Coordination Chemistry Reviews, 9 (1972/73) 107–143
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE CHEMISTRY OF d^1 COMPLEXES OF NIOBIUM, TANTALUM, ZIRCONIUM AND HAFNIUM †

D.A. MILLER and R.D. BEREMAN*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214 (U.S.A.)

(Received February 10th, 1972)

CONTENTS

ABBREVIATIONS

acac	acetylacetonato	dtc	diethyldithiocarbamate
bipy	2,2'-bipyridyl	dth	2,5-dithiohexane
bzac	benzoylacetonato	HMPA	$O{=}P[N(CH_3)_2]_3$
bzbz (or DBM)	dibenzoylmethane	ox	1:4 dioxane
bzta	benzoyltrifluoroacetonato	oxine	8-hydroxyquinoline

---

† Abstracted in part from the thesis of D.A. Miller, submitted to the Faculty of the Graduate School of the State University of New York at Buffalo in partial fulfillment of the requirements for the degree of Master of Arts.

* To whom correspondence should be directed.

C_2H_3CN	acrylonitrile	phen	1,10-phenanthroline
CH_3CN	acetonitrile	py	pyridine
DEF	$H-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$	Qu (or quin)	quinoline
diars	diarsine	salen	salicylidene
DMA	$CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$	T (or t)	tropolone
DME	dimethoxyethane	tta	thenoyltrifluoroacetone
DMF	$H\overset{\overset{O}{\|}}{C}-N(CH_3)_2$	TU	thiourea

A. INTRODUCTION

Recently, the chemistry of the d^1 transition metals has received considerable attention. This paper will review the chemistry of niobium, tantalum, zirconium and hafnium in the d^1 configuration. Although many of the compounds formed are air- and moisture-sensitive, a significant number has been obtained. Additional problems arise in attempts to isolate zirconium and hafnium compounds, because of the difficulty in their separation. The compounds and complexes which have been formed by these elements have been organized in tables with a short description of their preparation and properties. A discussion of some aspects of their chemistry is included in each section.

We offer here a non-critical collection and review of the literature in the hope it will inspire further work in the area.

B. NIOBIUM

The pentavalent oxidation state of niobium has been studied extensively, but only in recent years has niobium in the tetravalent state been explored. Since the compounds of Nb^{IV} are generally very air- and moisture-sensitive, synthetic problems have been numerous and conflicting results in many cases exist. Nevertheless, a significant number of compounds has been obtained.

The purpose of this chapter is to tabulate these compounds and discuss some of their chemistry. The chemistry of the halides and oxyhalides has been adequately reviewed[1-3] and only a brief summary will be presented here.

(i) Tetrahalides

NbF_4, NbI_4, $NbCl_4$ and $NbBr_4$ have each been prepared by several methods [1-3]. The most popular preparation involves the thermal gradient method [4,5]. For example, in the preparation of $NbCl_4$, a sealed evacuated tube contains Nb metal turnings at each end. Chlorine is introduced and one end of the tube is placed in a resistance furnace at 350°C where the hot Nb reacts to form $NbCl_5$, which is deposited in another section of the tube.

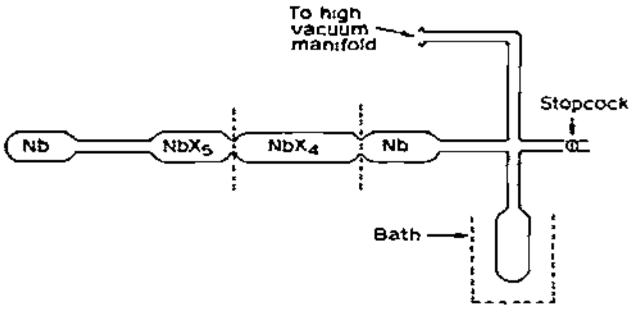


Fig. 1. Apparatus for the preparation of $NbCl_4$.

The portion of the tube which has reacted in the furnace is sealed off (see Fig. 1). The remaining tube is placed in a temperature gradient of 400°C at the Nb metal end and 250°C at the $NbCl_5$ end. After several days, blue-black $NbCl_4$ crystals collect in the middle portion of the tube[5].

The tetrahalides are diamagnetic, dark solids and will thermally disproportionate to form the corresponding trihalides and pentahalides[4,5,7]. The structures have been studied through X-ray powder diffraction patterns and there is some disagreement as to their interpretation[1].

(ii) Hexahaloniobates

The $NbCl_6{}^{2-}$ ion has been isolated as the sodium[8], potassium[8], rubidium[5], cesium[9], ammonium[9] and tetraalkylammonium salts[10,11]. They are stable in the absence of air and moisture and show face-centered cubic structure[8,12].

(iii) Oxyhalides

Several niobium oxyhalides have been formed: $NbOCl_2$ (ref. 9), $NbOI_2$ (ref. 13), $LiNbO_2F$ (ref. 14) and $KNbO_2F$ (ref. 14). $NbOCl_2$ is diamagnetic and very air-stable. The NbO_2F^- ion is very weakly paramagnetic[14]. $NbOCl_4^{2-}$ and $NbOF_4^{2-}$ have been prepared by reduction of the pentahalide with Zn in aqueous hydrochloric acid, or hydrofluoric acid. $NbOCl_5^{3-}$ is also thought to exist in concentrated hydrochloric acid[5a].

(iv) Niobium complexes

Many Nb^{IV} complexes have been formed as adducts of the niobium tetrahalides or as a result of the reduction of the pentahalides. These complexes are listed in Table 1 which follows along with some of their properties. In some cases the complexes have not been completely characterized, and in others conflicting data were available. In those instances, all sources were cited.

TABLE 1

Complex	*Color*	μ^a	*Preparation*	*Spectral features*[b]	*Ref.*
A. Niobium tetrahalides					
$NbCl_4$	Brown, purple black	0	Reduction of $NbCl_5$ with Sn^{II}, 220°C, 6–8 h or Nb, $NbCl_5$, 195–440°C	UV–vis: 12.5, 22.8, 27.8, 34.5	1–3, 9, 16
$NbBr_4$	Dark	0	$NbBr_5$, Nb, 200–300°C	UV–vis: 10.2, 19.3, 25.6, 33.3	1–3, 16
NbI_4	Dark	0	NbI_5, Nb, 230–270°C, 48 h	UV–vis: 8.0 to 40, absorbs continuously	1–3, 16
NbF_4	Black	0	NbF_5, Nb, 250–350°C		1–3, 16, 17
B. Niobium oxyhalides					
$NbOF_4^{2-}$	Violet		$NbCl_5$ in HF, reduce with Zn	ESR[c]: $\langle g \rangle = 1.897 \pm 0.006$ $\langle A \rangle = 215 \pm 5$	15
$NbOCl_2$	Brown		Reduction of $NbOCl_3$ with $SnCl_2$ in argon, 450°C, 6–8 h		9
$NbOCl_4^{2-}$	Blue		$NbCl_5$ in conc. HCl, reduce with Zn	ESR[d]: $g_\parallel = 1.943 \pm 0.006$, $g_\perp = 1.932 \pm 0.006$, $A_\parallel = 260 \pm 5$, $A_\perp = 122 \pm 5$	15
$NbOCl_5^{3-}$			$NbCl_5$ in conc. HCl, reduce with Zn	$g_\parallel = 1.9215$	50
$NbOI_2$	Black		Nb, Nb_2O_5, I_2, 500°C	$A_\parallel = 294.4$	3
C. Hexahaloniobates					
$(NH_4)_2NbCl_6$	Black		NH_4Cl and HCl, $NbCl_4$		9

Cs_2NbCl_6	Violet		$NbCl_4$, HCl, CsCl		9
Rb_2NbCl_6	Violet		RbCl, $NbCl_4$, HCl		9
Na_2NbCl_6			$NbCl_4$, NaCl (solid state reaction)		18
K_2NbCl_6			$NbCl_4$, KCl (solid state reaction)		18
$[(C_2H_5)_4N]_2NbCl_6$	Pale brown	1.16	Electrolytic reduction of $[(C_2H_5)_4N]NbCl_6$, chloroform–acetonitrile (9:1)	UV-vis.: 16.4sh^e, 23.8sh, b ($d \leftrightarrow d$), 31.4sh, 35.4, 38.0sh, 44.8 ($X\pi \rightarrow Nb$); (CH_3CN): 24.4sh (~ 100) ($d \leftrightarrow d$), 28.6sh (~ 420), 31.8sh (~ 2400), 34.8 (9600), 40.2 (9000) ($X \rightarrow Nb$); (CH_3CN_2 and $(C_2H_5)_4NbCl_6$): 19.4sh? 24.5sh ($d \leftrightarrow d$), 28.0sh, 31.6sh, 34.8, 40.5 ($X \rightarrow Nb$)	10
$[(C_2H_5)_4N]_2NbBr_6$	Yellow	1.20	Electrolytic reduction of $[(C_2H_5)_4N]NbBr_6$ chloroform–acetonitrile (9:1)	UV–vis.: 15.8sh?, 18.5sh ($d \leftrightarrow d$), 22.8sh, 26.4, 29.5, 32.2, 35.4, 37.4sh, 45.0 ($X\pi \rightarrow Nb$); (CH_3CN): 15.0sh, b?, 19.0sh? ($d \rightarrow d$), 27.0 (7800), 29.3 (11,500), 31.35 (12,800), 33.0sh?, 40.0sh ($X \rightarrow Nb$); (CH_3CN and $(C_2H_5)_4Br$): 15.9 (95), 21.5sh? ($d \leftrightarrow d$), 24.0 (~ 500), 26.7 (3500), 29.0 (10,500), 36.1 (3100), 36.4sh (~ 3000), 38.2 (3200)	10
D. Niobium with nitrogen ligands					
$NbCl_4(C_2H_5CN)_2$		1.59	$NbCl_4$ and ligand, 16 h, room temp.	IR: 466w, 379sh, 360s, 334s, 312sh, 284sh UV–vis.: (solid): 37.0, 30.6, 24.8sh, 23.0, 10.5; (C_2H_5CN): 37.0, 33.0sh, 25.1 (900)	21, 23
$NbBr_4(C_2H_5CN)_2$		1.48	$NbBr_4$ and ligand, 5 days, room temp.	IR: 448w, b, 385w, 343sh, 304m, 267sh, 259s, 228sh UV–vis.: (solid): 36.7, 29.6, 22.6sh, 20.8, 17.3sh, 11.2; (C_2H_5CN): 34.8 (16,000), 30.1sh, 25.9sh, 16.2sh, 10.7sh ESR^c: $g_\parallel = 1.9161$, $g_\perp = 1.9607$, $A_\parallel = 262.3$, $A_\perp = 139.9$	21, 23

TABLE 1 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
$Nb[N(C_2H_5)_2]_4$	Brown	0.8	$NbCl_5$ and $LiNEt_2$, 20h, room temp.	IR: 587s (M–N), 1000vs (NC_2), 1153s (NC_2), 1185vs (unassigned) UV–vis.: 12.4, 18.2 (200) ($d \rightarrow d$), 25.0sh (5000) (charge transfer) ESR: $\langle g \rangle = 1.952, g_\parallel = 1.923, g_\perp = 1.966$ $\langle A \rangle = 104, A_\parallel = 196, A_\perp = 58$	24–26
$Nb[N(CH_3)_2]_4$	Brown		$NbCl_5$ and $LiNMe_2$, 20 h, room temp.	IR: 540s (Nb–N), 938vs (NC_2), 1043m, 1143s, 1243m	24, 26
$NbCl_4(py)_2$	Purple brown	1.53 1.37 1.29 1.10	$NbCl_5$, pyridine, 5 weeks, 50°C or $NbCl_4$ and pyridine, several hours, room temp.	IR: 429m, 645, 687s, 758s, 864w, 948m, 1012s, 1046s, 1064s, 1088w, 1163w, 1173sh, 1212s, 1244m, 1573w, 1607s, 1662w IR: 361sh, 340sh?, 330s (Nb–X), 429mw (ligand), 238m (unassigned) UV–vis.: 20.6 (1000) Reflectance: 24.0, 20.0 Reflectance: 18.2, 24.3 ($d \rightarrow d$), 33.4sh, 35.6, 45.0 (X → Nb)	5, 16, 19, 20
$NbBr_4(py)_2$	Dark green	1.36 1.26 1.19	$NbBr_5$ + py, 12 h reflux or $NbBr_4$ and pyridine, 2–3 days	IR: 280w, sh?, 260sh, 245s, 230sh (Nb–X), 429w (ligand), 325w (unassigned) UV–vis.: 15.6 ($d \rightarrow d$), 25.4, 27.0, 31.0, 33.1, ~35.0, 45.0 (X → Nb) UV–vis.: 20.7, 22.8 (700)	5, 16, 19, 20
$NbI_4(py)_2$	Purple	1.05 0.67	NbI_4 and pyridine, room temp., several days	UV–vis.: 27.0, 16.4	5, 16
$NbF_4(py)_2$	Blue		NbF_4 and pyridine, room temp.	IR: 212w, 343m (Nb–N), 252s, 320w, 590vs (Nb–F), 367w, 410w, 505w, 525w (ligand)	30
$NbCl_4$ bipy	Light purple	1.06 1.26	$NbCl_5$, bipy, *n*-propyl cyanide, 2 days reflux	IR: 338s, 330sh, 228m, 247vw (Nb–X), 415mw, 355sh (ligand)	10, 16 19, 20

		1.41		UV–vis.: 17.0, 25.0sh ($d \rightarrow d$), 29.0, 31.0sh, 37.0, 45.0 (X → Nb)	
$NbBr_4$ bipy	Dark green	1.34	$NbBr_5$, bipy, 7 days	IR: 260sh, 240sh, 215s (Nb–X), 420m, 364m (ligand), 310sh UV–vis.: 17.0sh, 19.0 ($d \leftrightarrow d$), 46.3, 30.6, 35.6 (ligand), 45.0 (X→Nb)	10
NbI_4 bipy		0.77 0.56 0.73	Excess bipy, NbI_4 in benzene		16
$NbCl_4(CH_3CN)_2$	Pale red	1.37 1.22 1.55	Soln. of $NbCl_4$ in excess acetonitrile	UV–vis.: 23.0, 31–38.0 Reflectance: 24.4 ($d \leftrightarrow d$), 32.3, 37.2, 45.4 (Br→Nb); (CH_3CN) 15.4 (10), 26.3 (150), ~32.8sh, 38.0 (13,400), 43.1 (15,500) ($d \leftrightarrow d$) IR: ~370sh, 356s, 335s (Nb–X), 413sh, 400sh (ligand), 247w	10 16
$NbBr_4(CH_3CN)_2$		1,27	$NbBr_4$ in excess acetonitrile	UV–vis.: 26.0, 17.5sh IR: 250–310 (Nb–Br), 400 (CH_3–C–N) IR: 280s, 253s, 238sh (Nb–Br), 414mw, 400mw (ligand), 350m (unassigned) Reflectance: 16.6sh, 20.2sh ($d \leftrightarrow d$), 2.45, 29.9, 36.7, 44.9 (Br→Nb); (CH_3CN): 16.0sh ($d \leftrightarrow d$), 26.3sh, 30.8 (8400), 35.6 (7800), 38.2 (6800)	10 16, 22
$NbI_4(CH_3CN)_2$		0.89 0.51	NbI_4 in excess acetonitrile	UV–vis.: 26.0	16
$NbCl_4$·phen	Olive green, purple	1.05	$NbCl_5$, 1,10-phen, acetonitrile, 9 days reflux	IR: 360sh, 348s, 330s, 310s, 260m (Nb–X), 425m, 275mw, 237w (ligand) UV–vis.: 19.0b, 23.2 ($d \leftrightarrow d$), 28.2, 31.2, 36.6, 45.4 (X → Nb)	10 19
$NbBr_4$·phen	Brown	1.38	$NbBr_4$ in chloroform and acetonitrile, 7 days	IR: 263sh, 247sh, 230s (Nb–X), 430mw, 279m (ligand), 314m, 302w (unassigned) UV–vis.: 18.8sh, 21.5 ($d \leftrightarrow d$), 25.5, 29.0b, 37.0, 45.5 (X→Nb)	10

TABLE 1 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
NbN(CH$_3$)$_2$ N(C$_2$H$_5$)$_2$]$_3$	Red		Diethylamine and Nb(NMe$_2$)$_5$, 2 h reflux		24
Nb[N(n-C$_3$H$_7$)$_2$]$_4$	Red	0.8	NbCl$_5$ and LiNPr$_2$, 6 h, room temp.	ESR: $\langle g \rangle = 1.954, g_\parallel = 1.928, g_\perp = 1.967$, $\langle A \rangle = 95, A_\parallel = 196, A_\perp = 44$	24
Nb[N(n-C$_4$H$_9$)$_2$]$_4$	Red		NbCl$_5$ and LiNBu$^n{}_2$, 5 h, room temp.		24
Nb[NCH$_3$ · n-C$_4$H$_9$]$_4$	Red		NbCl$_5$ and LiNR$_2$, 6 h, room temp.	ESR: $\langle g \rangle = 1.9540, g_\parallel = 1.929, g_\perp = 1.966$, $\langle A \rangle = 107, A_\parallel = 195, A_\perp = 62$	24
Nb(NC$_5$H$_{10}$)$_4$	Brown		Piperidine and Nb(NEt$_2$)$_4$ in boiling benzene, 6 days	ESR: $\langle g \rangle = 1.954, g_\parallel = 1.926, g_\perp = 1.968$, $\langle A \rangle = 112, A_\parallel = 194, A_\perp = 71$	24
Nb[N(C$_2$H$_5$)$_2$]$_3$(NC$_5$H$_{10}$)	Brown		Piperidine and Nb(NEt$_2$)$_4$ in boiling benzene, 4 h		24
NbCl$_3$(CN)(CH$_3$CN)$_2$	Black		KCN and NbCl$_4$ in CH$_3$CN, room temp.	IR: 2940 (C–H), 2280, 2300 (C–N acetonitrile), 2160 (C≡N cyanide) UV–vis.: 22.0	27
K$_2$Nb(NCS)$_6$			NbCl$_4$, KCNS, acetonitrile, several days, extract with 1,2- dichloroethane and acetonitrile	IR: (Nujol mull): 2077m, 2020s, sh, 2005s, 1980s, 1948s, 1908m (C–N); (acetonitrile): 2080m, sh, 2035s, 888w; (Nujol): 504m, 342s (Nb–N–C–S); (acetonitrile): 512w, 392s, 330s (Nb–N–C–S) UV–vis.: 26.6 ($t_{1u} \rightarrow t_{2g}$), 38.5 (solvent to metal e$^-$ transition)	12
Nb(NCS)$_3$Cl	Greenish- black		KCNS, NbCl$_4$, several days, room temp.	IR: 1990 (C–N), 2290, 2305 (bridging NCS) UV–vis.: 18.0 (ligand field transition), 30.0 (internal transition of thiocyanate)	27

$NbCl_4 \cdot C_6H_{16}N_2$	Deep red		$NbCl_4$ and N,N,N',N'-tetramethylethylenediamine, 72 h, 100°C or 96 h at room temp.	UV–vis.: (benzene): 19.8 (30), 23.26 (13), 33.33 (1000); (solid): 19.42, 23.26, 33.33, 38.76	28
$NbBr_4 \cdot C_6H_{16}N_2$	Deep blue		$NbBr_4$ and N,N,N',N'-tetramethylethylenediamine, 72 h, room temp.	UV–vis.: (benzene): 17.86 (45), 21.98 (26), 30.45 (590); (solid): 17.49, 21.74sh, 30.1, 36.23, 38.76	28
$NbI_4 \cdot C_6H_{16}N_2$	Olive green		NbI_4 and N,N,N',N'-tetramethylethylenediamine, 72 h, room temp.	UV–vis.: (benzene): 15.75 (230), 18.18 (240), 22.22sh (820), 24.69sh (1200), 27.25 (2400), 33.11sh (5400); (solid): 15.75, 22.47, 24.94, 26.67, 31.75	28
$Nb(CNO)_3Cl$	Grey		$NbCl_4$ and KCNO, acetonitrile, several days, room temp.	IR: 2200 (C–N), 1400 (C–O) UV–vis.: 9.00, 15.0, 22.0	27
$NbCl_4$(salen)	Yellow		$NbCl_4$ and N,N-bis-(salicylidene)-ethylenediamine, benzene	UV: 27.3	27
$NbCl_4(\gamma\text{-pic})_2$	Dark brown	1.18 0.89	$NbCl_5$, γ-picoline, benzene, 7 days, 20°C (also in acetonitrile)	UV–vis.: 23.5, 19.5	16, 19, 21
$NbBr_4(\gamma\text{-pic})_2$	Green	1.29 0.58	$NbBr_5$, γ-picoline, 24 h, reflux (also acetonitrile)		16, 18
$NbI_4(\gamma\text{-pic})_2^{I}$		0.35 0.77	Excess γ-pic in acetonitrile with NbI_4		16
$NbI_4(\gamma\text{-pic})_2^{II}$		0.51 1.11	Excess γ-pic in acetonitrile and NbI_4		16
$NbCl_4 \cdot (C_2H_5)_3N$	Brown		$NbCl_4$ and triethylamine, 72 h, 250°C		28

TABLE 1 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
E. Niobium with sulfur ligands					
NbS_2		0.98	Thermal decomp. of NbS_2Cl_2 or NbS_2Br_2		29, 33
$Nb[S_2CN(CH_3)_2]_4$	Dark purple	1.32	$Nb[N(CH_3)_2]_4$ in cyclohexane, CS_2, reflux, 1 h	IR: 1510 (thioureide), 1138 (NC_2), 996 (C···S), 345 (Nb···S)	31, 32
$Nb[S_2CN(C_2H_5)_2]_4$	Dark purple, pale brown	0.5 1.55	$Nb[N(C_2H_5)_2]_4$ in cyclohexane, CS_2, reflux, 1 h or $NbCl_4$ and sodium diethyldithiocarbamate, acetonitrile, several days, room temp.	IR: 1504 (thioureide), 1147 (NC_2), 1002 (C···S), 364 (Nb···S) IR: 1499 (C···N), 1148 (NC_2), 1008 (C···S), 360 (Nb···S) IR: 1485 (C–N) UV: 19.5, 23.5, 16.0sh	27, 30, 31
$NbCl_4(C_4H_8S)_2$	Brown	1.32	$NbCl_4 + C_4H_8S$, several days	IR: ~ 340vw, b, 305sh (M–X), ~ 230, vw, b UV–vis.: (solid): 9.4, 13.0, 19.8sh ($d \leftrightarrow d$), 28.8, 31.2sh, 36.5 (X→M); (in C_4H_8S/C_6H_6): 9.2 (~ 10), 12.7 (20), 18.5 (~ 400) ($d \leftrightarrow d$), 24.75sh, ~ 29.5sh, b (X→M)	34
α-$NbBr_4(C_4H_8S)_2$	Brown	1.41	$NbBr_4 + C_4H_8S$, several days	IR: ~ 280sh, ~ 240vs, b (M–X) UV–vis.: (solid): 10.0, ~ 16.0sh ($d \leftrightarrow d$), 23.0b, ~ 30.0sh, 36.0 (X→M); (C_4H_8S/C_6H_6): ~ 11.0 (6), ~ 16.2sh ($d \leftrightarrow d$), 29.0sh, 32.3 (~ 5000) (X→M)	34
β-$NbBr_4(C_4H_8S)_2$	Light brown	1.30	$NbBr_4 + C_4H_8S$, several days	IR: 227 (M–X), 390w, 285w, 275w, 247sh (unassigned) UV–vis.: (solid): 9.5, 22.4sh ($d \leftrightarrow d$), 25.5, 29.2sh, ~ 33.0sh, 36.4 (X→M)	34

$NbCl_4S(CH_3)_2$	Brown, red-orange	0.44 0.36	$NbCl_4 + S(CH_3)_2$, 3–5 days, reflux	IR: 385vs, 362vs, 343s (M–X), 310ms, 250w (unassigned); (Nujol): 396m, sh, 368s, 340m, sh, 250w (Nb–X), 304wm, 278w, sh (Nb–S), 170w, 160w, sh, 130w, 110w, 76w; (C_6H_6): ~ 396m, 370s, 340m, 240w (Nb–X), 310w, sh, 280w, sh (Nb–S), 300w UV–vis.: (solid): 11.2, 16.0 ($d \leftrightarrow d$), 24.0, ~ 26.0b, 30.0sh, 36.0 ($X\pi \rightarrow M$); ($S(CH_3)_2$): 19.5 ($d \leftrightarrow d$), 30.8sh, 34.5 ($X \rightarrow M$)	35, 36
$NbBr_4S(CH_3)_2$	Red	0.50 0.38	$NbBr_4 + S(CH_3)_2$, 3–5 days, reflux	IR: (Nujol): 271s, 254m, 227m, 195m (Nb–X), 305m, 283m (Nb–S), 160w, 110w, sh, 98w UV–vis.: (C_6H_6): 6.9, 11.8, 17.4, 28.6, 30.9; ($S(CH_3)_2$): 11.9, 17.4, 29.0, 33.0; ($MgCO_3$): < 10.0, 15.4sh, ~ 24.0	35, 36
$NbCl_4[S(CH_3)_2]_2$	Dark red		$NbCl_4 + S(CH_3)_2$, 3–5 days, reflux		36
$NbBr_4[S(CH_3)_2]_2$	Brown green	1.42 1.36 1.21	$NbBr_4 + S(CH_3)_2$, 3–5 days, reflux	IR: ~ 265ms, b, ~ 230m, b (M–X), ~ 300sh, vb (unassigned); (Nujol): 270s, 256s, 227m, sh, 189w (Nb–X), 304m, sh, 278m, sh (Nb–S) UV–vis.: (solid): 25.0vb, 31.0sh ($X \rightarrow M$), 36.0; ($S(CH_3)_2$): ~ 10.7 (30), 18.2sh ($d \leftrightarrow d$), 31.2vb (~ 10,000) ($X \rightarrow M$) UV–vis.: ($S(CH_3)_2$): 11.9, 17.4, 29.0, 33.0; (C_6H_6): 6.9, 11.8, 17.4, 28.6, 30.9; ($MgCO_3$): 11.4, 17.5, 23.3, 24.4, 27.0, 28.6 IR: 270s, 256s, 227m, sh, 189w (Nb–X), 304m, sh, 278m, sh (Nb–X)	35, 36
$NbI_4[S(CH_3)_2]_2$	Dark brown	1.23 1.14	$NbI_4 + S(CH_3)_2$, 3–5 days, reflux	IR: (Nujol): 200s, 264m, sh, 14.4w (Nb–X), 316wm, 288m (Nb–S), 88w UV–vis.: ($S(CH_3)_2$): 11.1, 17.4, 20.8sh, 22.7, 29.0	36
$NbCl_4S(C_2H_5)_2$	Red-orange		$NbCl_4$, excess $S(C_2H_5)_2$, 3–5 days	IR: (Nujol): 390m, 360s, 340m, sh, 250w (Nb–X), 304m, 280w, sh (Nb–S), 162w, sh, 150m, 132w, sh, 110w;	35, 36

TABLE 1 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
				(C_6H_6): 398s, 370m, 250w (Nb–X), 300w, 280w (Nb–S) UV–vis.: (C_6H_{12}): 8.0, 12.1, 18.6, 26.7, 34.4, 43.5; (C_6H_6): 8.1, 12.4, 18.8	
$NbBr_4S(C_2H_5)_2$	Red		$NbBr_4$, excess $S(C_2H_5)_2$, 3–5 days	IR: (Nujol): 270s, 250m, 227m, 189 (Nb–X), 303m, 282s (Nb–S), 156m, 110w, 92w, 74w UV–vis.: (C_6H_6): 6.9 (79), 11.6 (12), 17.4 (150); ($MgCO_3$): 9.5, 14.6sh, 27.0sh, ~ 29.1	35, 36
$NbCl_4[S(CH_2)_4]_2$	Orange	1.34 1.25	$NbCl_4$ + $S(CH_2)_4$, 3–5 days, reflux	IR: (Nujol): 396m, 372s, 340m, sh, 245w (Nb–X), 302w, 278w (Nb–S), 235w, 162w, 148ms (other); (C_6H_6): 398m, 280m, 362s (Nb–X), 320w, 300w (other); ($S(CH_2)_4$): 396w, sh, 366s, 340m, 250w, sh (Nb–X), 304wm, 280w (Nb–S),230w (other) UV–vis.: (C_6H_6): 9.74 (12), 13.3 (29), 18.6 (194), 27.8 (1550); ($MgCO_3$): < 10.0, 13.0, 18.8sh, 22.8sh, 27.0; ($S(CH_2)_4$): 9.8, 13.3, 18.5	36
$NbBr_4[S(CH_2)_4]_2$	Green	1.38 1.27	$NbBr_4$ + $S(CH_2)_4$, 3–5 days, reflux	IR: (Nujol): 263s, 247m, 229wm, 200w, sh (Nb–X), 307wm, 278m, sh (Nb–S), 190wm, 96m, 85m (other); (C_6H_6): 266s, 253s, 229m, sh, 200w (Nb–X), 300m, sh (Nb–S), 400m, 300m, sh (other); ($S(CH_2)_4$): 266s, 253s, 227m (Nb–X) UV–vis.: (C_6H_6): 11.9 (12), 17.5 (240), 27.8 (2000); ($MgCO_3$): 11.0, 16.8, 25.4	36
$NbI_4[S(CH_2)_4]_2$	Dark brown	1.05 0.98	NbI_4 + $S(CH_2)_4$, 3–5 days, reflux	IR: (Nujol): 227w, sh, 200s, b, 149wm (Nb–X), 297m, 272wm (Nb–S), 138w, 98w (other) UV–vis.: 13.7 (118), 16.7 (1140), 19.3 (1530), 21.0 (1210), 27.0 (2400)	36
$NbCl_4(dth)_2$	Light	1.60	$NbCl_4$, dth,	IR: 310s, sh (Nb–Cl), 303s, 281s, 260w (Nb–S),	35, 37

	brown		4–5 days	245w (C–C–S), 235w, 204w (C–S–C), 180w, 119w, 97m, 81m (unassigned) UV–vis.: 12.3, 14.0, 18.8, 24.4, 31.0	
$NbBr_4(dth)_2$	Green	1.61	$NbBr_4$, dth, 4–5 days	IR: 245s, sh, 235s (Nb–I), 278m, 261m (Nb–S), 245 (C–C–S), 235 (C–S–C), 194w, sh, 185w, 164m, 135w, 118m, 113m, sh, 97m, 72m (unassigned) UV–vis.: 11.6, 13.7, 16.9, 22.7, 28.6	35, 37
$NbI_4(dth)_2$	Brown	1.28	NbI_4, dth, 10 days	IR: 165m, 142m (Nb–I), 276m, 254m (Nb–S), 230w, 213m (C–S–C), 123w, sh, 108m, 63w, 59w (unassigned) UV–vis.: 10.1, 12.7, 15.2, 18.4, 26.3	35, 37
$NbCl_4(TU)_2$	Red-brown	1.19	$NbCl_4$ and TU in acetonitrile, several days	IR: 695, 1510 UV–vis.: 25.0, 30.0	16
$NbI_4(TU)_3$	Black		NbI_4 and TU in acetonitrile, several days	IR: 700, 1510 UV–vis.: 34.0	16

F. Niobium with oxygen ligands

NbO_2		0.56	Nb_2O_5, H_2 1100°C		29
Nbt_4	Dark green	0.74	Tropolone and $NbCl_4$ in acetonitrile or toluene, triethylamine	UV–vis.: 44,3, 38.5, 30.8, 25.3 (intraligand), 20.38 ($\pi \rightarrow d$), 10.85 (2.89) ($d \rightarrow \pi$); (toluene): 26.38 (3.67) (intraligand), 20.2 ($\pi \rightarrow d$)	38
$Nb(tta)_4$	Dark green	1.61	$NbCl_4$ with (tta) thenoyltrifluoracetone	UV–vis.: 13.0, 20.5 ($d \leftrightarrow d$); (solution): 13.7, 20.8 (3000–5000) Reflectance: 44.4sh ($\pi_3 \rightarrow \pi_6$), 37.8sh (aromatic), 26.9 ($\pi_3 \rightarrow \pi_4$), 20.3 ($d \rightarrow \pi_4$); (toluene): 27.75 (4.84) ($\pi_3 \rightarrow \pi_4$), 20.75 (3.66) ($d \rightarrow \pi_4$), 13.95 (3.49) ($\pi_3 \rightarrow d$)	38, 39

TABLE I (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
Nb(bzta)$_4$	Dark green	1.43	$NbCl_4$ with (bztaH) benzoyltrifluoracetone	UV–vis.: 13.0, 21.0; (solution): 14.0, 21.7 (3000–5000) UV–vis.: 44.5sh ($\pi_3 \rightarrow \pi_5$), 38.8sh (aromatic), 30.1 ($\pi_3 \rightarrow \pi_4$), 21.0 ($d \leftrightarrow \pi_4$), 13.0 ($\pi_4 \rightarrow d$); (toluene): 21.55 ($d \rightarrow \pi_4$), 14.45 ($\pi_3 \rightarrow d$)	38, 39
Nb(bzbz)$_4$	Dark green	1.66	$NbCl_4$ with bzbzH (dibenzoylmethane)	UV–vis.: 10.0, 20.0; (solution): 12.0, 21.0 UV–vis.: 44.5sh ($\pi_3 \rightarrow \pi_5$), 28.0 (aromatic), 27.6 ($\pi_3 \rightarrow \pi_4$), 20.3 ($d \leftrightarrow \pi_4$), 12.8 ($\pi_3 \rightarrow d$); (toluene): 20.87 (3.48) ($d \rightarrow \pi_4$)	38, 39
$NbCl_2$(bzac)$_2$	Dark green	1.58	$NbCl_4$ in CH_3CN and dibenzoylmethane, reflux, 5 min.	UV–vis.: 44sh ($\pi_3 \rightarrow \pi_5$), 38.5sh (aromatic ring), 28sh ($\pi_3 \rightarrow \pi_4$), 17.4 ($d \rightarrow \pi_4$), 12.9 ($\pi_3 \rightarrow d$)	39
NbClt$_3$	Dark green	0.40	$NbCl_4$ in CH_3CN and tropolone, reflux	UV–vis.: 43.2sh, 39.2, 30.0sh, 25.6 (intraligand), 24.15 ($\pi \rightarrow d$); (acetonitrile): 30.2, 26.0 (intraligand), 20.6 ($\pi \rightarrow d$)	39
$Nb(OC_2H_5)_4$	Red-brown		$NaOC_2H_5$ and $NbCl(OC_2H_5)_3 \cdot (C_5H_5N)_2$	IR: 1030m, sh, 1040s, sh, 1100s, 1140m, sh	40
$NbCl_4(C_4H_8O)_2$	Pale yellow-brown	1.53	$NbCl_4$ and ligand, 72 h, room temp.	IR: ~ 333vs, 270mw, 235mw (Nb–X) UV–vis.: 25.5sh ($d \leftrightarrow d$), 31.6, 35.0sh, 37.4, 45.6 (X $\pi \rightarrow$ Nb)	10
$NbBr_4(C_4H_8O)_2$	Red-brown	1.35	$NbBr_4$ and ligand, 15 h, room temp.	IR: 290sh, 270s, 245sh (Nb–X), 330w (unassigned) UV–vis.: 19.4sh, 22.0 ($d \leftrightarrow d$), 24.6, 26.8, 30.2sh, b, 36.8, 45.0 (X $\pi \rightarrow$ Nb)	10
$NbCl_4(C_5H_{10}O)_2$	Pale yellow	1.54	$NbCl_4$ and ligand, 48 h, room temp.	IR: 347s, 332s, 278m, 247m (Nb–X), 417m, 295mw (ligand) UV–vis.: 25.8sh, vb ($d \leftrightarrow d$), 30.0sh, 33.4, ~ 37.1sh, 45.2 (X $\pi \rightarrow$ Nb)	10

$NbBr_4 \cdot C_5H_{10}O$	Light brown	1.51	$NbBr_4$ and ligand, 48 h, room temp.	IR: 248sh, 234vs (Nb–X), 415mw, 304m, 293ms (ligand) UV–vis.: 19.6sh, 22.0sh ($d \leftrightarrow d$), 24.7sh, 26.4, 29.6, 32.5, 36.0, 45.0 (X $\pi \rightarrow$ Nb)	10
$NbCl_4(C_4H_8O_2)_2$	Pale yellow	1.61	$NbCl_4$ and ligand, 1 week, room temp.	IR: 347sh, 334s, 288ms, 248m (Nb–X), 430w, 304ms (ligand) UV–vis.: 14.7?, 23.5 ($d \leftrightarrow d$), 29.6sh, 32.0sh, 34.0, 36.5sh, ~ 45.0? (X $\pi \rightarrow$ Nb)	10
$NbBr_4 \cdot 2C_4H_8O_2$	Red-brown	1.55	$NbBr_4$ and ligand, 1 week, room temp.	IR: 240s, vb (Nb–X), 438w, 312s (ligand) UV–vis.: 18.8sh, 22.0sh ($d \leftrightarrow d$), 24.4, 26.0, 30.2, 32.7, 36.0, 45.4 (X $\pi \rightarrow$ Nb)	10
$NbO(CH_3COCH_2 \cdot COCH_3)_2$	Violet		HCl soln. of $NbCl_5$ reduced with metallic zinc in acetylacetone	ESR: $\langle g \rangle = 1.906 \pm 0.006$ $\langle A \rangle = 159 \pm 5$ $g_{\parallel}$ 1.093 ± 0.006 $g_{\perp}$ 1.964 ± 0.006 $A_{\parallel}$ 249 ± 5 $A_{\perp}$ 108 ± 5	15
$Nb(bzac)_4$ dioxane	Dark green	1.44	$NbCl_4$, triethylamine, benzoylacetone	UV–vis.: 43.8sh ($\pi_3 \rightarrow \pi_5$), 38.8 (aromatic), 30.1 ($\pi_3 \rightarrow \pi_4$), 21.9 ($d \rightarrow \pi_4$), 12.9 ($\pi_3 \rightarrow d$), (toluene): 22.45 ($d \rightarrow \pi_4$), 15.05 ($\pi_3 \rightarrow d$)	39
$NbCl_4(dioxane)_2$	Dark purple	1.47	$NbCl_4$, 5 min, reflux, dioxane	IR: 1253s, 1113s, 1094m, sh, 1076m, 897m, 871s, 820sh, 799s, 620	39
$Nb(oxine)_4$	Dark purple	1.60	8-Hydroxyquinoline and $NbCl_4$ in acetonitrile or toluene, 3 min, reflux	UV–vis.: 12.0, 17.9 ($d \leftrightarrow d$); (solution): 12.4, 19.2 (3000–5000) UV–vis.: 38.3, 24.3 (intraligand), 17.7 ($\pi \rightarrow d$), 12.3 ($d \rightarrow \pi$); (toluene): 25.05 (intraligand), 19.15 ($\pi \rightarrow d$), 12.53 ($d \rightarrow \pi$); (dioxane): 25.23 (intraligand), 19.15 ($\pi \rightarrow d$), 12.53 ($d \rightarrow \pi$)	38, 39
$Nb(acac)_4$-dioxane	Dark green	1.73	$NbCl_4$, dioxane, Tl acac, 5 min, reflux	UV–vis.: 9.0, 15.0 UV–vis.: 45.2sh ($\pi_3 \rightarrow \pi_5$), 34.1 ($\pi_3 \rightarrow \pi_4$), 23.4 ($d \rightarrow \pi_4$), 15.4 ($\pi_3 \rightarrow d$); (toluene): 24.1 (3.26), 19.23 (3.11) ($\pi_3 \rightarrow d$)($d \rightarrow \pi_4$)	38, 39

TABLE 1 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
Nb(acac)$_4$	Dark purple	1.51 1.47	NbCl$_4$ and Tl acac in toluene or acetonitrile	UV–vis.: 7.0, 15.0 (3000–5000) UV–vis.: 45.6 ($\pi_3 \rightarrow \pi_5$), 33.9 ($\pi_3 \rightarrow \pi_4$), 23.9 ($d \rightarrow \pi_4$), 16.6 ($\pi_3 \rightarrow d$); (toluene): 24.37 (3.08), ($d \rightarrow \pi_4$), 19.45 (2.95) ($\pi_3 \rightarrow d$)	38, 39
G. Niobium with mixed ligands					
(pyH)$_2$Nb(OC$_2$H$_5$)Cl$_5$	Orange		Electrolytic reduction, few minutes, NbCl$_5$, HCl, ligand	IR: 1070, 1090	41
[(CH$_3$)$_4$N]$_2$Nb(OC$_3$H$_7$)Cl$_5$	Pink		NbCl$_5$, HCl, propanol, ligand, electrolytic reduction		41
(QuH)$_2$Nb(OC$_2$H$_5$)Cl$_5$	Violet	1.72	NbCl$_5$, quin, ethyl alcohol, HCl, several hours, electrolytic reduction	IR: 1070, 1090 (C–O), 3000 (C–H)	41
(QuH)$_2$Nb-(i-OC$_3$H$_7$)Cl$_5$	Violet	1.74	quin, HCl, i-propanol, NbCl$_5$, immediate, electrolytic reduction	IR: 1030, 1100 (C–O), 3000 (C–H)	41
[(CH$_3$)$_4$N]$_2$Nb-(OCH$_3$)Cl$_5$	Pink		HCl, NbCl$_5$, ligand, methanol, few minutes, electrolytic reduction	IR: 1130 (C–O) UV–vis.: 19.6	41
(QuH)$_2$Nb-(OCH$_3$)Cl$_5$	Violet		NbCl$_5$, ligand, CH$_3$OH, HCl, 20 min, electrolytic reduction	IR: 1110 (C–O), 3000 (C–H)	41
(pyH)$_2$Nb-(OCH$_3$)Cl$_5$	Red-brown	1.72	Electrolytic reduction of NbCl$_5$ in methanol, pyridinium chloride	IR: 1095 (C–O)	46

$Nb(OCH_3)Cl_5^{2-}$ (not isolated in this ESR study – see ref. 41)			Electrolytic reduction of $NbCl_5$ in HCl-saturated alcohols	UV–vis.: 19.9 ($b_2 \rightarrow b_1$), 23.6 (charge transfer band) ESR: $A_\parallel$ 248 ± 6 gauss $A_\perp$ 144 ± 10 gauss $g_\parallel$ 1.965 ± 0.008 $g_\perp$ 1.809 ± 0.010	42
$(QuH)_2Nb\text{-}(OCH_3)Cl_5$	Red		$NbCl_5$, quin, methanol, HCl, 10 min, electrolytic reduction	IR: 3000 (C–H)	41
$(4\text{-picH})_2Nb\text{-}(OC_2H_5)Cl_5$	Orange		$NbCl_5$, pic, ethanol, HCl, few minutes, electrolytic reduction		41
$(QuH)_2Nb\text{-}(OC_2H_5)Cl_5$	Violet		$NbCl_5$, quin, ethanol, HCl, 10 min, electrolytic reduction		41
$(pyH)_2Nb\text{-}(i\text{-}OC_3H_7)Cl_5$	Orange		$NbCl_5$, py, isopropanol, HCl, immediate, electrolytic reduction		41
$Nb_2Cl_5(OC_2H_5)_3\cdot(bipy)_2$	Dark blue-green	1.39	Electrolytically reduced Nb^{IV} and bipyridyl in ethanol	IR: 1600, 760 (coord. bipy)	47
$[(CH_3)_2NH_2]_2Nb\text{-}(OC_2H_5)Cl_5$	Peach		$NbCl_5$, ligand, CH_3OH, HCl, 1 min, electrolytic reduction	IR: 1070, 1100 (C–O) UV–vis.: 19.6	41
$[(C_5H_5N)_2NbCl\text{-}(OC_2H_5)_3]_2$	Red		py and $NbCl_4$ in ethyl alcohol, 1 h	IR: 1010m, 1040m, 1080s, 1120s, sh, 1140m	40
H. Niobium with other ligands					
$(\pi\text{-}C_5H_5)_2NbI_2$	Black	1.80	$(\pi\text{-}C_5H_5)_2NbCl_2OH$ reduced by benzyl mercaptan in a methanol or benzene solution in NH_4I, 25°C, 20 h	IR: 3090m, 1430m, 1115vw, 1060vw, 1010m, 1000m, 857m, 810s	43

TABLE I (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
$NbCl_4(Ph_3P)_{3/2}$	Yellow		$NbCl_4$ and Ph_3P in benzene, stirred, several days	UV–vis.: 26.0	16
$NbSe_2$			Thermal decomposition of $NbSe_2Cl_2$ or $NbSe_2Br_2$		33, 44
$NbCl_4(diars)_2$	Green	1.7	Diarsine with $NbCl_4$, $NbCl_5$ or $NbOCl_3$, 250°C	UV–vis.: 10.7, 13.8, 15.3w, sh, 17.3, 22.7sh ESR: $g_{\parallel} = 1.951$, $g_{\perp} = 2.002$	45
$NbBr_4(diars)_2$	Green	1.9	Diarsine with $NbBr_4$, $NbBr_5$ or $NbOBr_3$, 100°C	UV–vis.: 10.6, 13.8, 16.7, 21.2	45
$NbI_4(diars)_2$	Yellow	1.6	Diarsine with NbI_4, NbI_5 or $NbOI_3$, 70°C	UV–vis.: 10.25, 13.1sh, 15.2, 19.7sh	45

a Magnetic moments are at ambient room temperature unless otherwise noted.

b IR values are given in cm^{-1}; UV–vis. values are in ($cm^{-1} \times 10^3$); ESR splitting parameters, $A_{\parallel}$, $A_{\perp}$ and $\langle A \rangle$ are in ($cm^{-1} \times 10^4$) unless otherwise noted.

c Values in gauss.

d More recent details on the ESR study of $NbOCl_4^{2-}$ are given in the section covering the magnetic properties of Nb^{IV}.

e w = weak-strength peak; m = medium-strength peak; s = strong peak; sh = shoulder; b = broad. Assignments are given as in reference noted.

1. *Chemistry*.

The methods of preparation for the complexes are summarized in the table, with specific techniques available in the respective references. The reaction times vary greatly ranging from immediate reactions to several weeks. In most cases, much care is taken to protect the reactants from air and moisture.

The magnetic properties of these complexes have proven most interesting. The expected spin-only magnetic moment of a d^1 transition element is 1.73 B.M. Although this value is found in some of the complexes, many show much lower values. Some are diamagnetic, which has been attributed to Nb—Nb interactions in polymeric compounds[5,35,48]. The structure of NbI_4, for example, has been described as octahedral crystals opposite edges being shared. Nb—Nb metal bonds are formed with the overlap of, possible, the d_{xy} orbitals, resulting in electron pairing (see Fig. 2).

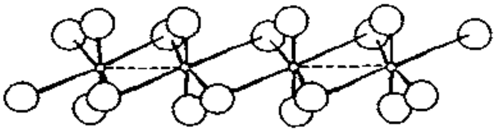


Fig. 2. Structure[1] of NbI_4.

8-Coordinate complexes have been prepared and studied[31,37,38,45] and shown to be paramagnetic with magnetic moments ranging from 1.6 to 1.9 B.M. Since the formation of Nb—Nb bonds in these complexes is sterically hindered, this provides further evidence for the Nb—Nb interactions in some of the d^1 complexes. Still another example where bulky ligands prevent Nb—Nb interaction is the dicyclopentadienylniobium diiodide complex, which is proposed to have a structure with canted cyclopentadienyl rings and iodine atoms at angles dictated by Nb—I bond distances and van der Waals radii[43]. This predicted geometry would not allow the molecular packing needed for Nb—Nb interactions and the complex is paramagnetic with a magnetic moment of 1.8 B.M., near that for a spin-only d^1 complex. Controversy still exists concerning the magnetic moments of $NbX_4 \cdot 2py$ (X = = Cl, Br, I) which decrease[5] in the order Cl > Br > I. This order has been related to the magnitude of the tetragonal distortion of the complexes, Δ, which should depend on the net difference in ligand field strength between the pyridine and halogens.

As suggested by Fowles et al.[10], the situation is not as simple as stated above. Since the effective magnetic moment arising from the $^2T_{2g}$ ground term in a cubic ligand field depends on Δ, the separation between the orbital levels of the $^2T_{2g}$ terms created by a noncubic ligand field, on λ, the spin—orbit coupling constant, and on *k*, the orbital reduction factor, all of these factors, not just Δ, must be considered.

The coordination number of niobium(IV) is usually six, but as expected for a second-row transition element, a great number of eight-coordinate complexes exists. There is evidence[38] for a nine-coordinate Nb(acac)$_4$-dioxane. The eight-coordinate complexes could be either square anti-prism or dodecahedral structures. The latter structure is usually assigned from the optical spectrum[35].

The six-coordinate complexes, NbX_4L_2, could have D_{4h} or C_{2v} symmetry and both exist. Fowles et al. have assigned the geometry of a series of compounds, mainly N-containing[10], while Hamilton and McCarley have worked with sulfur-containing compounds[36].

Lower coordination numbers are also known for niobium(IV). In a series of sulfur adducts, $S(CH_3)_2$, $S(C_2H_5)_2$ and $S(CH_2)_4$ with niobium tetrahalide, it was found that diadducts were formed with $S(CH_2)_4$ but that the bulkier methyl sulfide and ethyl sulfide formed monoadducts. In addition, the order of increasing space requirements, $S(CH_2)_4 <$ $< S(CH_3)_2 < S(C_2H_5)_2$ corresponds to the order of decreasing stability of the diadducts[36]. Electron spin resonance studies of solutions of niobium(IV) chloride in substituted pyridines have also shown mono- and diadducts to be present.

Coordination numbers of four are usually of the $Nb(NR_2)_4$ type. The magnetic moments for these compounds were found to be about 0.8 B.M., less than the predicted value[25] of 1.73 B.M. However, in this case, the difference could not be explained in terms of a dimeric complex. Molecular weight determinations showed that only monomers were present. A small θ value and the appearance of an ESR signal at room temperature seemed to rule out the possibility of strong magnetic interactions. Further investigation is warranted.

Relatively few non-oxo anionic complexes exist. The hexahalo- and pentachloroalkoxoniobates have been well characterized. The hexathiocyanato niobate(IV) complex has also been well characterized and shown to be N-coordinated[12].

2. *Magnetic properties*

Complexes of the type $NbCl_4 \cdot 2L$ with L = pyridine and various substituted pyridines have recently been under investigation in ESR studies[49]. The ESR spectra of these complexes show variations in splitting parameters which are related to the electronic effects of the substituent. Simple molecular orbital calculations with the ESR parameters indicate a considerable amount of delocalization of electron density into p_π orbitals of the four equatorial chlorides.

In all the substituted pyridine complexes investigated, except for the 4-ethyl and 4-phenyl complexes, $g_\perp$ is greater than $g_\parallel$ (see Table 2). Typically among d^1 transition metal complexes, $g_\parallel$ is greater than $g_\perp$. Exceptions to this generalization occur only with transition metal complexes where the ligands in both axial and equatorial sites have similar electron donating properties. That is, a pyridine donating electrons to niobium in axial sites must be similar to the chloride ion in $NbCl_6^{2-}$. In $NbO(acac)_2$, the equatorial and axial oxygens must interact with the metal in a similar way. Thus, the tetragonal field and cubic field for those complexes where $g_\perp$ is greater than $g_\parallel$ are of the same order. The two most bulky ligands, 4-ethylpyridine and 4-phenylpyridine may, through a steric mechanism, bring about a larger tetragonal distortion than the other pyridine complexes.

Electron spin resonance studies of $NbCl_4$ in concentrated hydrochloric acid show two species to be present[50]. These are identified as the oxopentachloroniobate(IV) ion and the

TABLE 2

ESR parameters of Nb^{IV} complexes with substituted pyridines[a].

L	$A_\parallel$	$A_\perp$	$\langle a \rangle_{calc}$	$g_\perp$	$g_\parallel$	$\langle g \rangle_{calc}$
Pyridine	262.3	139.9	180.7	1.9161	1.9607	1.9458
3-Ethyl	267.3	140.0	182.4	1.9262	1.9542	1.9449
3-Methyl	253.9	137.6	176.4	1.9161	1.9601	1.9454
3-Amino	242.7	127.0	165.6	1.9197	1.9634	1.9488
3-Bromo	265.2	140.9	169.0	1.8623	1.9564	1.9250
4-Ethyl	251.8	134.1	173.3	1.9238	1.8965	1.9056
4-Methyl	268.8	139.6	182.7	1.9242	1.9556	1.9451
4-Amino	248.1	128.9	168.6	1.9205	1.9557	1.9440
4-Phenyl	254.2	133.9	174.0	1.9229	1.8930	1.9030

[a] ESR splitting parameters given in gauss.

oxotetrachloroaquoniobate(IV) ion from their electron spin resonance parameters. A third species, the hexachloroniobate(IV) ion, is also present and can be isolated as the cesium salt. Solutions of niobium(IV) produced by zinc reduction of Nb^{IV} in hydrocloric acid or HCl-saturated ethanol contain the oxotetrachloroaquoniobate(IV) ion and the oxotetrachloroethanolatoniobate(IV) ion respectively. Calculations of the normalization constant for the ground state $B_2 >^*$ molecular orbital for the oxo species also indicate considerable delocalization of unpaired spin density into the equatorial chlorine $p-\pi$ orbitals.

In the investigation of hexacoordinate complexes of niobium(IV) chloride by ESR methods, several oxygen donors as well as the oxochloro species were examined[51] to determine the extent of axial π bonding, since oxygen would be observed in different states of bonding to metal (Table 3). In nearly all cases, the hyperfine parameters are significantly different from those of the oxochloro species, and it is concluded that only coordinate bonding to oxygen is present.

In the case of HMPA, two species are detected, which are likely mono and bis complexes, since the bulkiness of the ligand would probably hinder rapid coordination. It is seen that where the nature of the groups bonded to the oxygen utilize the oxygen's π-bonding capability, the A values are significantly higher indicating that π-bonding to the oxygen by Nb is important in delocalization. $g_\parallel$ and $g_\perp$ for DMA, DMF and DEF are extremely close. Also, $g_\parallel > g_\perp$, as was found in the oxochloro species.

The investigation of *cis* complexes of the type $NbCl_4L_4$, where L is various nitriles, has recently been completed. The spectra are very complex and quite different from those complexes above which are known to be axially symmetric (C_{4v} or D_{4h}). While an interpretation is not complete, it appears that in some cases $A_\parallel$ and $A_\perp$ may be of the same order and second-order corrections may be very significant[52].

TABLE 3

ESR parameters[a] of hexacoordinate complexes of Nb^{IV}, $NbCl_4L_2$

L	$g_\parallel$	$g_\perp$	$\langle g \rangle$	$A_\parallel$	$A_\perp$	$\langle a \rangle$	$N_{\pi 2}^{2}$ [b]
DMF	1.9014	1.8953	1.8971	282.95	140.03	187.67	0.813
Dioxane	1.9065	1.8759	1.8861	277.0	138.85	184.91	0.786
DME	1.9069	1.8779	1.8876	277.78	135.62	183.00	0.809
HMPA	1.8991	1.8869	1.8910	289.49	149.20	195.99	0.798
second species	1.8869	(1.8869)	(1.8869)	301.51	(149.20)	(199.97)	0.867
THF	1.9131	1.8943	1.9006 1.8920	270.8	122.3	171.8 177.1	0.845
DMA	1.8988	1.8969	1.8975	285.51	141.51	189.51	0.820
DEF	1.8954	1.8990	1.8978	282.46	139.14	186.91	0.816
$NbOCl_5^{3-}$	1.9215			294.4			0.95
$NbOCl_4(H_2O)^{2-}$	1.9165	1.8833	1.8943	277.0	130.6	179.4	0.83
$NbOCl_4(HOC_2H_5)^{2-}$	1.9194	1.8946	1.9029	269.3	131.8	177.6	

[a] ESR splitting parameters given in gauss.

[b] $N_{\pi 2}^{2}$ is the normalization constant for the ground-state molecular orbital $B_2>^* = N_{\pi 2}(dxy - \lambda_{\pi 2}\phi_\pi)$ and would be equal to 1 if the MO were ionic or equal to 0.5 if the MO were perfectly covalent.

C. TANTALUM

As in the case of niobium, tantalum in its tetravalent state has only recently been studied. The compounds formed are usually air- and moisture-sensitive, and since the tantalum pentahalides are not easily reduced, not many Ta^{IV} compounds have been prepared.

This section will tabulate these compounds as well as discuss some of their properties, comparing them, in many cases, with niobium(IV).

(i) Tetrahalides

$TaCl_4$, $TaBr_4$ and TaI_4 have been obtained by a variety of methods[1,3]. Since the tantalum pentahalides are more difficult to reduce than those of Nb, and NbF_5 is the least easily reduced of the niobium halides, it is understandable that the preparation of TaF_4 is proving to be a problem and the compound has not yet been obtained.

The methods of preparation of the tantalum tetrahalides have been adequately reviewed[53–55]. The tantalum tetrahalides are diamagnetic, dark crystals. $TaCl_4$ and $TaBr_4$ are isomorphic with corresponding niobium halides and have been classified as an orthorhombic unit cell with four TaX_4 units per unit cell[5]. Some controversy exists as to the assignment of the basic unit cell.

TaI_4 appears to exist in two different forms, depending on how it is prepared, and neither is indexed on the same basis as NbI_4. One form exists when TaI_4 is prepared by reducing TaI_5 vapor at high temperature by aluminum, and the other comes about when the TaI_4(pyridine)$_2$ complex is thermally decomposed[6].

(ii) Hexahalotantalates

$TaCl_6^{2-}$ has been prepared with Cs (ref. 56), K (ref. 57) and Rb (ref. 58) as cations. It is thermally stable. K_2TaCl_6 and Rb_2TaCl_6 are reported to be tetragonal, while Cs_2TaCl_6 is a cubic salt of the K_2PtCl_6 type.

(iii) Oxyhalides

Some oxyhalides of tantalum(IV) have been obtained. These include $TaOCl_2$ and $TaOI_2$. Not much information is available for $TaOI_2$, and $TaOCl_2$ is known to be quite stable, diamagnetic, and is assumed to involve Ta—Ta bonding.

(iv) Tantalum complexes

A number of Ta^{IV} complexes has been obtained by reducing the tantalum pentahalide or by reacting the tetrahalide with the ligands. These, as well as the compounds previously mentioned, are listed in Table 4.

The spin-only value of the magnetic moment of tantalum(IV) complexes is expected to be 1.73 B.M., but most complexes exhibit values considerably below this. Lower values are probably again due to large spin—orbit coupling constants[5] for Ta^{IV}.

$BaTaS_3$ is in the form of black crystals which were found to consist of hexagonal close-packing of BaS_3 layers with Ta cations in one fourth of the octahedral holes. The point group assigned[60] is D_{3h} (Fig. 3).

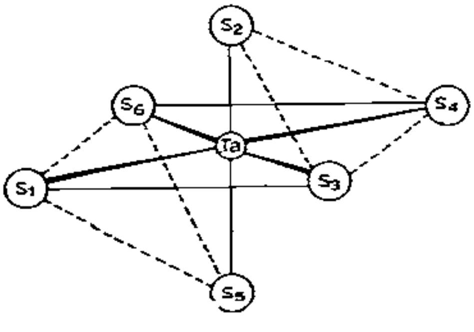


Fig. 3. Structure of $BaTaS_3$. Dashed lines indicate BaS_3 layers.

Many of the complexes of Ta^{IV} have been found to be of six-coordinate octahedral

TABLE 4

Tantalum compounds

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
A. Tantalum tetrahalides					
$TaCl_4$	Brown-black		$TaCl_5$, Ta, 280–630°C		1, 3, 6
$TaBr_4$	Brown-black		$TaBr_5$, Al, 250–500°C, 7 days		1, 3, 6
TaI_4	Brown-black		TaI_5, Al, 350–500°C, 7 days		1, 3, 6
B. Hexahalotantalate complexes					
K_2TaCl_6	Dark lilac		Fusion of KCl and $TaCl_4$, 20–25 h		57
Rb_2TaCl_6	Dark lilac		Fusion of RbCl and $TaCl_4$, 20–25 h		57, 58
Cs_2TaCl_6	Dark lilac		P, $CsTaCl_6$, CsCl, 20–25 h		56, 57
C. Tantalum with nitrogen ligands					
$TaCl_4$·phen	Dark blue, grey-green	0.95 0.67	$TaCl_4$ and phen, 10 days, reflux	IR: 325s, 288m (Ta–Cl), 427w, 275sh (ligand), ~380sh, 255w, sh	10, 19
$TaBr_4$·phen	Dark blue-green	0.91	$TaBr_4$ and phen, 5 days, reflux	IR: 265m, 255m, ~225sh, 214s (Ta–Br), 429mw, 285sh (ligand), 390mw, 325m	10, 19
$TaCl_4(py)_2$	Purple	1.31 0.69	$TaCl_5$ and pyridine, 5 weeks, 50°C	IR: 318sh?, 310s (Ta–Cl) IR: 434m, 638m, 683s, 757s, 870w, 950w, 1015s, 1032m, 1052s, 1069s, 1168w, b, 1219s, 1613s	5, 10, 19

$TaBr_4(py)_2$	Chocolate	1.02 0.43	$TaBr_5$ and pyridine, 8 months, 20°C	IR: ~ 215sh, 208s (Ta–Br), 432w (ligand) IR: 433m, 640m, 685s, 757s, 860m, 944m, 1010s, 1027m, 1049s, 1066s, 1090w, 1162m, 1217s, 1242w, 1570w, 1607s, 1638w	5, 10, 19
$TaCl_4(CH_3CN)_2$	Dark brown	0.45	$TaCl_4$ in acetonitrile, 2 weeks	IR: 2315m, 2292s, ~ 1600b, sh, 1360m, ~ 1310b, sh, 1258w, 1211w, ~ 1092m, b, 1025ms, 949w, ~ 850sh, vb, ~ 800m, 760ms, 657w, 526mw, 475w	10
$TaBr_4(CH_3CN)_2$	Dark red-brown	0.46	$TaBr_4$ and acetonitrile, 2 weeks	IR: 2305sh, 2288ms, ~ 1640mw, b, 1510m, 1360m, 1309mw, 1264w, 1098w, 1021ms, 951w, 865sh, ~ 830sh, ~ 800m, 740m, 672w, ~ 530w, ~ 455m	10, 19
$TaCl_4(C_2H_5CN)_2$		0.45	$TaCl_4$, excess ligand, 16 h, 25°C	IR: 457mw, b, 393sh, 334sh, 324sh, 312s, 284sh IR: 2261ms, 1597m, 1411ms, 1280w, 1089w, 975s, 953s, 894mw, 678m, 584w UV–vis.: (solid): 37.2, 28.5sh, 23.4b, 16.2sh, 10.7sh; (C_2H_5CN): 37.9sh, 34.5sh, 10.1sh, 26.5sh, 18.0sh, 15.2sh, 13.3sh, 12.7sh	23
$TaBr_4(C_2H_5CN)_2$		0.52	$TaBr_4$ and ligand, 3 days, reflux	IR: 456w, b, 383w, b, 307w, b, 256sh, 246sh, 230sh, 215s IR: 2262ms, 1595m, 1410ms, 1274w, 1090w, 971sh, 952s, 676m UV–vis.: 36.5, 34.8sh, 29.6, 24.4, 21.6sh, 19.2sh, 10.7sh; (C_2H_5CN): 33.3 (35,000), 32.3sh, 32.1sh, 26.0 (4000), 20.0sh, 18.1sh, 15.2sh, 12.9sh	23
$TaCl_4$·bipy	Dark green	0.81	$TaCl_4$ and bipy, 6 days, reflux	IR: ~ 335sh, 316s, 290ms, 248w, b (Ta–Cl), 422vw, 372sh, 357sh (ligand), 455vw (unassigned)	10, 19
$TaBr_4$·bipy	Dark green	0.89	$TaBr_4$ and bipy, reflux, several days	IR: 265sh, 248sh, 220s, b (Ta–Br), 419m, 364s (ligand), 325ms	10
$TaCl_4$·γ-picoline	Dark brown	0.77	$TaCl_5$ and picoline, 6 days, 20°C		19

TABLE 4 (continued)

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
$TaBr_4 \cdot \gamma$-picoline	Dark brown	0.77	$TaBr_5$ and picoline, 5 days, reflux		19
$Ta(bzbz)_4$	Yellow	0.53	$TaCl_4$, triethylamine, dibenzoylmethane, reflux, 2 min	UV–vis.: 44sh ($\pi_3 \rightarrow \pi_5$?), 38.2 (aromatic), 26.5 ($\pi_3 \rightarrow \pi_4$), 13.5 ($\pi_3 \rightarrow d$ and $d \rightarrow \pi_4$); (toluene): 28.25 (4.45) ($\pi_3 \rightarrow \pi_4$), 16.1 (3.02) ($\pi_3 \rightarrow d$ and $d \rightarrow \pi_4$); (dioxane): 37.8 (aromatic), 28.55 ($\pi_3 \rightarrow \pi_4$), 16.0 ($\pi_3 \rightarrow d$ and $d \rightarrow \pi_4$)	39
D. Tantalum with sulfur ligands					
$TaCl_4[S(CH_3)_2]_2$	Dark green	0.85	$TaCl_4$ and ligand, several days	IR: 345m, b, 313s (Ta–Cl), 379sh, w, ~ 290sh (unassigned) UV–vis.: (solid): 14.0 ($d \leftrightarrow d$), 28.4b, ~ 33.0sh, 37.0 ($\pi \rightarrow$ Ta); ($S(CH_3)_2$): 15.0, 21.2 ($d \leftrightarrow d$), 29.9sh ($\pi \rightarrow$ Ta)	34
$TaBr_4[S(CH_3)_2]_2$	Red-brown	0.80	$TaBr_4$ and ligand, several days	IR: ~ 245–210b, (Ta-Br), 333vw, ~ 316vw, b, 292w (unassigned) UV–vis.: (solid): ~ 10.2sh, 13.6, 20.0sh ($d \leftrightarrow d$), 25.0, ~ 27.5sh, 35.5 ($\pi \rightarrow$ Ta). ($S(CH_3)_2$): ~ 13.5sh, 14.1 (36), 20.0 (790) ($d \leftrightarrow d$), ~ 31.5sh, 34.4 (~ 15,000) ($\pi \rightarrow$ Ta)	34
$TaCl_4(C_4H_8S)_2$	Dark green	0.97	$TaCl_4$ with tetrahydrothiophene, several days	IR: 325s, vb (Ta–Cl), 393w, 240m (unassigned) UV–vis.: (solid): 14.0 ($d \leftrightarrow d$), 30.6, 36.8 ($\pi \rightarrow$ Ta); (C_4H_8S/C_6H_6): 14.9 (40), 20.6 (400?) ($d \leftrightarrow d$), 29.4sh, 32.8sh ($\pi \rightarrow$ Ta)	31
$TaBr_4(C_4H_8S)_2$	Maroon red	0.97	$TaBr_4$ with ligand, several days	IR: ~ 250sh, 230s, 213s (Ta–Br), ~ 330w, 285w (unassigned) UV–vis.: (solid): 14.6, 18.9 ($d \leftrightarrow d$), 26.4, ~ 30.0sh, 36.8 ($\pi \rightarrow$ Ta); (C_4H_8S/C_6H_6): 13.4 (~ 40), 19.5 (~ 800) ($d \leftrightarrow d$), 29.0sh, 32.3sh ($\pi \rightarrow$ Ta)	34

$BaTaS_3$	Black		BaS, Ta, S, 2 weeks at 600°C and 1 week at 1000°C	29, 60
TaS_2		0.57	TaO_2, CS_2	29
E. Tantalum with oxygen ligands				
TaO_2			Ta_2O_5, C, 1700°C	29
$TaOCl_2$			$TaCl_5$, Ta, Ta_2O_5, temperature gradient, 500–400°C	59
$TaOI_2$				3

geometry. The geometry of some of the tantalum compounds with nitrogen-containing ligands has been predicted[10], as well as that of those with sulfur-containing ligands[34], from the infrared spectra of the complexes.

D. ZIRCONIUM

The chemistry of zirconium and hafnium closely resemble one another and problems are encountered in their separation. Reduction to an oxidation state of less than four is difficult and few Zr^{3+} and Hf^{3+} compounds have been prepared. Zirconium compounds are listed in Table 5.

(i) Trihalides

The zirconium trichlorides, tribromides, and triiodides have been prepared in a variety of ways, many of which have been previously reviewed[61]. The zirconium tetraiodides are most easily reduced, followed by the bromides and chlorides[62]. When aluminum is used as the reducing agent, the product is contaminated with the oxides and halides of the aluminum and zirconium metal[63,64]. With zirconium metal as the reducing agent, products with purities of 99.2% have been obtained[65]. Many preparations based on reduction by Zr metal have been found, with the temperature, pressure, form of the Zr metal, and reaction time varying[62,65]. Zr will preferentially reduce its own halides. These methods also allow a separation of zirconium and hafnium.

Zirconium trifluoride has been prepared[66] from zirconium hydride in a H_2—HF mixture at 750°C. Zirconium tetrafluoride has not been reduced successfully by Zr metal. These reduction reactions have been studied in detail[67,68].

Zirconium trihalides are dark moisture-sensitive solids. The structures of the trihalides have been studied by X-ray powder diffraction and are found to consist of distorted hexagonal close packing of the halogen atoms. Infinite chains along an axis formed by MX_6 octahedra are joined at opposite faces and the metal atoms are regularly spaced midway between the halogen atoms[69–71]. The point group is D_{3d}. There are nine Zr orbitals available for bonding: $2A_{1g}$ (s, d_{z^2}), A_{2u} (p_z), $2E_g$ ($d_{x^2-y^2}$), d_{xy}, and d_{xz}, d_{yz} pairs, and E_u (p_x, p_y pair). Six bonds are formed when these combine under a trigonal ligand field with the corresponding symmetry orbitals of the halogen. After σ bonding, there are three orbitals left on each Zr available for metal—metal interaction with the remaining electron per metal atom. These consist of a σ-type metal orbital of A_{1g} symmetry along the chain axis, and two other degenerate orbitals of E_g symmetry. These orbitals and higher energy Zr atomic orbitals can interact with the corresponding orbitals of the neighboring metal atoms in the chain to give an appropriate molecular orbital[69].

The trihalides will undergo disproportionation, e.g. ZrI_3 will disproportionate[72,73] at 300–480°C, viz.

$$2\,ZrI_3 \rightarrow ZrI_2 + ZrI_4 \tag{1}$$

TABLE 5

Zirconium compounds

Complex	Color	μ	Preparation	Spectral features	Ref.
A. Zirconium trihalides					
$ZrCl_3$	Blue-black, yellow-green	0.4	$ZrCl_4$ reduced with Zr, Al, or H, 250°C, 6–7 days	IR: 446b, 333s, 267m, 218m UV–vis.: 17.3s, 21.0sh	1, 61, 62, 69, 70, 86–88
$ZrBr_3$	Light blue brown-black	0.4	$ZrBr_4$ reduced with Zr, Al, or H, 250°C, 6–7 days	IR: 443b, 273m, 246s UV–vis.: 16.2	1, 61, 62, 69, 75, 86, 87, 93
ZrI_3	Green-black, black	0.4	ZrI_4 reduced with Zr, Al, or H, 275°C, 6–7 days		1, 61, 62, 69, 73, 78, 80, 86, 87
ZrF_3	Bluish-gray	1.73	ZrH with H_2–HF, 750°C		66
K_2ZrF_3	White				95
B. Zirconium with nitrogen ligands					
$ZrCl_3(py)_2$	Chocolate	1.29	$ZrCl_3$ and py, shaken 3–5 days with CH_3CN	IR: 418s, 293b, 270sh UV–vis.: (solid): 27.6b, 33.9m, 37.6m, 44.7s; (CH_3CN): 13.25sh (12), 29.2sh (1800), 31.3 (1900), 39.4b (50,000)	1, 80, 81
$ZrBr_3(py)_2$	Red-brown	1.24	$ZrBr_3$ and py, shaken 3–5 days with CH_3CN	IR: 417s, 382w, 220b UV–vis.: (solid): 25.6b, 30.0sh, 37.6m, 44.8s; (CH_3CN): 13.0sh (6), 28.25sh (1500), 40.0b (50,000)	1, 80, 81
$ZrI_3(py)_2$	Yellow	1.16	ZrI_3 and py, shaken 3–5 days with CH_3CN	IR: 472b, 417s, 320s UV–vis.: (solid): 13.4sh, w, 24.2sh, 27.5m, 36.8sh, 45.0s; (CH_3CN): 28.6 (1400), 34.3 (1500), 39.4b (50,000)	80, 81

TABLE 5 (continued)

Complex	*Color*	μ	*Preparation*	*Spectral features*	*Ref.*
$2ZrCl_3 \cdot 5CH_3CN$	Red-brown	0.46	$ZrCl_3$ and ligand, 3–5 days	IR: 440b, 294s UV–vis.: (solid): 15.5w, 22.0sh, 29.5b, 37.5sh, 46.3s; (CH_3CN): 15.4 (13), 21.9 (220), 31.1 (1300), 36.8b, sh (1800), 46.6 (3000)	1, 80, 81
$2ZrBr_3 \cdot 5CH_3CN$	Brown	0.29	$ZrBr_3$ and ligand, shaken 3–5 days	IR: 461b, 395s, 296w, 223b UV–vis.: (solid): 12.4sh, 27.6b, 37.2b, sh, 44.8s; (CH_3CN): 38.8 (2000), 40.9 (2200)	1, 61
$2ZrI_3^{5-}(CH_3CN)_5$	Yellow-brown	1.10	ZrI_3 and ligand, shaken 3–5 days	IR: 459b, 395, 278 UV–vis.: (solid): 14.5sh, w, 21.4sh, w, 31.5b, 37.9sh, 45.5s; (CH_3CN): 14.3 (7), 20.0sh (200), 25.0 (800), 31.8sh, 35.5 (1100), 42.2 (1800)	1, 61
$2ZrCl_3^{3-}(bipy)_3$	Chocolate	1.35	$ZrCl_3$ and ligand, few hours	IR: 434sh, 416sh, 403sh, 347sh, 315sh, 292, 278sh UV–vis.: (solid): 14.5sh, w, 21.4sh, w, 31.5b, 37.9sh, 45.5s; (CH_3CN): 14.3 (7), 20.0sh (200), 25.0 (800), 31.7sh, 35.5 (1100), 42.2 (1800)	1, 61
$ZrBr_3(bipy)_3$	Dark brown	1.20	$ZrBr_3$ and ligand, few hours	UV–vis.: (solid): 14.0sh, w, 25.7sh, w, ~ 32.0b, 37.1sh, 45.3; (CH_3CN): 31.9, 35.5 (1700), 40.9 (1800), 42.2 (2200)	1, 61
$2ZrI_3(bipy)_3$	Yellow-green	0.96	ZrI_3 and ligand, few hours	UV–vis.: (solid): 12.8sh, w, 26.0b, 37.0sh, 45.1s; (CH_3CN): 13.2sh, w, 14.0sh, w, 31.6 (1510), 40.5 (1900)	1, 61
$2ZrCl_3(phen)_3$	Purple-brown	1.27	$ZrCl_3$ and ligand, few hours	IR: 410s, 360w, 302s, 265m, 252sh UV–vis.: (solid): 21.2sh, 24.4m, 29.4sh, 32.4sh, 36.3b, 45.0s; (CH_3CN): 25.4sh, 26.2 (500), 37.9 (1300), 43.4 (1800)	1, 80, 81

$ZrCl_3(py)_3$		0.39			79
ZrN	Dark gray-brown				82, 83
C. Zirconium with mixed ligands					
$(C_5H_5)_2ZrP\text{-}(C_2H_5)_2$	Brown-red		$(C_5H_5)_2ZrBr_2$, $LiP(C_2H_5)_2$, 280–282°C		84
$(C_5H_5)_2ZrP\text{-}(C_4H_9)_2$	Brown-red		$(C_5H_5)_2ZrBr_2$, $LiP(N\text{-}C_4H_9)_2$, 238–240°C		84
$(\pi\text{-}C_5H_5)_2Zr\text{-}(PPh_2)_2^-Na^+$			Reduction of zirconocene dichloride with alkali metal organophosphide	ESR: coupling constant 11.7 G, $\langle g \rangle$ 1.989	85

A close study of $ZrCl_3$, however, reveals a non-stoichiometric disproportionation. At 300°C

$$6\ ZrCl_3 \rightarrow 5\ ZrCl_{2.8} + ZrCl_4 \tag{2}$$

When the resulting $ZrCl_{2.8}$ is heated to 310–400°C

$$2\ ZrCl_{2.8} \rightarrow ZrCl_{1.6} + ZrCl_4 \tag{3}$$

The $ZrCl_{2.8}$ has the same X-ray powder pattern as $ZrCl_3$ and is explained in the following way. The loss of $ZrCl_4$ leaves gaps in the linear chains of the $ZrCl_6$ octahedra. The gaps form an ordered arrangement of a region of the lattice ion plane. Shearing takes place on the plane, resulting[74] in $ZrCl_{2.8}$. The disproportionation of $ZrCl_3$ has been studied thermodynamically, and at 700°C the equilibrium constant for the reaction in molten solutions of KCl is[94] 1.10×10^{-3}.

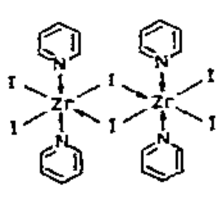
The low magnetic moments, ~ 0.4 B.M., of the zirconium trihalides is due either to strong antiferromagnetic interaction or to spin–orbit coupling.

A magnetically dilute sample of $ZrCl_3$ has a moment of 0.9 which supports an antiferromagnetic interaction mechanism[75].

ZrX_3L_3 compounds are six-coordinate adn distorted octahedra. In the reduced states of Zr, ligand field stabilization energy becomes important in determining the stereochemistry. Since the ligand field splittings are known to be large, the configurations giving the greatest ligand field stabilization energy are favored[76]. The diffuse reflectance spectra have been studied and it is assumed that the bands arise from $^2E_g \leftarrow {}^2T_{2g}$-transitions on Zr atoms[77] (note this assumes pure O_h geometry). The Δ (crystal field splitting energy) of Zr^{III} has been found to be 20% larger than for Ti^{III} and the increase is attributed to going from a $3d^n$ to a $4d^n$ compound[78].

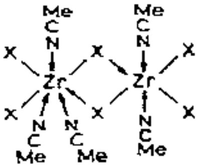
(ii) Complexes of Zr^{3+}

The complexes of Zr^{3+} formed with N-containing ligands are very air- and moisture-sensitive. Although the $ZrCl_3 \cdot 3py$ complex has a magnetic moment of 0.39 B.M., the EPR spectrum in pyridine suggests that a paramagnetic species of unknown character may be present. The $[ZrX_2 \cdot 2py]_2$ complexes show still lower magnetic moments than spin-only and are believed to be halogen-bridged dimers, viz.



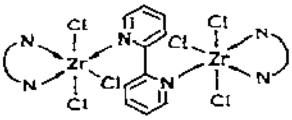
In CH_3CN, this species breaks down to form $[ZrI_2py(CH_3CN)_2]^+I^-$, which accounts for its high conductivity[80].

The $2ZrX_3 \cdot 5CH_3CN$ complexes involve interactions between neighboring metal atoms, either directly or through bridging, viz.



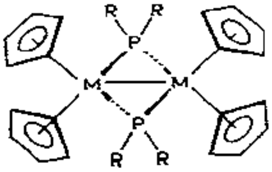
or through a Zr—$CH_3CN \rightarrow$ Zr linkage[80]. Since CH_3CN is not released when heated in vacuo to 100°C and the IR spectrum does not show the C≡N stretching frequency of a free ligand, the presence of uncoordinated CH_3CN trapped in the lattice seems unlikely[81].

The bipyridyl complexes, $2ZrX_3 \cdot 3(bipy)$ are also postulated to have a dimeric type structure, viz.



The bonding in the Zr nitrides appears to be of a mixed type, largely ionic with some metallic bonding. The cation sub-lattice consists of Zr^{3+} ions with the equilibrium $N \rightleftharpoons N^{3-} + 3\ e^-$ occurring in the anionic sub-lattice. The nitrides show high electrical conductivity and metallic luster, which can be explained in terms of the partial metallic character of the bonding[82,83].

Compounds of the type $(C_5H_5)_2ZrPR_2$ have been prepared; where R is C_2H_5 or n-C_4H_9, a dimeric structure has been proposed[84], viz.



When zirconocene dichloride is reduced with $NaPPh_2$, the ESR spectrum indicates that anion radicals of the type $[(\pi\text{-}C_5H_5)_2Zr^{III}(PPh_2)_2]^-$ may be formed[85].

E. HAFNIUM

The chemistry of hafnium in the trivalent oxidation state has not been explored to a great extent. The hafnium tetrahalides are difficult to reduce, and the trihalides, when formed, tend to be unstable, disproportionating and hydrolyzing easily. Hafnium compounds are listed in Table 6.

(i) Trihalides

Hafnium trichloride has been prepared by reacting $HfCl_4$ with Hf metal as reducing agent at high temperatures[62,89]. $HfBr_3$ has been prepared in a similar manner, as well as by reacting $HfBr_4$ with Al. The reaction is carried out[90] in a spherical bomb tube at 470°C, or in a two-zone tube at 600–650°C. HfI_3 has been prepared by the reduction of HfI_4 with Hf (refs. 62, 91) and also[78] by reacting HfI_4 with aluminum at 350–385°C.

The trifluoride has been prepared[92] by the reaction

$$HfN + 3\ Hf \rightarrow HfF_3 + NH_3 \qquad (4)$$

However, the HfF_3 reacts immediately.

$$HfF_3 + HF \rightarrow HfF_4 + 1/2\ H_2 \qquad (5)$$

A satisfactory preparation of HfF_3 has not been found. The tetraiodides are the easiest to reduce, followed by the tetrabromide and then the tetrachloride.

The hafnium trihalides, like their zirconium counterparts, are dark solids. Hafnium triiodide is reported to exist in both a green and a black form, depending on the preparation temperature, but may depend only on particle size[91]. The structure of HfI_3 is isomorphous with the trihalides of zirconium. X-ray diffraction shows hexagonal close-packed halogen atoms consisting of infinite chains formed by HfI_6 octahedra joined at opposite faces with the metal atoms regularly spaced midway between the halogen atoms[69]. The trihalides disproportionate to form the dihalides and tetrahalides[62,90]. This disproportionation often produces problems in the preparation of the trihalides.

Little information is available on the magnetic properties of the hafnium trihalides. The magnetic moment reported for HfI_3, in one case, is in excess of spin-only value, and is thought to be due to strong ferromagnetic coupling[78]. In another study, however, μ is reported[91] to be 0.62 B.M.

(ii) Other hafnium(III) compounds

HfN has been prepared[82,83] in which nearly all of the nitrogen can be converted to NH_3. The bonding is mainly ionic, but to some extent metallic. The cation sub-lattice consists entirely of Hf^{3+} ions. In the anionic sub-lattice, the equilibrium $N \rightleftharpoons N^{3-} + 3\ e^-$ occurs and accounts for the metallic properties which HfN displays.

The only other compound of Hf^{3+} so far reported is the $HfCl_3 \cdot 4(py)$ complex which was found to be diamagnetic. However, the EPR spectrum[79] indicates the existence of a

TABLE 6

Hafnium compounds

Complex	*Color*	*μ*	*Preparation*	*Spectral features*	*Ref.*
A. Hafnium trihalides					
$HfCl_3$	Blue-black, brown		Reduction of $HfCl_4$ with Al or Hf		62, 89
$HfBr_3$	Blue-black, brown		Reduction of $HfBr_4$ with Al or Hf	UV–vis.: 13.8, 24.8	62, 90, 93
HfI_3	Green-black, red-brown	0.62	Reduction of HfI_4 with Al or Hf, 500–550°C, few days	UV–vis.: 38.5, 29.0, 14.3–11	62, 78, 91
HfF_3			HfN and HF		92
B. Other hafnium compounds					
HfN					82, 83
$HfCl_3\cdot(py)_4$					79

paramagnetic species "of an unknown character".

REFERENCES

1 J.H. Canterford and R. Colton, *Halides of the Second and Third Row Transitions Metals*, Wiley-Interscience, London, 1968.
2 V. Gutmann (Ed.), *Halogen Chemistry*, Academic Press, London, 1967, pp. 123, 178.
3 F. Fairbrother, *The Chemistry of Niobium and Tantalum*, Elsevier, Amsterdam, 1967, pp. 122–133.
4 H. Schafer, C. Groser and L. Bayer, *Z. Anorg. Allg. Chem.*, 265 (1951) 258.
5 R.E. McCarley and B.A. Torp, *Inorg. Chem.*, 2 (1963) 540.
6 R.E. McCarley and J.C. Boatman, *Inorg. Chem.*, 2 (1963) 547.
7 J.D. Corbett and P.W. Seabaugh, *J. Inorg. Nucl. Chem.*, 6 (1958) 207.
8 E.K. Smirnova and I.V. Vasilhova, *Vestn. Leningrad. Univ., Fiz., Khim.*, 20 (1965) 161.
9 I.S. Morozov and N.P. Lipatova, *Zh. Neorg. Khim.*, 11 (1966) 550.
10 G.W. Fowles, D.J. Tidmarsh and R.A. Walton, *Inorg. Chem* , 8 (1969) 631.
11 W.D. Benzinger, *Diss. Abstr. B.*, 28 (1968) 4056.
12 G.F. Knox and T.M. Brown, *Inorg. Chem.*, 8 (1969) 1401.
13 H. Schaefer and R. Gerken, *Z. Anorg. Allg. Chem.*, 317 (1962) 105.
14 W. Ruedorff and D. Krug. *Z. Anorg. Allg. Chem.*, 329 (1964) 211.
15 I.F. Gainullin, N.S. Garifyanov and B.M. Kozyrev, *Dokl. Akad. Nauk SSSR*, 180 (1968) 858.
16 D.J. Machin and J.F. Sullivan, *J. Less-Common Metals*, 19 (1969) 405.
17 H. Schafer and H.G. Schnering, *Angew. Chem.*, 76 (1964) 833.
18 B.G. Korshunov and V.V. Safonov, *Russ. J. Inorg. Chem.*, 6 (1961) 385.
19 M. Allbutt, K. Feenan and G.W.A. Fowles, *J. Less-Common Metals*, 6 (1964) 299.
20 C. Djordjevic and V. Katovic, *Chem. Commun.*, (1966) 224.
21 F.E. Dickson, R.A. Hayden and W.F. Fateley, *Spectrochim. Acta, Part A*, 25 (1969) 1875.
22 T.A. Doughtery, *U.S. At. Energy Comm.*, 21 (1967) 25817.
23 G.W.A. Fowles and K.F. Gadd, *J. Chem. Soc. A.*, (1970) 2232.
24 D.C. Bradley and I.M. Thomas, *Can. J. Chem.*, 40 (1962) 449.
25 D.C. Bradley and M.H. Chisholm, *J. Chem. Soc. A.*, (1971) 1511.
26 D.C. Bradley and M.H. Gitlitz, *J. Chem. Soc. A.*, (1969) 980.
27 D.J. Machin and J.F. Sullivan, *J. Less-Common Metals*, 19 (1969) 413.
28 T.M. Brown and G.S. Newton, *Inorg. Chem.*, 5 (1966) 1117.
29 E.I. Krylov, *Zh. Neorg. Khim.*, 3 (1958) 1487.
30 J.N. Smith and T.M. Brown, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 441.
31 D.C. Bradley and M.H. Gitlitz, *J. Chem. Soc. A.*, (1969) 1152.
32 D.C. Bradley and M.H. Gitlitz, *Chem. Commun.*, 13 (1965) 289.
33 V.H. Schafer and W. Beckmann, *Z. Anorg. Allg. Chem.*, 347 (1966) 255.
34 G.W. Fowles, D.J. Tidmarsh and R.A. Walton, *J. Inorg. Nucl. Chem.*, 31 (1969) 2373.
35 J.B. Hamilton, *Diss. Abstr. B.*, 29 (1969) 3247.
36 J.B. Hamilton and R.E. McCarley, *Inorg. Chem.*, 9 (1970) 1333.
37 J.B. Hamilton and R.E. McCarley, *Inorg. Chem.*, 9 (1970) 1339.
38 R.L. Deutscher and D.L. Kepert, *Chem. Commun.*, 3 (1969) 121.
39 R.L. Deutscher and D.L. Kepert, *Inorg. Chim. Acta*, 4 (2970) 645.
40 R.A.D. Wentworth and C.H. Brubaker, Jr., *Inorg. Chem.*, 3 (1964) 47.
41 R.A.D. Wentworth and C.H. Brubaker, Jr., *Inorg. Chem.*, 2 (1963) 551.
42 P.G. Rasmussen, H.A. Kuska and C.H. Brubaker, Jr., *Inorg. Chem.*, 4 (1965) 343.
43 P.M. Treichel and G.P. Werber, *J. Organometal Chem.*, 12 (1968) 479.
44 F. Kadijk and F. Jellinik, *J. Less-Common Metals*, 23 (1971) 437.
45 R.J.H. Clark, D.L. Kepert, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, (1965) 2865.
46 R.A.D. Wentworth and C.H. Brubaker, Jr., *Inorg. Chem.*, 1 (1962) 971.
47 C. Djordjevic and V. Katovic, *J. Chem. Soc. A.*, (1970) 3382.
48 P.W. Seabaugh and J.D. Corbett, *Inorg. Chem.*, 4 (1965) 176.

49 R.D. Bereman and D.P. Johnson, submitted for publication.
50 R.D. Bereman and D.P. Johnson, *J. Inorg. Nucl. Chem.*, 34 (1972) 679.
51 R.D. Bereman and D.P. Johnson, *J. Inorg. Nucl. Chem.*, in press.
52 R.D. Bereman and D.P. Johnson, unpublished results.
53 H. Schafer, H. Scholtz and R. Gerken, *Z. Anorg. Allg. Chem.*, 331 (1964) 154.
54 H. Schafer and L. Grau, *Z. Anorg. Allg. Chem.*, 275 (1954) 198.
55 H. Schafer, R. Gerken and H. Scholtz, *Z. Anorg. Allg. Chem.*, 335 (1965) 96.
56 S.M. Horner, F.N. Collier, Jr. and S.Y. Tyree, Jr., *J. Less-Common Metals*, 13 (1967) 85.
57 E.K. Smirnova and I.V. Vasil'kova, *Zh. Neorg. Khim.*, 12 (1967) 566.
58 V.V. Safonov, B.G. Korshunov, Z.N. Shevtsova and L.G. Shadrova, *Russ. J. Inorg. Chem.*, 9 (1964) 763.
59 H. Schafer, E. Sibbing and R. Gerken, *Z. Anorg. Allg. Chem.*, 307 (1961) 163.
60 R.A. Gardner, M. Vlasse and A. Wold, *Inorg. Chem.*, 8 (1969) 2784.
61 E.M. Larsen, *Advan. Inorg. Chem. Radiochem.*, 13 (1970) 1.
62 E.M. Larsen and J.J. Leddy, *J. Amer. Chem. Soc.*, 78 (1956) 5983.
63 O. Ruff and R. Wallstein, *Z. Anorg. Allg. Chem.*, 128 (1923) 96.
64 R.C. Young, *J. Amer. Chem. Soc.*, 53 (1931) 2148.
65 B. Swaroop and S.N. Flengas, *Can. J. Chem.*, 42 (1964) 1495.
66 V.P. Ehrlich and G. Kaupa, *Z. Anorg. Allg. Chem.*, 333 (1964) 209.
67 L.I. Nekrasov, N.J. Kobozev and Z. Braun, *Zh. Fiz. Khim.*, 44 (1970) 2398.
68 P. Ehrlich, F. Ploger and E. Koch, *Z. Anorg. Allg. Chem.*, 333 (1964) 209.
69 L.F. Dahl, T. Chiang, P.W. Seabaugh and E.M. Larsen, *Inorg. Chem.*, 3 (1964) 1236.
70 J.A. Watts, *Inorg. Chem.*, 5 (1966) 281.
71 F.R. Sale and R.A.J. Shelton, *J. Less-Common Metals*, 9 (1965) 64.
72 F.R. Sale, *J. Less-Common Metals*, 19 (1969) 53.
73 F.R. Sale and R.A.J. Shelton, *J. Less-Common Metals*, 9 (1965) 60.
74 D.B. Copeley and R.A.J. Shelton, *J. Less-Common Metals*, 20 (1970) 359.
75 J. Lewis, D.J. Machin, I.E. Newnham and R.S. Nyholm, *J. Chem. Soc., London*, (1962) 2036.
76 R. Colton and J.H. Canterford, *Aust. J. Chem.*, 21 (1968) 9.
77 R.J.H. Clark, *J. Chem. Soc., London*, (1964) 417.
78 W.A. Baker, Jr. and A.R. Janus, *J. Inorg. Nucl. Chem.*, 26 (1964) 2087.
79 D.A. Wasmund, *Diss. Abstr. B.*, 30 (1970) 4549.
80 G.W.A. Fowles and G.R. Willey, *J. Chem. Soc. A.*, (1968) 1435.
81 G.W.A. Fowles, B.J. Russ and G.R. Willey, *Chem. Commun*, (1967) 646.
82 M.E. Straumanis, *Anisotropy Single Cryst.: Refract Compounds, Proc. Int. Symp., Dayton, Ohio*, 1 (1967) 121.
83 M.E. Straumanis and C.A. Faunce, *Z. Anorg. Allg. Chem.*, 353 (1967) 329.
84 K. Issleib and H. Hackert, *Z. Naturforsh. B.*, 21b (1966) 519.
85 J.G. Kenworthy, J. Myatt and P.F. Todd, *Chem. Commun.*, (1969) 263.
86 J.E. Newnham and J.A. Watts, *J. Amer. Chem. Soc.*, 28 (1960) 2113.
87 E.M. Larsen, F. Gil-Arnao, J.W. Moyer and M.J. Camp, *Chem. Commun.*, (1970) 281.
88 S.I. Troyanov, V.I. Tsirel'nikov and L.N. Komissarova, *Izv. Vyssh. Ucheb., Zaved., Khim. Khim. Tekhnol.*, 12 (1969) 851.
89 S.I. Troyanov, A.S. Ismailovich, V.I. Tsirel'nikov, L.N. Komissarova, *Russ. J. Inorg. Chem.*, 14 (1969) 452.
90 W.C. Schumb and C.K. Morehouse, *J. Amer. Chem. Soc.*, 69 (1947) 2696.
91 A.W. Struss and J.D. Corbett, *Inorg. Chem.*, 8 (1969) 227.
92 J. Straumanis, *Inorg. Chem.*, 5 (1966) 2027.
93 H.L. Schafer and H.W. Wille, *Z. Anorg. Allg. Chem.*, 351 (1967) 279.
94 B. Swaroop and S.N. Flengas, *Can. J. Chem.*, 44 (1966) 199.
95 P. Ehrlich, *Angew. Chem.*, 64 (1952) 617.