J. inorg. nucl. Chem., 1967, Vol. 29, pp. 1003 to 1012. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON SOME METAL-HYDRAZINE COMPLEXES

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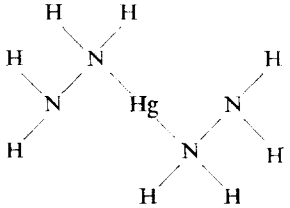
(*First received* 4 *July* 1966; *in revised form* 14 *November* 1966)

Abstract—Under different conditions of preparation, uranyl chloride reacted with hydrazine giving rise to hydrated and/or hydroxylated species of compositions $(UO_2Cl_2)_2 \cdot N_2H_4 \cdot 6H_2O$; $[UO_2(OH)Cl]_2 \cdot 3N_2H_4$ and $[UO_2(OH)Cl]_2 \cdot N_2H_4 \cdot 6H_2O$, whereas from uranyl sulphate, the normal complex of composition $UO_2SO_4 \cdot 2N_2H_4$ was obtained except in the case when aqueous solutions of uranyl sulphate and hydrazine sulphate were employed. Also the normal complexes with hydrazine of thorium, cerium and nickel of compositions $Th(SO_4)_2 \cdot 2N_2H_4$, $Ce(SO_4)_2 \cdot 2N_2H_4$ and $NiSO_4 \cdot 3N_2H_4$ have been prepared. All these compounds were studied by thermogravimetry, DTA, X-ray and i.r. analyses. The order of stabilities of the hydrazine complexes with the metallic sulphates have been discussed.

INTRODUCTION

Though the preparation of a large number of solid complexes of hydrazine has been reported in literature, these have been confined mostly to those of the non-hydrolysable elements.(1) Moreover, the thermal characteristics of these metallic hydrazinates have not been studied except for the known fact that some of these explode on heating. Another interesting feature of these compounds is that in many of the reported complexes, the full co-ordination number of the metal atom is not satisfied(2) unless hydrazine is considered to act as a bidentate ligand giving rise to three membered rings which are considered unstable from steric considerations. Only a few papers have appeared on the i.r. and X-ray investigations of these complexes. Among these may be mentioned the works of Brodersen, Ferrari and Sacconi.(3–7) Brodersen investigated the hydrazine complexes of mercuric chloride by i.r. spectroscopy and X-ray analysis and postulated a structure



for $Hg(N_2H_4)_2Cl_2$ and a chain like structure for $Hg(N_2H_4)Cl_2$. The hydrazine complexes of the chlorides of manganese, nickel, iron, cobalt, copper, zinc and cadmium were studied by Sacconi *et al.* and from the vibrational frequencies of the metal nitrogen linkages in the i.r. spectrum they have shown that the order of stabilities of

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(1) L. F. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine.* J. Wiley, New York (1951).

(2) J. C. Bailar, *Chemistry of Co-ordination Compounds.* Reinhold, New York (1956).

(3) K. Brodersen, *Z. anorg. Chem.* **290,** 24 (1957).

(4) A. Ferrari, A. Braibanti and G. Bigliardi, *Z. Kristallogr.* **117,** 241 (1962); *Acta crystallgr.* **16,** 498 (1963).

(5) A. Ferrari, A. Braibanti and G. Bigliardi and F. Dallaville, *Z. Kristallogr.* **119,** 284 (1963).

(6) A. Ferrari, A. Braibanti and A. B. Lanfredi, *Ann. chim.* **48,** 1238 (1958).

(7) L. Sacconi and A. Sabitini, *Nature, Lond.* **186,** 549 (1960); *J. inorg. nucl. Chem.* **25,** 1389 (1963).

the hydrazine complexes of these divalent metals as Mn < Fe < Co < Ni < Cu > Zn > Cd. FERRARI *et al.* reported from an X-ray investigation of the chloride complexes with hydrazine of zinc, cadmium and manganese of the formula $M(N_2H_4)_2$-Cl_2 that the moles of hydrazine form bridges between the two metal atoms. They have also suggested that in the nitrate complexes of zinc, cadmium and cobalt of the formula $M(N_2H_4)_3(NO_3)_2$, the most probable arrangement is as three parallel N—N bridges between two metal atoms.

Therefore a study of the hydrazine complexes of the hydrolysable elements, uranium, thorium and cerium was considered interesting. Earlier studies on the uranium chloride complexes were carried out by KALNINS *et al.*(8) who have reported the formation of $UO_2Cl_2{\cdot}4N_2H_4$, $UCl_4{\cdot}6N_2H_4$ and $UCl_4{\cdot}7NH_4$ based on equilibrium vapour pressure studies. SAHOO and PATNAIK(9) prepared a complex of composition $UF_4{\cdot}2N_2H_4$ by exposing a mixture of uranyl nitrate, hydrofluoric acid and hydrazine to sunlight. In a similar way they obtained a complex of thorium fluoride, $ThF_4{\cdot}$-$N_2H_4{\cdot}HF$. The various nickel salts as chloride, sulphate, thiocyanate form complexes with hydrazine.(1)

The present work deals with the complexes of hydrazine with uranyl chloride, uranyl sulphate, thorium sulphate, cerium sulphate and nickel sulphate from the point of view of their composition, thermal, i.r. and X-ray characteristics. Nickel is included in this series for comparison as it forms well characterized complexes.

EXPERIMENTAL

Reagents

Uranyl chloride ($UO_2Cl_2{\cdot}H_2O$). High purity U_3O_8 was dissolved in hydrochloric acid by the addition of a few drops of nitric acid, followed by evaporation thrice with hydrochloric acid. It was allowed to crystallize over sodium hydroxide, the crystals of uranyl chloride removed and dried *in vacuo*.

Uranyl sulphate ($UO_2SO_4{\cdot}H_2O$). Pure U_3O_8 was dissolved in nitric acid, fumed with sulphuric acid twice. The sulphate was dissolved in the minimum amount of water, reprecipitated by addition of acetone, filtered and dried *in vacuo*.

Thorium sulphate ($Th(SO_4)_2{\cdot}2H_2O$). Thorium nitrate was fumed with sulphuric acid twice. The sulphate was dissolved in the minimum amount of water, reprecipitated by addition of alcohol, filtered and dried *in vacuo*.

Cerium (IV) *sulphate*. $Ce(SO_4)_2{\cdot}4H_2O$; E. Merck GR.

Nickel sulphate. $NiSO_4{\cdot}H_2O$; BDH AR Grade.

Hydrazine hydrate. BDH LR.

All the other reagents were BDH AR grade.

Preparation of the complexes

Method (1). To an alcoholic solution of the substance, hydrazine hydrate was added slowly and with stirring till the precipitation was complete, as seen by the solution turning just alkaline. The precipitated hydrazinate was filtered off, washed with alcohol and ether and dried *in vacuo* to constant weight.

Method (2). The original compound and hydrazine hydrate in excess were mixed together under a layer of carbon tetrachloride. The precipitated hydrazinate was transferred by suction to a sintered glass crucible, washed with carbon tetrachloride, alcohol and finally with ether. The crucible with the precipitate was dried *in vacuo* to constant weight.

Method (3). The compound and the corresponding salt of hydrazine were dissolved in water and mixed together. Liquor ammonia was added drop by drop till there was slight excess of alkali. The

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(8) I. KALNINS and G. GIBSON, *J. inorg. nucl. Chem.* **7**, 55 (1958); *ibid.* **11**, 115 (1959).

(9) B. SAHOO and D. PATNAIK, *Curr. Sci.* **30**, 263 (1961).

hydrazine formed, *in situ*, reacts with the metallic salt to form a precipitate which was filtered, washed with alcohol, ether and dried *in vacuo*.

All the three above mentioned methods were used in the preparation of the complexes with hydrazine of uranium whereas only the second method was tried in the preparation of the complexes of thorium, cerium and nickel.

Determination of the chemical composition

The composition of the complexes were determined by finding out the percentages of metal, hydrazine and chloride or sulphate. The difference, if any, between the total percentage of the above and 100% was taken to be as due to water and/or hydroxyl groups. The Karl Fischer method of estimation of the water molecules could not be used in the present case as one of the constituents of Karl Fischer viz. Iodine reacts with hydrazine. As no other methods were available for determination of the water content, the water moles were calculated after assigning first the (OH) groups necessary to satisfy the valence of the metal atom. The results are shown in Tables 1, 2 and 3.

TABLE 1.—COMPOSITION OF THE COMPLEXES OF URANYL CHLORIDE WITH HYDRAZINE

Method of preparation	Analysis (%)				Mole ratio				Probable formula
	UO_2	Cl	N_2H_4	Difference H_2O or OH	UO_2	Cl	N_2H_4	H_2O or OH	
1	64·40	17·55	4·12	13·93	0·24	0·49	0·13	0·77	$(UO_2Cl_2)_2N_2H_4 \cdot 6H_2O$
2	73·80	9·43	12·25	4·52	0·27	0·27	0·38	0·27	$(UO_2(OH)Cl)_2 \cdot 3N_2H_4$
3	68·88	9·04	4·07	18·01	0·26	0·25	0·12	1·00	$(UO_2(OH)Cl)_2 \cdot N_2H_4 \cdot 6H_2O$

TABLE 2.—COMPOSITION OF THE URANYL SULPHATE COMPLEXES WITH HYDRAZINE

Method of preparation	Analysis (%)				Mole ratio				Probable formula
	UO_2	SO_4	N_2H_4	Difference H_2O or OH	UO_2	SO_4	N_2H_4	H_2O or OH	
1	63·11	21·88	15·22	0·21	0·23	0·23	0·47	—	$UO_2SO_4 \cdot 2N_2H_4$
2	62·67	21·91	14·89	0·53	0·23	0·23	0·46	—	$UO_2SO_4 \cdot 2N_2H_4$
3	76·81	13·80	4·46	4·93	0·28	0·14	0·14	0·29	$(UO_2)_2(OH)_2SO_4 \cdot N_2H_4$

TABLE 3.—COMPOSITION OF THE COMPLEXES OF METALLIC SULPHATES WITH HYDRAZINE

Metallic salt	Analysis (%)			Mole ratio			Probable formula
	Metal	Sulphate	Hydrazine	Metal	Sulphate	Hydrazine	
Thorium sulphate	47·85	38·59	13·52	0·21	0·40	0·42	$Th(SO_4)_2 \cdot 2N_2H_4$
Cerium sulphate	35·30	48·77	15·69	0·25	0·50	0·49	$Ce(SO_4)_2 \cdot 2N_2H_4$
Nickel sulphate	23·62	38·56	37·90	0·40	0·40	1·19	$NiSO_4 \cdot 3N_2H_4$

Thermolysis studies

For the thermogravimetric studies, the Stanton Thermobalance (High Temperature Model) was used. From these thermograms, the differential curves were plotted for resolving some of the steps

TABLE 4

$$(\mathrm{UO_2Cl_2})_2\cdot\mathrm{N_2H_4}\cdot 6\mathrm{H_2O} \xrightarrow[\substack{145^\circ\ (\text{Exo})\\ 180^\circ\ (\text{Endo})}]{135^\circ,\,195^\circ} \begin{matrix}\mathrm{UO_2Cl_2}\cdot\mathrm{H_2O}\\ \mathrm{Cl}(19\cdot17)19\cdot78\,\%\end{matrix} \xrightarrow[270^\circ\ (\text{Endo})]{295^\circ} \begin{matrix}\mathrm{U_2O_5Cl_2}\\ \mathrm{Cl}(10\cdot96)11\cdot32\,\%\end{matrix} \xrightarrow[410^\circ\ (\text{Endo})]{425^\circ} \mathrm{U_3O_8}$$

$$(\mathrm{UO_2(OH)Cl_2})_2 3\mathrm{N_2H_4} \xrightarrow[\substack{240^\circ\ (\text{Exo})\\ 330^\circ\ (\text{Exc})}]{250^\circ} \begin{matrix}\mathrm{UO_2(OH)Cl}\\ \mathrm{Cl}(11\cdot12)11\cdot01\,\%\end{matrix} \xrightarrow[490^\circ\ (\text{Endo})]{610^\circ} \begin{matrix}\mathrm{U_{15}O_{36}Cl_{14}}\\ \mathrm{Cl}(10\cdot88)10\cdot70\,\%\end{matrix} \xrightarrow[810^\circ\ (\text{Endo})]{790^\circ} \mathrm{U_3O_8}$$

$$(\mathrm{UO_2(OH)Cl})_2\cdot\mathrm{N_2H_4}\cdot 6\mathrm{H_2O} \xrightarrow[\substack{140^\circ\ (\text{Exo})\\ 180^\circ\ (\text{Endo})}]{175^\circ} \begin{matrix}\mathrm{U_2O_5Cl}\\ \mathrm{Cl}(6\cdot02)6\cdot00\,\%\end{matrix} \xrightarrow[\substack{275^\circ\ (\text{Endo})\\ 360^\circ\ (\text{Endo})}]{365^\circ} \mathrm{U_3O_8}$$

$$\mathrm{UO_2SO_4}\cdot 2\mathrm{N_2H_4} \xrightarrow[\substack{150^\circ\ (\text{Exo})\\ 200^\circ\ (\text{Exc})}]{185^\circ} \begin{matrix}\mathrm{UO_2SO_4}\\ \mathrm{SO_4}(26\cdot34)26\cdot23\,\%\end{matrix} \xrightarrow[800^\circ\ (\text{Endo})]{810^\circ} \mathrm{U_3O_8}$$

$$(\mathrm{UO_2})_2(\mathrm{OH})_2\mathrm{SO_4}\cdot\mathrm{N_2H_4} \xrightarrow[165^\circ\ (\text{Exo})]{150^\circ} (\mathrm{UO_2})_2(\mathrm{OH})_2\mathrm{SO_4}. \xrightarrow[780^\circ\ (\text{Endo})]{760^\circ} \mathrm{U_3O_8}$$

$$\begin{tikzcd}
\mathrm{Th(SO_4)_2}\cdot 2\mathrm{N_2H_4} \arrow[r, "80^\circ", "110^\circ\ (\text{Exo})"'] & 2\mathrm{Th(SO_4)_2}\cdot 3\mathrm{N_2H_4} \arrow[r, "265^\circ", "260^\circ\ (\text{Exo})"'] & \begin{matrix}\mathrm{Th(SO_4)_2}\\ \mathrm{SO_4}(45\cdot03)45\cdot28\,\%\end{matrix} \arrow[d, "580^\circ", "\substack{540^\circ\\ (\text{Endo})}"'] \\
 & \mathrm{ThO_2} & \begin{matrix}2\mathrm{ThO_2}\cdot 3\mathrm{SO_3}\\ \mathrm{SO_4}(38\cdot20)37\cdot50\,\%\end{matrix} \arrow[l, "865^\circ\ (\text{Endo})", "840^\circ"']
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{Ce(SO_4)_2}\cdot 2\mathrm{N_2H_4} \arrow[r, "80^\circ", "\substack{105^\circ\ (\text{Exo})\\ 150^\circ\ (\text{Exo})}"'] & 2\mathrm{Ce(SO_4)_2}\cdot 3\mathrm{N_2H_4} \arrow[r, "275^\circ", "255^\circ\ (\text{Exo})"'] & \begin{matrix}\mathrm{Ce(SO_4)_2}\\ \mathrm{SO_4}(45\cdot68)45\cdot93\,\%\end{matrix} \arrow[d, "465", "\substack{420^\circ\\ (\text{Endo})}"'] \\
 & \mathrm{CeO_2} & 3\mathrm{CeO_2}\cdot 4\mathrm{SO_3} \arrow[l, "965^\circ\ (\text{Endo})", "965^\circ"']
\end{tikzcd}$$

$$\mathrm{NiSO_4}\cdot 3\mathrm{N_2H_4} \xrightarrow[\substack{225^\circ\ (\text{Exo})\\ 250^\circ\ (\text{Exo})}]{265^\circ} \mathrm{NiSO_4} \xrightarrow[780^\circ\ (\text{Endo})]{765^\circ} \mathrm{NiO}$$

Note: The figures above the arrows represent the peak decomposition temperatures in DTG and those below that in the DTA graph. Enclosed in brackets are given the nature of reactions.

The analysis data for the products obtained are given below the respective products in enclosed brackets and the theoretical values are given alongside.

and to know the peak decomposition temperatures. The intermediate products of decomposition were verified by chemical analysis and in some cases by X-ray data. The data are tabulated in Table 4.

For the differential thermal analysis, a known weight of the substance was mixed with an equal weight of alumina and packed in a platinum crucible of capacity 1 ml. This was kept in a ceramic block alongside a similar crucible containing calcined alumina packed in a similar manner. A differential chromel alumel–chromel thermocouple was introduced into the specimen and alumina. The ceramic block was kept in a horizontal tubular furnace, heated at a constant rate of 10°C/min and the differential e.m.f. from the thermocouple was recorded as a function of time on a Kipp monograph BD I strip chart recorder.

The DTA data was used to confirm the steps as obtained in the thermogram and also to obtain a measure of the heat evolved during the decomposition of the metallic sulphate hydrazinates to the respective metallic sulphates. This was done by calibration of the DTA apparatus using silver nitrate. This was chosen as the standard since the temperature of fusion of silver nitrate is at 212°C which is near the temperature of the decomposition of these complexes and there is no hydrazinate, whose heat of decomposition is reported in literature. From the area of the peak and the amount of standard substance taken, the constant for the experimental set up can be determined. Since this is dependent on the size, shape, type of sample holder, furnace atmosphere, heating rate, type of thermocouple etc. identical conditions were maintained for the standard and the complexes under investigation.[10]

X-ray analysis. The X-ray analysis of the complexes as well as some of the products of decomposition were taken using the Bragg-Brentens para focussing method and are given in Table 5. The chloride complexes of uranium as well as the sulphate complex $(UO_2)_2(OH)_2SO_4{\cdot}N_2H_4$ and the thorium complex gave only a diffusive pattern and as such the X-ray data for these compounds could not be obtained.

TABLE 5.—DIFFRACTOMETRIC X-RAY DATA OF THE COMPLEXES OF HYDRAZINE WITH URANYL, CERIUM AND NICKEL SULPHATES AND $U_{15}O_{36}Cl_{14}$

$U_{15}O_{36}Cl_{14}$		$UO_2SO_4{\cdot}2N_2H_4$		$Ce(SO_4){\cdot}2N_2H_4$		$NiSO_4{\cdot}3N_2H_4$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
8·34	9	8·59	19	7·90	80	7·14	100
7·56	93	8·50	19	6·10	12	5·15	32
3·76	21	7·36	100	4·74	66	4·69	14
3·57	86	6·15	14	4·53	13	4·50	74
3·51	44	5·60	12	4·09	70	3·71	27
3·37	11	4·29	16	3·80	34	3·57	60
3·30	11	4·21	16	3·53	74	3·29	15
3·23	100	3·71	48	3·29	79	3·24	15
3·17	60	3·47	64	3·04	100	3·23	14
2·90	9	3·13	100	2·76	37	3·17	7
2·58	26	2·87	26	2·73	42	3·04	20
2·25	9	2·79	12	2·60	29	3·03	23
2·21	9	2·67	27	2·54	23	2·96	9
2·07	9	2·53	26	2·37	18	2·92	14
2·06	12	2·26	12	2·31	25	2·79	10
2·03	17	2·17	14	2·26	18	2·64	14
2·00	14	2·14	8	2·17	9	2·58	16
1·97	26	2·09	18	2·07	15	2·51	10
1·79	14	2·05	12	2·03	31	2·35	9
1·78	16	2·03	12	1·94	15	2·34	13
1·74	12	2·02	16	1·86	13	2·19	9
1·67	8	1·87	22	1·83	8	2·18	9
1·66	8	1·75	12	1·70	20	2·11	6
1·61	9	1·74	14			2·08	5
1·59	8	1·69	16			1·97	9
1·58	9	1·57	14			1·86	6
		1·42	13			1·59	8
		1·41	15				
		1·40	12				

I.R. analysis. I.r. spectra of these complexes were taken on Perkin-Elmer (Model 21) using fluorolube in the 4000–1200 cm^{-1} and paraffin in the lower region of 1200–400 cm^{-1}. The vibrational frequencies with their assignments are shown in Tables 6 and 7. These have been made on the basis of the assignments by NAKAMATO.[11]

RESULTS AND DISCUSSION

As seen from Table 1, the composition of the uranyl chloride complexes with hydrazine vary depending on the method of preparation and that all are either hydrated and/or hydroxylated. On the other hand, the complexes of hydrazine with uranyl sulphate prepared by methods (1) and (2) are of the composition

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[10] W. WENDLANDT, *Techniques of Inorganic Chemistry*, (Edited by H. B. JONASSON and A. WEISSBERGER). Vol. I. Interscience, New York (1963).

[11] K. NAKAMATO, *Infrared Spectra of Inorganic and Co-ordination Compounds*. Interscience, New York (1963).

TABLE 6.—I.R. SPECTRA OF THE CHLORIDE COMPLEXES AND THEIR ASSIGNMENTS

$(UO_2Cl_2)_2{\cdot}N_2H_4{\cdot}6H_2O$		$(UO_2(OH)Cl)_2{\cdot}3N_2H_4$		$(UO_2(OH)Cl)_2{\cdot}N_2H_4{\cdot}6H_2O$		
Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Assignment
		3600	sp, s			(OH) stretching
		3450	vs, b	3500	vs, b	(OH) stretching (NH) stretching
3350	s, b	3355	vs, b	3360	s, b	(NH) stretching
		3230	vs, b	3220	s, b	(NH) stretching
1632	s	1612	m	1612	m, b	H_2O and NH_2 bending
1535	w	1525	m	1525	m, b	NH_2 bending NH_2 bending
1425	s	1425	s	1420	s	NH_2 bending
1110	w	1112	w	1100	m	NH_2 bending
1015	w	1014	w	1024	w	NH_2 bending
975	w	977	w	968	w	N–N stretching
925	vs	932	vs	915	vs	UO_2 asymmetric stretching
818	w	815	w	825	w	UO_2 symmetric stretching

Note. No assignments could be made in the region below 800 cm^{-1} as the bands observed were extremely weak and broad.

$UO_2SO_4{\cdot}2N_2H_4$ whereas that prepared by method (3) is again a hydroxylated species. Method (2) which was employed in the preparation of the complexes of the sulphates of thorium, cerium and nickel gave the normal complexes of the composition $M(SO_4)_x\ yN_2H_4$.

$(UO_2Cl_2)_2{\cdot}N_2H_4{\cdot}6H_2O$. The thermogram and DTA reveal that hydrazine and four of the six water molecules are removed first. The stages of decomposition of this complex are $UO_2Cl_2{\cdot}H_2O$, $U_2O_5Cl_2$ and U_3O_8. A compound of the composition $UO_2Cl_2{\cdot}H_2O$ has been reported,(12) the decomposition of which was studied by PRIGENT.(13) An intermediate product of composition $HU_2O_5Cl_3$ reported by him was not observed in the present case. Instead, $UO_2Cl_2{\cdot}H_2O$ decomposes directly to $U_2O_5Cl_2$ which is converted to U_3O_8 at 400°C with no further gain or loss up to 800°C. X-ray data of the products obtained at 400°C and 800°C both gave characteristic U_3O_8 pattern [*d* values were 4·15(100% I/I_0); 3·43(100% I/I_0) and 2·64(90% I/I_0)] except for the difference that the U_3O_8 obtained by heating to 800°, was more crystalline and gave a sharp pattern.

The i.r. spectra was in general broad. Especially the region below 800 cm^{-1} was weak making the assignment in this region particularly difficult so that it has not been included in Table 6.

$(UO_2(OH)Cl)_2{\cdot}3N_2H_4$. Decomposes to U_3O_8 though the intermediate formation of $UO_2(OH)Cl$ and $U_{15}O_{36}Cl_{14}$. A product of the composition $UO_2(OH)Cl$ has been reported.(12) The composition $U_{15}O_{36}Cl_{14}$ assigned to the second decomposition stage was based on TG and analysis data of the product. Such an odd composition had to be

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(12) J. W. MELLOR, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XII. Longmans-Green, London (1946).

(13) J. PRIGENT and M. GUEGUIN, *C. r. hebd. Séanc. Acad. Sci., Paris* **258**, 4069 (1964).

TABLE 7.—I.R. SPECTRA OF THE SULPHATE COMPLEXES AND THEIR ASSIGNMENTS

$(UO_2)_2(OH)_2SO_4{\cdot}N_2H_4$		$UO_2SO_4{\cdot}2N_2H_4$		$Th(SO_4)_2{\cdot}2N_2H_4$		$Ce(SO_4)_2{\cdot}2N_2H_4$		$NiSO_4{\cdot}3N_2H_4$		
Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Wave numbers (cm^{-1})	Intensity	Assignment
3500	s, b									(OH) stretching
*3300	s, b	3300	s, b	3400	s, b	3350	s, sp	3215	s, sp	NH stretching
						3250	s, sp			NH stretching
						3100	s, sp	3140	s, sp	NH stretching
						2960	s, sp			NH stretching
*1632	s	1600	m	1585	m	1658	m, sp	1625	s	NH_2 bending
		1502	m	1510	w	1613	m, sp	1605	w	NH_2 bending
						1585	m, sp			NH_2 bending
						1545	m, sp	1257	w	NH_2 bending
1230	s	1205	m	1175	m	1160	s, b	1224	s	ν_3 mode of SO_4
1135	s	1150	m			1135	s	1100	s	ν_3 mode of SO_4
1050	s	1070	m	1065	w	1115	s			ν_3 mode of SO_4
				1085	w					NH_2 bending
1007	m	972	s, b	980	m, b	1003	w	985	w	ν_1 mode of SO_4
945	s	960	s							UO_2^{2+} asymmetric stretching
		902	w							N-N stretching
860	m	850	s							UO_2^{2+} symmetric stretching
650	s	645	s	641	m	673	s	614	s	ν_4 mode of SO_4
630	s	612	s	604	s	656	s			ν_4 mode of SO_4
						643	w			ν_4 mode of SO_4
605	s	600	w			603	s			ν_4 mode of SO_4
590	s	582	s	527	s	553	m	614	s	M–N-stretching
						505	s			M–N-stretching
480	m					460	m			ν_2 mode of SO_4
						430	m			ν_2 mode of SO_4

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* The wave numbers 3300 and 1632 cm^{-1} in the case of $(UO_2)_2(OH)_2SO_4$ can represent the H_2O stretching and bending modes also.

visualized since the X-ray analysis of the same (which may as well be a mixture) did not tally with any of the reported X-ray patterns of compounds containing uranium, oxygen and chlorine.

I.R. spectra is similar to the complex already discussed except that a sharp absorption peak is obtained at 3600 cm^{-1} confirming the presence of (OH) group. In addition, the spectra of the product obtained on decomposition of the complex at 250°C showed a peak at 3575 cm^{-1} confirming the assignment of $UO_2(OH)Cl$ for this compound.

$(UO_2(OH)Cl)_2 \cdot N_2H_4 \cdot 6H_2O$. On heating gives only one intermediate product of composition U_2O_5Cl before final conversion to oxide, U_3O_8. This assignment was based on weight loss and analysis of product formed on heating the substance at 225°C. X-ray analysis of this compound gave no useful information as no crystalline pattern was obtained. Further, the i.r. spectra could not yield any precise information as regards N–H stretching and bonding modes. The region below 800 cm^{-1} showed only extremely weak bonds so that no assignments could be made for these.

$UO_2SO_4 \cdot 2N_2H_4$. The thermogram reveals two clear steps showing the decomposition stages as UO_2SO_4 and U_3O_8, the intermediate product of UO_2SO_4 having been verified by analysis data. The DTA, however, shows that the evolution of hydrazine takes place in two stages.

The i.r. spectra shows the N–H stretching and bending modes at 3300 cm^{-1}, 1600 and 1502 cm^{-1} in addition to the weak bond at 902 cm^{-1} due to N–N stretching. The ν_3 frequency of SO_4 molecule splits up into three components in the complex showing that the sulphate symmetry is reduced to C_{2v}. This means that two oxygen atoms of the sulphate molecule are co-ordinated in the complex. Because of this reduced symmetry, the ν_1 mode appears in the spectrum. Also the ν_4 mode is split up into three bands. All these definitely show that sulphate is doubly co-ordinated. The appearance of M–N frequency at 582 cm^{-1} proves that the nitrogen of the hydrazine molecule is co-ordinated to the metal atom.

$(UO_2)_2(OH)_2)SO_4 \cdot N_2H_4$. Only two steps are seen in the thermogram. On heating it evolves hydrazine followed by decomposition of $(UO_2)_2(OH)_2SO_4$ to U_3O_8. Spectra is similar to that of $UO_2SO_4 \cdot 2N_2H_4$, except for the (OH) band at 3500 cm^{-1}.

$Th(SO_4)_2 \cdot 2N_2H_4$. The thermogram reveals that 0·5 mole of hydrazine is evolved first followed by 1·5 mole later. The evolution of hydrazine in two stages is confirmed by DTA graph. An absolutely flat region corresponding to thorium sulphate could not be obtained from the thermogram. It appears from the analysis data of the product obtained on heating the complex at 600°C that an intermediate stage of composition $2ThO_2 \cdot 3SO_3$ is formed before final conversion to the oxide, ThO_2.

In the i.r. spectrum there is a complete broadening effect of the vibrational frequencies. The N–H stretching mode appears as a broad strong band at 3400 cm^{-1} and the N–H bending modes are seen at 1585, 1510 and 1085 cm^{-1}. ν_3 and ν_4 modes of the sulphate molecule split up into two bands and the ν_1 mode makes its appearance. Possibly the sulphate is co-ordinated through only one of the oxygen atoms. The M–N stretching mode appears as a strong band at 527 cm^{-1} showing that nitrogen of the hydrazine molecule is co-ordinated to the metal atom. The broadening of the bands can be explained as due to the mutual interaction of many different groups present in the solid state.

$Ce(SO_4)_2 \cdot 2N_2H_4$: There are four distinct steps in the thermogram. The first two correspond to the evolution of hydrazine in two stages, corroborated by the two DTA peaks. The first step corresponds to removal of 0·5 mole hydrazine followed by 1·5 mole subsequently. This indicates that the complex is at least a dimer. The cerium sulphate formed decomposes to CeO_2 through an intermediate stage of composition 3 $CeO_2·4SO_3$. The latter was verified by chemical analysis.

The i.r. spectra of the complex is very interesting. Four peaks are observed in the N–H stretching region. In the spectra of solid hydrazine, only two bands are observed. The presence of more than two bands in the spectrum can be explained on the basis that part of the hydrazine is loosely bound in the complex, whereas part of it is firmly bound. Compounds similar to the thorium and cerium complexes where an extra molecule of the ligand is loosely attached have been observed in the case of uranium, thorium and scandium.[14] This is also confirmed by the fact that on heating to 120° when part of the hydrazine is lost as seen from TG and taking the spectra of the product, the N–H stretching region shows only one band. The ν_3 and ν_4 modes of sulphate split up into three bands each. Moreover, the ν_1 mode appears in the spectrum. It can, therefore, by concluded that the sulphate molecule occupies two co-ordination positions in the complex. The appearance of M–N vibrational modes shows that nitrogen of the hydrazine molecule is co-ordinated to metal.

$NiSO_4·3N_2H_4$. The thermogram showed two clear steps representing decomposition to nickel sulphate and further to nickel oxide.

The N–H stretching region in the i.r. spectrum shows two sharp bands at 3215 cm^{-1} and 3140 cm^{-1} and three bands at 1625, 1605 and 1257 as the $N–H_2$ bending modes. The ν_3 mode of sulphate is split up into two bands and the ν_1 mode makes its appearance. Sulphate is therefore co-ordinated to the metal atom through only one of its oxygen atoms. Only a single band is observed in the ν_4 region. Since by comparison with nickel sulphate, this band is very strong, it should be a superimposition of ν_4 mode of sulphate and the M–N stretching frequency. Hydrazine is therefore co-ordinated to the nickel atom.

Strength of the M–N *bonding.* A study of the heat evolved as seen from Table 8 during the exothermic evolution of hydrazine when the hydrazinates are decomposed shows the order as Ni > U > Th > Ce. The heat evolved is a measure of the bond strength of hydrazine molecules to the respective sulphates. It therefore follows that the bonding is strongest in nickel, followed by uranium, thorium and cerium in the order mentioned. This order is also confirmed from the metal nitrogen frequencies

TABLE 8.—HEATS EVOLVED ON THE DECOMPOSITION OF HYDRAZINE SULPHATE COMPLEXES TO SULPHATES

Complex	Wt. taken (g)	Area of peak (cm^2)	Area (cm^2/g)	Heat of reaction (cal/g)	kcal/g mole
$UO_2SO_4·2N_2H_4$	0·1501	3·41	22·73	173	74·39
$Th(SO_4)_2·2N_2H_4$	0·4002	3·96	9·90	75	36·60
$Ce(SO_4)_2·2N_2H_4$	0·2621	2·24	8·54	65	25·74
$NiSO_4·3N_2H_4$	0·1875	11·12	59·30	452	113·20

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(14) A. E. COMYNS, *Chem. Rev.* **60**, 115 (1960).

shown in the i.r. spectra of these complexes. These reveal that the bond is strongest in nickel sulphate hydrazinate followed by uranyl sulphate hydrazinate. Thorium and cerium sulphate hydrazinates show almost the same strength for the metal–nitrogen bond, if we take the average of the two M–N frequencies of cerium.

Acknowledgements— The authors wish to thank Dr. M. D. KARKHANAVALA, Chemistry Division, Atomic Energy Establishment Trombay and SHRI V. B. KARTHA, Spectroscopy Division, Atomic Energy Establishment Trombay for useful discussions regarding X-ray and i.r. analysis respectively.