)
Zr(acac)$_4$	D.R.	44.5		35.4	33.5 sh	
	Dioxane			36.7	32.0 sh	
Nb(acac)$_4$(dioxane)	D.R.	45.2 sh		34.1	23.4	15.4
	Toluene				24.10(3.26)	19.23(3.11)
	Dioxane				24.10(3.26)	19.23(3.11)
Nb(bzac)$_4$. dioxane	D.R. [a]	43.8 sh	38.8	30.1	21.9	12.9
	Toluene				22.45	15.05
Nb(BTA)$_4$	D.R. [a]	44.5 sh	38.8 sh	30.1	21.0	13.0
	Toluene				21.55	14.45
	Dioxane			30.0 (4.61)	21.55(3.26)	14.45(3.23)
Nb(TTA)$_4$	D.R.	44.4	37.8 sh	26.9	20.3	12.9
	Toluene			27.75(4.84)	20.75(3.66)	13.95(3.49)
	Dioxane			27.85	20.75	13.95
Zr(TTA)$_4$	Dioxane			28.7	30 sh	
Nb(DBM)$_4$	D.R.	44.5 sh	38.0	27.6	20.3	10.2
	Toluene				20.87(3.48)	12.80(3.69)
Ta(DBM)$_4$	D.R.	44 sh	38.2	26.5	13.5 [b]	
	Toluene			28.25(4.45)	16.1 [b](3.04)	
	Dioxane		37.8	28.55	16.0 [b]	
NbCl$_2$(DBM)$_2$	D.R. [c]	44 sh	38.5 sh	28 sh	17.4	12.9
TaCl$_4$(DBM)	D.R.	43 sh	37.4	26.6	19.7	
[TaCl$_3$(DBM)]$_2$O	D.R.	45 sh	38	26 sh	21.4	

[a] The complexes Nb(bzac)$_4$. dioxane and Nb(BTA)$_4$, also show a weak shoulder in their diffuse reflectance spectra at 26.5 and 27.0 kK respectively. [b] It is assumed that the π_3 to d and d to π_4 transitions are coincident for this complex. [c] Additional bands at 23.5 and 9.0 (sh) kK are assigned to d to d transitions.

Table III. Absorption Maxima (kK) in the Diffuse Reflectance (D.R.) and Solution Spectra in the Visible and Ultra Violet Regions for Tropolonate and 8-Hydroxyquinolinate Complexes. (Log$_{10}$ of Molar Extinction Coefficient in Parentheses, where measured).

		Intraligand Transitions					π to d	d to π
NbT$_4$	D.R. [a]	44.3 sh	38.5	30.8		25.3	20.38(3.15)	10.85(2.89)
	Toluene					26.38(3.67)	20.2	
NbClT$_3$	D.R.	43.2 sh	39.2	30 sh		25.6	24.15	
	Acetonitrile			30.2		26.0	20.6 sh	
LiT	[b]	42.92	37.74	29.76	27.1			
		42.19				25.00		
Nb(oxine)$_4$	D.R.		38.3			24.3	17.7	12.3
	Toluene					25.05	19.15	12.53
	Dioxane					25.23	19.15	12.53

[a] The diffuse reflectance spectrum of NbT$_4$ also shows bands at 13.8 and 7.1 kK. [b] Taken from reference 22.

The tetrakis complex is much less soluble in common organic solvents than are the other niobium chelates, and also has a much lower magnetic moment than the other tetrakis-chelate niobium complexes (Table I). There is also a much greater difference between the solution and diffuse reflectance spectra for this complex (Table III) than for any of the other complexes measured (Table II). These properties are indicative of a polymeric structure for the solid complex. It is relevant that metals such as indium(III), tin(IV), and lead(IV), which form only tris-complexes with β-diketones can form tetrakis-complexes with tropolone.[16]

The black crystalline Nb(acac)$_4$(dioxane) was isolated from the reaction of niobium tetrachloride with acetylacetonatothallium(I) in dioxane. The compound was less reactive with air than the dioxane-free Nb(acac)$_4$. The infra red spectrum is similar to that found when dioxane is coordinated through one oxygen atom.[17] The visible spectrum of Nb(acac)$_4$(dioxane) in toluene or dioxane is significantly different to that of Nb(acac)$_4$ in toluene (Table II), indicating that the dioxane is firmly bound to the Nb(acac)$_4$. Similarly the magnetic properties are different to those found for Nb(acac)$_4$ (Table I). The complex is tentatively assigned a nine coordinate structure. Tetrakisacetylacetonatoniobium(IV) did not form a similar compound with tetrahydrofuran, nor could dioxane solvates be prepared of Th(acac)$_4$, Nb(TTA)$_4$, or Zr(acac)$_4$.

The green product isolated from the reaction of niobium tetrachloride with benzoylacetone (Hbzac) and triethylamine in dioxane shows peaks in its infrared spectrum which are assigned to dioxane. It was not possible to tell whether the dioxane was coordinated as the infra red spectrum is too complex. The ultra violet and visible spectral, and magnetic properties of the complex are similar to those of Nb(BTA)$_4$, sugge-

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sting that the dioxane is not coordinated. Attempts to prepare a benzoylacetonate complex from other solvents were unsuccessful as only tars were produced.

A tetrakisdibenzoylmethanate complex of tantalum was prepared in the same way as the corresponding niobium complex. A large amount of yellow compound was also produced, but this could be removed by washing with acetonitrile. Similar yellow solids were also obtained with acetylacetone and 8-hydroxyquinoline, and it appears that oxygen abstraction from the ligand is occurring in these cases. When an acetonitrile solution of dibenzoylmethane and tantalum tetrachloride were refluxed in the absence of triethylamine in the cold, a small amount of the red tantalum(V) complex $TaCl_4(DBM)$ was formed, while under reflux oxygen abstraction again occurred with the formation of the mustard-coloured tantalum(V) complex $[TaCl_3(DBM)]_2O$. This compound showed a fairly strong band in its infra red spectrum at 809 cm^{-1} attributable to a Ta–O–Ta group. This greater tendency of tantalum tetrachloride compared with niobium tetrachloride to undergo oxygen abstraction reactions with β-diketones, is also shown by the reaction with dioxane. Niobium tetrachloride forms the simple adduct $NbCl_4(dioxane)_2$, whereas tantalum tetrachloride forms $TaOCl_3(dioxane)_2$. Strong bands in the infra red spectrum of the latter at 935 and 919 cm^{-1} are attributed to the Ta=0 group. Although $NbCl_4(dioxane)_2$ has been described previously, attempts to isolate a product from the reaction with tantalum tetrachloride were unsuccessful.[18] Oxygen abstraction from dioxane has previously been found to occur with molybdenum pentachloride, with the formation of $MoOCl_3 . 1\frac{1}{2}$ dioxane and 2,2′-dichlorodiethyl ether.[19]

Discussion

The infra red spectra show that the β-diketonate ligands are bidentate, and all the tetrakis β-diketone compounds are therefore eight coordinate.

Visible and Ultra Violet Spectra. The diffuse reflectance spectra of the niobium compounds show two bands below 25 kK plus a series of two to four bands at higher energies (Tables II and III). Only the two or three lower energy bands can be seen in solution due to the high extinction coefficients of the higher energy bands, and to absorption by the solvent. Representative spectra are shown in Figures 1 and 2.

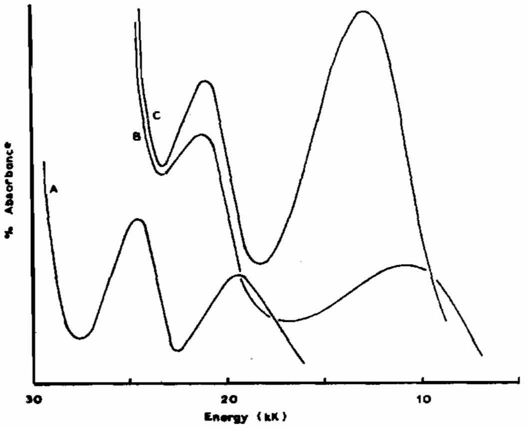

Figure 1. Solution spectra in toluene. (A) $Nb(acac)_4$, (B) NbT_4, (C) $Nb(DBM)_4$.

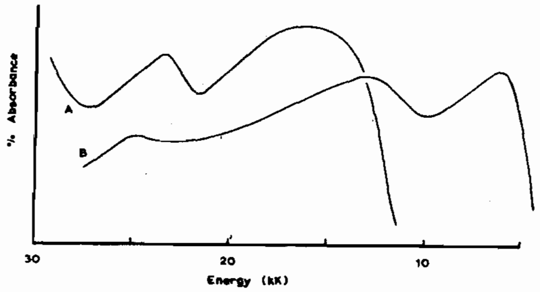

Figure 2. Diffuse reflectance spectra. (A) $Nb(acac)_4$, (B) NbT_4.

Hückel semiempirical calculations have given energy levels for the π-electrons in β-diketonates.[20,21] Each β-diketonate has six π-electrons which occupy the π_1, π_2, and π_3 orbitals, the antibonding π_4^* and π_5^* remaining unoccupied. In metal complexes, partially filled *d*-orbitals must lie in energy between the π_3 and π_4^* orbitals, otherwise oxidation or reduction of the metal would occur.

The two bands in the ultra violet region between about 26 and 39 kK appear to be common to all complexes and to the lithium and sodium salts of each particular ligand.[22,23] The lowest allowed ligand transition, π_3 to π_4^*, has been calculated to lie at approximately 33.5 kK for the acetylacetonate ion and for ionic complexes.[20] Consequently the band at 34 kK in the diffuse reflectance spectra of the niobium acetylacetonate complexes can be confidently assigned to the π_3 to π_4^*, intraligand transition. The strong bands which lie between 26 and 34 kK for the other β-diketonate complexes are also assigned to this transition.[23]

The highest energy absorption maximum in the diffuse reflectance spectra of the β-diketonate complexes is common to most complexes of the ligands, and has been assigned to a π_3 to π_4^* transition.[23] However as the band is not found in the sodium salts of the ligands,[23] it may be due to a charge transfer transition, for example π_2 to *d*, or π_3 to a higher metal orbital, or to a π_3 to π_5^* intraligand transition.

There are three possible asignments for the two lowest energy absorption maxima found in the niobium complexes. These are: (i) metal *d* to *d* transitions, (ii) intraligand singlet to triplet transitions, or (iii) charge transfer transitions.

(i) Metal *d* to *d* transitions. The intensities appear too high for *d–d* bands,[24,25] and the relative energies

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do not correlate with the expected ligand field strengths. For the two most likely stereochemistries, the square antiprism and the dodecahedron,[26] the Laporte selection rule is invalid, but nevertheless low intensities ($\epsilon < 30$) are observed for the *d*–*d* bands in other dodecahedral niobium(IV) complexes.[9]

(ii) Intraligand singlet to triplet transitions. This assignment can be rejected as no band is found for the tantalum dibenzoylmethanate complex, and the intensities are too high for a spin forbidden transition of this type.[23,27]

(iii) Charge transfer. From the energy of the first Laporte allowed transition of the NbCl$_6^{2-}$ anion (31.65 kK), the optical electronegativity of octahedral niobium(IV) has been calculated to be 1.85.[18] Assuming that the optical electronegativity of eight coordinate niobium(IV) is similar and using an optical electronegativity of 2.7 for the acetylacetonate ion,[28] and applying the same correction for the spin pairing energy of the central metal ion as was used in the calculation of the electronegativity of niobium(IV) (2.8 kK), the energy of the π_3 to *d* charge transfer transition of Nb(acac)$_4$ is calculated to be 23 kK.[28,29] This is in good agreement with the observed absorption maximum at 24 kK in the solution spectra of Nb(acac)$_4$. Using an optical electronegativity of 1.6 for octahedral zirconium(IV),[29] a similar calculation places the first charge transfer band of Zr(acac)$_4$ at 33 kK, and a pronounced shoulder on the band assigned to the ligand π_3 to π_4^* transition is seen at approximately 32 kK in the solution spectra of the complex (Table II).

The assignment of the other bands[30] is clear from Table II.

The bands above 25 kK of 8-hydroxyquinolinate and tropolonate complexes are assigned to intraligand transitions as before.[22,31] The two lowest energy bands in the diffuse reflectance spectra of tetratropolonatoniobium(IV) are somewhat anomalous. This may be indicative of a polymeric structure for the complex in the solid state as mentioned above. The solution spectra of the complex fits in well with the spectra of the other niobium complexes. As well as the expected bands due to intraligand transitions, the diffuse reflectance spectra of NbClT$_3$ shows a single band at 20.2 kK, and the solution spectrum in acetonitrile of the complex shows bands at 20.6 and 24.1 kK. The solution also has a significant conductance (46 cm^2 ohm^{-1} mole^{-1} for a 2×10^{-3} *M* solution, compared with a value of about 150 cm^2 ohm^{-1} mole^{-1} for a 1:1 electrolyte) which is indicative of some dissociation in solution. The band at 24.1 kK in the solution spectrum may then be due to a transition of the dissociated species.

Table IV. Temperature dependence of magnetic susceptibilities (cgs units, uncorrected for ligand or metal diamagnetism)

Nb(TTA)$_4$		Nb(DBM)$_4$	
Temp. (°K)	$10^6\chi_M$	Temp. (°K)	$10^6\chi_M$
307.9	656	308.0	546
293.1	704	291.3	660
266.4	805	263.7	759
236.1	957	234.8	891
204.4	1118	197.7	1120
179.6	1288	175.6	1301
146.5	1602	145.2	1668
105.2	2218	110.4	2197
75.0	3173	72.2	3360

Magnetic and Electron Spin Resonance Measurements. The room temperature effective magnetic moments of the simple tetrakis-chelate complexes (Table I) are as predicted for a *d* electron in an orbitally non-degenerate ground state, with some reduction due to spin-orbit coupling with higher ligand field levels.[32] The magnetic susceptibilities of Nb(TTA)$_4$ and Nb(DBM)$_4$ were studied as a function of temperature (Table IV) and found to obey the Langevin-Debye equation ($\chi_A = C/T + N\alpha$) as expected.[32] The temperature independent paramagnetism was 170 ± 10 and 180 ± 10 cgsu respectively.

The electron spin resonance spectra of Nb(acac)$_4$ and Nb(DBM)$_4$ at room temperature consist of a broad asymmetric signal, and show the shape expected for a broad signal with $g_\perp$ greater than $g_\parallel$.[33] The values of $g_\perp$ are 1.95 and 1.98 respectively; values of $g_\parallel$ were not estimated. The observation that $g_\perp$ is greater than $g_\parallel$ is consistent with a dodecahedral, rather than a square antiprismatic structure for these compounds.[34] (It may be relevant that Nb(acac)$_4$ is not isomorphous with the square antiprismatic Zr(acac)$_4$.[14]) The apparently low calculated magnetic moments are therefore probably due to uncertainties in the diamagnetic corrections for the ligands, and because no correction was made for the niobium core electrons.

Both the troplonate complexes NbT$_4$ and NbClT$_3$ have abnormally low magnetic moments, consistent with a polymeric structure.

The magnetic moment of NbCl$_2$(DBM)$_2$ is typical for that of a six coordinate niobium(IV) complex.[30,35]

The low magnetic moment of the tantalum dibenzoylmethanate complex is probably due to the higher spin-orbit coupling constant expected for tantalum(IV) compared with niobium(IV). Some six coordinate complexes of tantalum(IV) have similar low magnetic moments.[9]

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