

1060. Nitrate-complexes of Groups IVA and IVB.

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The hexanitrate-complexes $\text{Cs}_2\text{Sn}(\text{NO}_3)_6$, $(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$, and $(\text{NMe}_4)_2\text{-Hf}(\text{NO}_3)_6$ have been prepared by the action of dinitrogen tetroxide in methyl cyanide or of liquid dinitrogen pentoxide on the corresponding hexachloro-complexes. Attempts to prepare similar complexes of Ge(IV), Pb(IV), and Ti(IV) were unsuccessful.

In the present Paper we shall use the term nitrate to designate a compound of the type $\text{Zr}(\text{NO}_3)_4$, and reserve the term nitrate-complex for compounds of the type $(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$. Our terminology therefore is different from that suggested by Hardy and Field^{1,2} who use the term nitrate-complex for simple covalent nitrates such as $\text{Pd}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$. The tetranitrates of titanium,³ zirconium,² and hafnium² [as the adduct $\text{Hf}(\text{NO}_3)_4 \cdot \text{N}_2\text{O}_5$] have recently been characterised, but the corresponding nitrate-complexes of the type $\text{M}^{\text{IV}}\text{M}^{\text{IV}}(\text{NO}_3)_6$ have not been described previously. Similarly, nitrate-complexes of the quadrivalent Group IVB elements germanium, tin, and lead have not been reported, although tin tetranitrate has been prepared⁴ by reaction of the tetrachloride with chlorine nitrate, and methyltin(IV) nitrates are known.⁵ Current work⁶ on the preparation of nitrate-complexes of niobium(V), tantalum(V), and protactinium(V) [$\text{RM}^{\text{VO}}(\text{NO}_3)_4$] from the hexachloro-complexes suggested that an investigation of the Group IVA nitrate-complexes was worthwhile, especially since the known nitrates of these elements are readily obtained from the corresponding chlorides. In addition, we have tried to prepare germanium and lead tetranitrates. Since the preparative methods, reaction of $\text{Cs}_2\text{M}^{\text{IV}}\text{Cl}_6$ with liquid dinitrogen pentoxide or of $\text{R}_2\text{M}^{\text{IV}}\text{Cl}_6$ ($\text{R} = \text{NMe}_4^+$, NEt_4^+ , etc.) in anhydrous methyl cyanide with dinitrogen tetroxide, could easily yield mixtures, for example of CsNO_3 and $\text{M}^{\text{IV}}(\text{NO}_3)_4$, analytically indistinguishable from a nitrate-complex $\text{Cs}_2\text{M}^{\text{IV}}(\text{NO}_3)_6$, X-ray powder diffraction photographs and infrared spectra have been employed to ascertain whether the reaction products are genuine compounds.

A selection of the reactions investigated is listed in Table I. The transition-metal elements zirconium and hafnium form white, moisture-sensitive hexanitrate-complexes with tetramethylammonium as the cation, but zirconium does not do so with caesium, and titanium

TABLE I.

Reactions of chloro-complexes with N_2O_5 and N_2O_4 .

Complex	Reaction*	Products	Identification
Cs_2GeCl_6	A	CsNO_3 ; GeO_2	Analysis; infrared
$(\text{NEt}_4)_2\text{GeCl}_6$	B	NEt_4NO_3 ; GeO_2	Analysis
Cs_2SnCl_6	A	$\text{Cs}_2\text{Sn}(\text{NO}_3)_6$	Analysis; infrared; X-rays
Cs_2PbCl_6	A	CsNO_3 ; $\text{Pb}(\text{NO}_3)_2$	Analysis; infrared; X-rays
$(\text{QH})_2\text{PbCl}_6^\dagger$	B	—; $\text{Pb}(\text{NO}_3)_2$	Infrared; X-rays
$(\text{NMe}_4)_2\text{PbCl}_6$	A	$\text{Pb}(\text{NO}_3)_2?$	White Pb(II) ppt. with NH_4OH
Cs_2TiCl_6	A	CsNO_3 ; $\text{Ti}(\text{NO}_3)_4$	Infrared; X-rays
$(\text{NMe}_4)_2\text{TiCl}_6$	A; B	NMe_4NO_3 ; $\text{TiO}(\text{NO}_3)_2$	Analysis; infrared; X-rays
Cs_2ZrCl_6	A	CsNO_3 ; $\text{Zr}(\text{NO}_3)_4$	Analysis; infrared
$(\text{NMe}_4)_2\text{ZrCl}_6$	B	$(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$	Analysis; infrared; X-rays
$(\text{NMe}_4)_2\text{HfCl}_6$	B	$(\text{NMe}_4)_2\text{Hf}(\text{NO}_3)_6$	Analysis; infrared; X-rays

* A, Liquid N_2O_5 at room temperature; B, N_2O_4 in methyl cyanide at room temperature.

† QH = quinolinium.

¹ B. O. Field and C. J. Hardy, *Quart. Rev.* 1964, **18**, 361.

² B. O. Field and C. J. Hardy, *J.*, 1964, 4428.

³ B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 1962, 76; *J.*, 1963, 5278; M. Schmeisser, *Angew. Chem.*, 1955, **67**, 493.

⁴ M. Schmeisser and K. Bründle, *Angew. Chem.*, 1957, **69**, 781.

⁵ C. C. Addison, W. B. Simpson, and A. Walker, *J.*, 1964, 2360.

⁶ D. Brown, and P. J. Jones, unpublished results.

appears to form no stable complex. The hexanitrate-complexes are soluble in anhydrous methyl cyanide or nitromethane and are immediately decomposed by water. The different behaviour observed with the tetramethylammonium and caesium cations may be due to lattice-energy stabilisation of the complexes in the former owing to the difference in cation size (~ 2.1 Å and 1.69 Å, respectively, the former being calculated from C-N and C-H bond lengths in NMe_3 and CH_4 , respectively, ignoring a small correction due to H atom radius). Of the Group IVB elements, only tin(IV) forms a hexanitrate-complex, $\text{Cs}_2\text{Sn}(\text{NO}_3)_6$, which is a white, moisture-sensitive compound soluble in liquid dinitrogen pentoxide but insoluble in anhydrous methyl cyanide. The three complexes are thermally unstable, slowly evolving oxides of nitrogen at 150° [$\text{Cs}_2\text{Sn}(\text{NO}_3)_6$], 130° [$(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$], and 230° [$(\text{NMe}_4)_2\text{Hf}(\text{NO}_3)_6$]. The infrared spectral data are given in Table 2 in terms of assignments⁷ of the covalently-bonded nitrate-groups. In each, splitting of the symmetric (ν_1) and asymmetric (ν_4) stretching vibrations of covalent nitrate-groups is observed, and although

TABLE 2.
Infrared spectra of hexanitrate-complexes (cm.^{-1}).

	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5
$(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$	1600 } 1572 } vs 1544 }	1294 } 1280 } vs	1021 } 1010 } vs	803 } 794 } s	762s	731m
$(\text{NMe}_4)_2\text{Hf}(\text{NO}_3)_6$	1598 } 1572 } vs 1517 }	1288 } 1269 } vs	1021 } 1008 } vs 981 }	801sh } 795 } s	775sh } 769 } s	736m
$\text{Cs}_2\text{Sn}(\text{NO}_3)_6$	1561 } 1546 } vs 1534 }	1288 } 1270 } vs	970 } 949 } vs	792 } 784 } s 779 }	756 } 752 } s 742 }	701 } 681 } m

this is not well defined it is reproducible for different preparations and is therefore not considered to be due to instrumental aberrations. The separation of ν_4 and ν_1 ($250 \rightarrow 320$ cm.^{-1}) for the hexanitratozirconate(IV), which is likely to contain unidentate nitrate groups, is markedly less than the separation of the vibrations observed in this region ($292 \rightarrow 407$ cm.^{-1}) by Field and Hardy² for zirconium tetranitrate which, on the basis of the large separation of these vibrations, they suggest may contain bidentate nitrate-groups. However, the smaller separation in the former instance can equally well be explained by the increased number of anionic groups bonded to the Zr^{4+} in the hexanitrate-complex. The spectrum of caesium hexanitratostannate(IV) is dominated by an extremely intense broad band (ν_2) around 970 cm.^{-1} . The reason for the unusual appearance of this band is at present unknown. Ionic nitrate vibrations, ~ 1370 cm.^{-1} for CsNO_3 and ~ 1330 cm.^{-1} for NMe_4NO_3 , were absent from the infrared spectra of these three complexes but were observed in the spectra of the products from all other reactions. Samples were examined as mulls in hexachlorobutadiene to permit easier detection of the ionic nitrate vibrations in this region.

X-Ray powder diffraction reflections for tetramethylammonium hexanitratohafnate(IV) are listed in Table 3. The compound is obviously of low symmetry, and the data have not been interpreted. No reflections due to tetramethylammonium nitrate were observed on the

TABLE 3.
X-Ray powder diffraction data for $(\text{NMe}_4)_2\text{Hf}(\text{NO}_3)_6$.

$\text{Sin}^2\theta_{\text{obs}}$	I_{est}	$\text{Sin}^2\theta_{\text{obs}}$	I_{est}	$\text{Sin}^2\theta_{\text{obs}}$	I_{est}	$\text{Sin}^2\theta_{\text{obs}}$	I_{est}
0.0077	S	0.0238	S	0.0513	W-	0.1051	W+
0.0090	M(b)	0.0270	W-	0.0589	W	0.1081	W+(b)
0.0109	M	0.0292	W	0.0620	W-	0.1160	M-
0.0119	M(b)	0.0316	W+	0.0672	S-	0.1406	W-
0.0135	W-	0.0426	S	0.0769	S-	0.1483	M-
0.0148	M-	0.0446	M	0.0965	W-	0.1533	M-
0.0180	M	0.0475	M-	0.0999	M	0.1727	W+
0.0225	S-(b)	0.0568	M-	0.1031	W-	0.1974	W

⁷ B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J.*, 1957, 4222.

films obtained for this complex. Likewise, caesium nitrate reflections were absent from the powder patterns of caesium hexanitrostannate(IV) but such films were generally of poor quality and were therefore not measured.

In addition to the unsuccessful attempts to prepare quadrivalent lead nitrate-complexes listed in Table I, lead dioxide was observed to dissolve in liquid dinitrogen pentoxide at room temperature, but vacuum-evaporation of the resulting solution yielded only lead(II) nitrate. Tetraethylammonium hexachloroplumbate(IV) reacted in a similar manner to the tetramethylammonium complex, the resulting solid containing only bivalent lead. The apparent non-existence of nitrate-complexes of lead(IV) is not too surprising in view of the increasing stability of the dipositive state of Group IVB elements with increasing atomic number. The case of germanium(IV), however, is somewhat different in view of the numerous quadrivalent compounds known for this element. Reactions examined, but not listed in Table I, include germanium tetrachloride in carbon tetrachloride with dinitrogen pentoxide in which the germanium was rapidly and quantitatively precipitated as a white solid containing no nitrate. It may be that the lack of success with germanium(IV) is due to its acidic nature.

EXPERIMENTAL

The moisture-sensitive reaction products were handled in a dry atmosphere after isolation and vacuum-drying. X-Ray powder diffraction photographs of samples mounted in thin-walled quartz capillaries were taken with a 19-cm. Debye-Scherrer camera using filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54051 \text{ \AA}$). Infrared spectra of the solid samples as mulls in Nujol or hexachlorobutadiene, mounted between 1-mm. silver chloride plates, were measured in the 2–15 μ region with a Hilger H800 spectrometer using a rock-salt prism. The complexes did not react with the mulling agents.

Materials.—Titanium, zirconium (British Drug Houses), and germanium (Johnson Matthey) tetrachlorides were purchased commercially, and hafnium tetrachloride was prepared from the metal and chlorine at 450°.

The hexachloro-complexes were prepared by published methods, *e.g.*, from hydrochloric acid⁸ solution (Sn, Pb, and Ti), from thionyl chloride solution⁹ (Ge, Pb, Ti, Zr, and Hf), or from thionyl chloride-iodine monochloride mixtures¹⁰ (Zr), the references referring to the type of reaction. The purity of the complexes was checked by analysis before use.

Solvents were dried, and dinitrogen pentoxide and tetroxide were prepared and used as described elsewhere.¹¹ The caesium hexanitrostannate(IV), completely soluble in dinitrogen pentoxide, and the tetramethylammonium hexanitratozirconate(IV) and hexanitratohafnate(IV), which were soluble in methyl cyanide-dinitrogen tetroxide mixtures, were isolated by vacuum-evaporation of the solvents at room temperature.

Analysis.—Titanium, zirconium, and hafnium were weighed as the dioxides following upon precipitation of the hydroxides and ignition. Tin was determined by titration against standard iodine solution^{12a} after reduction to Sn(II) using a Jones reductor, and nitrate by precipitation with Nitron^{12b} after hydrolysis of the complexes. Caesium¹³ was weighed as caesium hexachlorostannate(IV).

$\text{Cs}_2\text{Sn}(\text{NO}_3)_6$ [Found: Sn(IV), 15.65; NO_3 , 49.25; Cs, 35.0. Reqd.: Sn(IV), 15.7; NO_3 , 49.2; Cs, 35.1%]. $(\text{NMe}_4)_2\text{Zr}(\text{NO}_3)_6$ [Found: Zr(IV), 14.9; NO_3 , 60.8. Reqd.: Zr(IV), 14.9; NO_3 , 60.85%]. $(\text{NMe}_4)_2\text{Hf}(\text{NO}_3)_6$ [Found: Hf(IV), 25.6; NO_3 , 53.3. Reqd.: Hf(IV), 25.55; NO_3 , 53.25%].

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