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DIMETHYL SULPHOXIDE COMPLEXES OF TITANYL, ZIRCONYL AND THORIUM PERCHLORATES

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Abstract—$TiO{\cdot}5DMSO(ClO_4)_2$, $ZrO{\cdot}8DMSO(ClO_4)_2$ and $Th{\cdot}12DMSO(ClO_4)_4$ are prepared by reaction of the respective metal perchlorates with an excess of dimethyl sulphoxide. The last two complexes yield $ZrO{\cdot}6DMSO(ClO_4)_2$ and $Th{\cdot}6DMSO(ClO_4)_4$ on heating around 185°C, while the titanyl complex explodes at 190°C. The extra DMSO molecules in the zirconyl and thorium complexes seem to be held in the lattice. In the parent complexes, the co-ordinated DMSO molecules are bonded by oxygen to the metal atoms while in the DMSO complexes of zirconyl and thorium perchlorates, obtained by heating at 185°C, the bonding involves the sulphur, indicating a change in the bonding during the process of heating.

THE solubility of a number of inorganic compounds in dimethyl sulphoxide (DMSO) and its various physico-chemical properties are given by SCHLÄFER and SCHAFFERNICHT.(1) COTTON and FRANCIS,(2,3) and SELBIN *et al.*(4) prepared a number of DMSO complexes of transition and nontransition metal ions and studied their infra-red spectra.(3,4,5) SCHLÄFER and OPITZ(6,7) studied electronic spectra and thermal behaviour of the DMSO complexes of chromium, manganese, nickel, iron, cobalt and copper perchlorates. WEAVER and KEIM(8) studied conductivity, molecular weight by cryoscopic method and differential thermal analysis of the DMSO complexes of iron, cobalt and nickel chlorides. The DMSO complex of thorium nitrate(2) is known. DMSO complexes of titanyl, zirconyl and thorium perchlorates have not been prepared before. In this paper, the preparation of the DMSO complexes of titanyl, zirconyl and thorium perchlorates and their infra-red spectra and thermal behaviour are described.

EXPERIMENTAL

Reagents used

(1) Dimethyl sulphoxide: Water white DMSO, obtained through the courtesy of Crown Zellerbach Co., U.S.A., was used without further purification

(2) Crystals of titanyl perchlorate,(9) $TiO(ClO_4)_2{\cdot}6H_2O$, zirconyl perchlorate,(10) $ZrO(ClO_4)_2{\cdot}8H_2O$ and thorium perchlorate,(11) $Th(ClO_4)_4{\cdot}8H_2O$, were prepared by the methods described earlier.

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(1) H. L. SCHLÄFER and W. SCHAFFERNICHT, *Angew. Chem.* **72,** 618–26 (1960).
(2) F. A. COTTON and R. FRANCIS, *J. Amer. Chem. Soc.* **82,** 2986 (1960).
(3) F. A. COTTON and R. FRANCIS, *J. Phys. Chem.* **64,** 1534 (1960).
(4) J. SELBIN, W. E. BULL and L. H. HOLMES JR., *J. Inorg. Nucl. Chem.* **16,** 219 (1961).
(5) D. W. MEEK, D. K. STRAUB and R. S. DRAGO, *J. Amer. Chem. Soc.* **82,** 6013 (1960).
(6) H. L. SCHLÄFER and H. P. OPITZ, *Z. Electrochem. Phys. Chem.* **65,** 372 (1961).
(7) H. L. SCHLÄFER and H. P. OPITZ, *Z. Anorg. Chem.* **313,** 178 (1961).
(8) E. E. WEAVER and W. KEIM, *Proc. Indiana Acad. Sci.* **70,** 123 (1961).
(9) V. KRISHNAN and C. C. PATEL, *Chem. and Industry,* 321 (1961).
(10) P. RAMAMURTHY and C. C. PATEL, *Z. Naturwissenschaften,* **22,** 310 (1961).
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Preparation

The method of dissolving the metal perchlorate in an excess of the DMSO and distilling off the latter under reduced pressure, even in a nitrogen atmosphere, always met with an explosion. An alternative method of precipitation of the DMSO complexes by another solvent was, therefore, used. Since a hydrate of a metal perchlorate when dissolved in an excess of DMSO produced a considerable amount of heat, the salt was added slowly to the constantly stirred DMSO maintained at 20°C by cooling. After stirring the mixture for half an hour, an excess of pure dry benzene was added to the solution when white precipitates of the DMSO complex separated out gradually, leaving behind no metal perchlorate in the mother liquor. The precipitates were washed by decantation with benzene to free them from DMSO, filtered and then dried in a desiccator over fused calcium chloride. The complex was then analysed by the methods described below. In this way complexes of titanyl, zirconyl and thorium were prepared.

Analyses

Titanium, zirconium and thorium in the complexes were estimated as their ignited oxides after decomposing the complexes by boiling with concentrated nitric acid and precipitating the hydroxides by addition of dilute ammonium hydroxide.

Perchlorate was converted into chloride by fusing the complex (about 0·1 g) with sodium nitrite at 500°C in a nickel crucible[12] and estimating the chloride formed by Volhard's method.

DMSO in the complex was estimated by oxidizing it by potassium permanganate to dimethyl sulphone,(13) $(CH_3)_2SO_2$. For this, the complex (~0·5 g) was dissolved in 50 ml 2N H_2SO_4 and an excess of known volume of 0·1 N $KMnO_4$ was added to the solution. After the reaction, the excess $KMnO_4$ was determined by titration with standard ferrous sulphate solution and the amount of DMSO in the complex was computed. This method gave an accuracy of ±1·0 per cent. The average analytical results of different samples of the complexes are given in Table 1. The complexes were found to be free from any water. The complexes have the molar formulae $TiO\cdot 5DMSO(ClO_4)_2$, $ZrO\cdot 8DMSO)(ClO_4)_2$ and $Th\cdot 12DMSO(ClO_4)_4$.

TABLE 1.—ANALYSIS OF DMSO COMPLEXES OF METAL PERCHLORATES

Complex	Composition (%)			Mole ratio		
	Metal	ClO_4	DMSO	Metal	ClO_4	DMSO
Titanium	7·45	29·87	59·54	1	1·92	4·9
Zirconium	9·54	22·13	67·81	1	2·12	8·3
Thorium	14·74	25·51	59·50	1	3·95	12·14

Properties

The complexes are obtained as white crystals which are slightly hygroscopic. They are soluble in polar solvents like alcohol and acetonitrile and insoluble in nonpolar solvents. The DMSO complexes exert a vapour-pressure of about 3 mm of mercury at 20–40°C.

Thermal studies

Owing to the explosive nature of these complexes, the differential thermal analysis (DTA)was carried out by diluting the complexes with alumina (Complex:alumina::1:10 by weight) as the latter minimized the violence of the explosion and retained the solid products of explosion in the cuvette. The DTA was carried out in a manual apparatus(14) with chromel–alumel thermocouples and a heating rate of 10°C/min. The DTA curves are given in Fig. 1. The sharp exothermic peak in the titanyl complex at 190°C is due to the explosion giving amorphous titanium dioxide, while that at 260°C is due to the disorder to order transformation of titania.(15) The zirconyl and thorium

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(12) E. Kurz, G. Kober and M. Berl, *Analyt. Chem.* **30**, 1983 (1958).

(13) T. B. Douglas, *J. Amer. Chem. Soc.* **68**, 1072 (1946).

(14) N. S. K. Prasad and C. C. Patel, *J. Indian Inst. Sci.* **36**, 23 (1954).

(15) G. V. Jere and C. C. Patel, *J. Sci. Industr. Res.* (India) **20 B**, 292 (1961).

complexes gave endothermic peaks around 190°C due to partial loss of DMSO. The products of analysis showed that the zirconyl complex lost two molecules of DMSO, while the thorium complex lost six molecules per mole of the complex. The sharp exothermic peak at 275°C is due to the explosion of the zirconyl complex while the similar peak at 290°C is for the explosion of thorium complex, giving the corresponding metal dioxides.

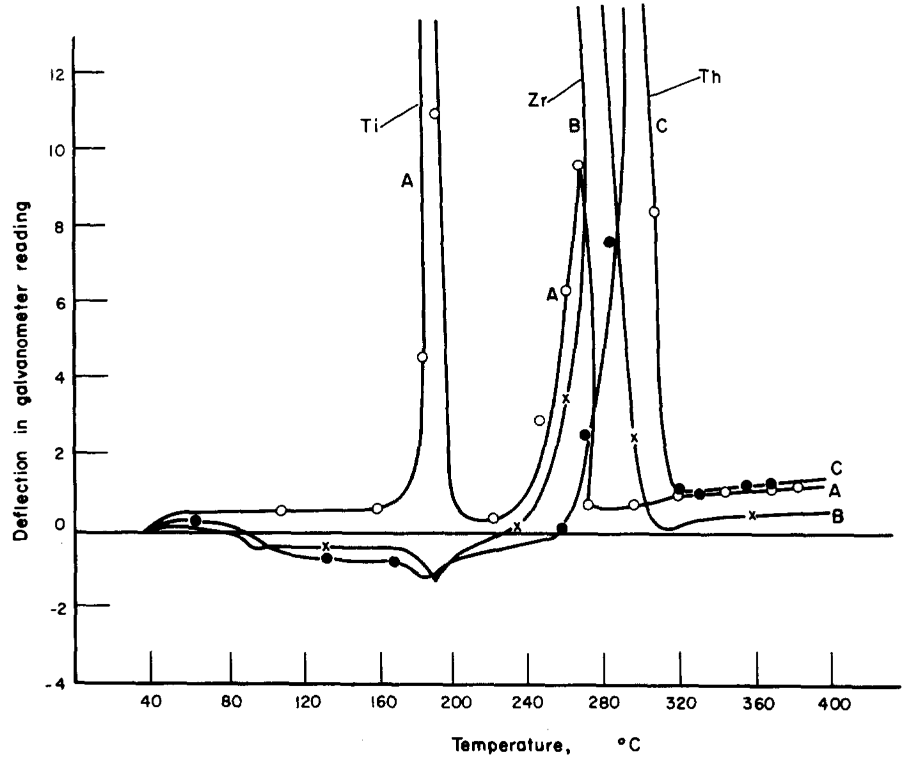

FIG. 1

Infrared absorption studies

The infra-red spectra of the unheated DMSO complexes were taken in Nujol mulls with a Perkin-Elmer infracord spectrophotometer, model 137, in rock salt region and are given in Fig. 2. The spectra of the complexes $ZrO \cdot 6DMSO(ClO_4)_2$ and $Th \cdot 6DMSO(ClO_4)_4$, formed on heating around 185°C were taken with a Perkin-Elmer single beam spectrometer model 112 using KBr disk technique, since the preparation of the mull was difficult for the heated samples. The spectra are reproduced in Fig. 3. The assignments of different bands of the spectra are based on the work of COTTON.[3,16]

TABLE 2.—ANALYSIS OF THE ZIRCONYL AND THORIUM COMPLEXES OBTAINED AROUND 185°C

	Composition (%)			Mole ratio		
Samples	Metal	ClO_4	DMSO	Metal	ClO_4	DMSO
Zirconyl complex	12·00	25·69	59·82	1	1·96	5·8
Thorium complex	20·84	36·22	42·71	1	4·06	6·1

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[16] W. D. HORROCKS JR. and F. A. COTTON, *Spectrochim. Acta* **17**, 134 (1961).

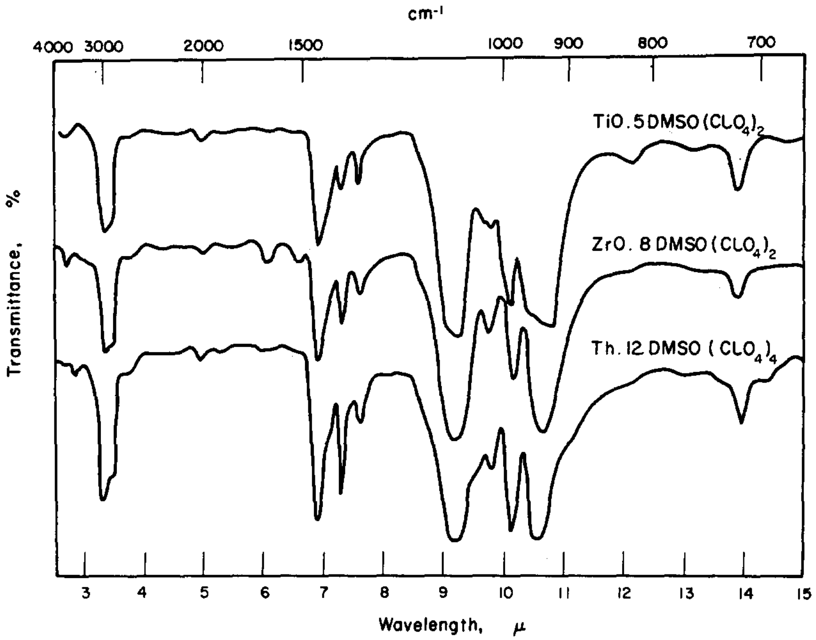


FIG. 2

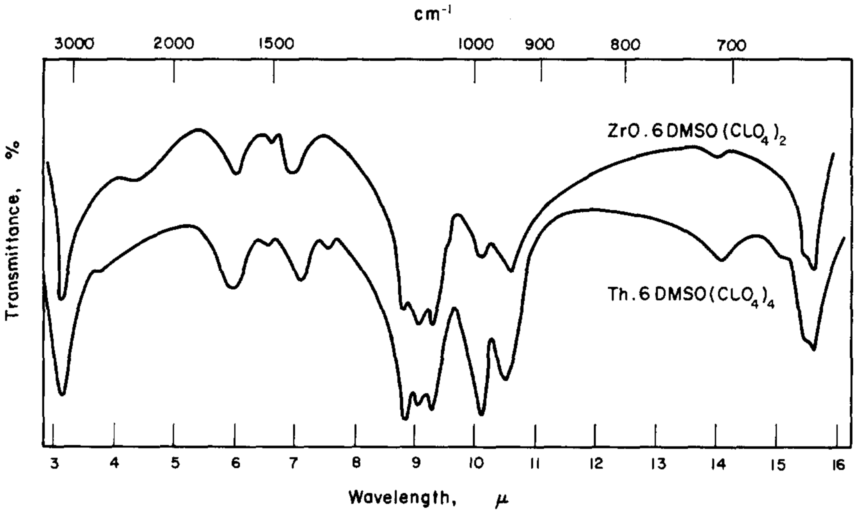


FIG. 3

DISCUSSION

Dimethyl sulphoxide with a semi polar S → O linkage has a pyramidal structure with unshared pairs of electrons on both sulphur and oxygen. It has a tendency to complex formation with metal ions by donating a pair of electrons from either sulphur or oxygen. Hence it is interesting to find out whether the DMSO is bonded through oxygen or sulphur to the metal ions. If all the DMSO molecules are coordinated, titanium will have a co-ordination number 6 while zirconium and thorium will have 9 and 12 respectively, assuming that the perchlorate ions do not take part in co-ordination. It will, therefore, be of interest to ascertain whether all the DMSO molecules are co-ordinated or some of them coordinated and some differently held in the crystals.

The DTA gives only one exothermic peak for the titanyl complex, at 190°C, while the zirconyl and thorium complexes give small endothermic peaks, almost at the same temperature, losing 2 and 6 molecules of DMSO respectively (Fig. 1). The loss of DMSO from the two complexes can be represented as follows:

$$\mathrm{ZrO{\cdot}8DMSO(ClO_4)_2} \xrightarrow{\text{at } 185^\circ\text{C}} \mathrm{ZrO{\cdot}6DMSO(ClO_4)_2} + \mathrm{2DMSO}$$

$$\mathrm{Th{\cdot}12DMSO(ClO_4)_4} \xrightarrow{\text{at } 180^\circ\text{C}} \mathrm{Th{\cdot}6DMSO(ClO_4)_2} + \mathrm{6DMSO}$$

The formation of $\mathrm{ZrO{\cdot}6DMSO(ClO_4)_2}$ and $\mathrm{Th{\cdot}6DMSO(ClO_4)_4}$ was confirmed by chemical analysis of the products. The endothermic loss of DMSO from the parent complexes at practically the same temperature as the boiling point of DMSO(17) (187°C at 760 mm of Hg) probably indicates that two molecules of DMSO in zirconyl and six molecules of DMSO in thorium complexes are either loosly bonded or held in the lattice of the crystals.

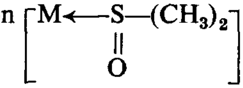
The explosion temperatures of titanyl, zirconyl and thorium complexes of DMSO are 190, 270 and 290°C. The rise in explosion temperature from titanyl through thorium complex cannot be taken as an increase in the bond strength between the metal ion and the DMSO since these explosions are dependent on the supply of oxygen from the perchlorate for the oxidation of the coordinated DMSO. This has been verified by the DTA of a similar complex, $\mathrm{Th{\cdot}6DSMO{\cdot}Cl_4}$, which explodes at 485°C leaving behind $\mathrm{ThO_2}$. Further, it is known that the perchlorates of titanyl,(18) zirconyl(19) and thorium(19) start decomposing at 190, 260 and 290°C respectively. This shows that the complexes explode at, more or less, the same temperature as the decomposition of the respective metal perchlorates.

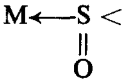
The infra-red spectra of $\mathrm{TiO{\cdot}5DMSO(ClO_4)_2}$, $\mathrm{ZrO{\cdot}8DMSO(ClO_4)_2}$ and $\mathrm{Th{\cdot}12DMSO(ClO_4)_4}$ (Fig. 2) are similar except for the diffuse band at 1026 $\mathrm{cm^{-1}}$ with the titanyl complex in contrast to the well defined bands at 1024 $\mathrm{cm^{-1}}$ and 1044 $\mathrm{cm^{-1}}$ for the zirconyl and thorium complexes respectively. The occurrence of this well defined band is due to S=O and indicates the presence of some unbonded lattice held DMSO in the latter two complexes, as shown by the DTA method. The absence of the bands around 1026 $\mathrm{cm^{-1}}$ in the complexes of $\mathrm{ZrO{\cdot}6DMSO(ClO_4)_2}$ and $\mathrm{Th{\cdot}6DMSO(ClO_4)_4}$ (Fig. 3) shows that no free DMSO is present in these complexes and that all the DMSO molecules are coordinated to the central metal ion in the heated complexes. The occurrence of another S—O stretching frequency at 934 $\mathrm{cm^{-1}}$, 938 $\mathrm{cm^{-1}}$ and 946 $\mathrm{cm^{-1}}$ in the parent complexes of titanyl, zirconyl and thorium respectively (Fig. 2) show that the π-bond character of the S—O bond in bound DMSO is lowered on complex formation as a result of bond formation by donation of a lone pair of electrons on the oxygen to the metal ions $[\mathrm{M \leftarrow O{-}S{-}(CH_3)_2}]$. The production of two very strong bands at 1148 and 1125 $\mathrm{cm^{-1}}$ in $\mathrm{ZrO{\cdot}6DMSO(ClO_4)_2}$

(17) *Technical Information on Dimethylsulphoxide.* Crown Zellerbach Corporation, Chemical Products Division, Camas, Washington (1961).

(18) V. KRISHNAN and C. C. PATEL. In press.

(19) P. RAMAMURTHY and C. C. PATEL. Unpublished work.

and 1144 and 1113 cm^{-1} in Th·6DMSO(ClO$_4$)$_4$ (Fig. 3) is due to the S—O stretching vibration appearing as a result of the rearrangement in bonding between DMSO and the metal ions. It seems that in the rearrangement, the bonding has occurred by donation of a lone pair of electrons from sulphur to the metal ion  $\left[\mathrm{M}\leftarrow\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}-(\mathrm{CH_3})_2\right]$

This type of bonding is known in palladium (S—O str., 1116 cm^{-1}) and platinum (S—O str., 1157 and 1134 cm^{-1}) DMSO complexes.[3] The endothermic peaks in the DTA curves of zirconyl and thorium complexes are very small. The peaks are due to the overall energy effect of endothermic heat of dissociation of M←—O—S < and exothermic heat of formation of  $\mathrm{M}\leftarrow\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}<$ and the loss of loosely held DMSO molecules in the lattice of the complex.

The methyl rocking vibrations in the parent complexes are very strong around 985 cm^{-1} and in the heated complexes around 1000 cm^{-1}. This is due to the distribution of half of the potential energy associated with the S—O stretching vibration to the rocking vibrations of methyl groups of DMSO.[16]

Nature of perchlorate in the complexes

In the parent complexes, the perchlorate groups give bands around 2000(w) and 1096 (*vs.* b) cm^{-1}, showing the T$_d$ symmetry of the perchlorate ions.[20] In the complexes obtained by heating the parent complexes, the appearence of the bands around 1120 (*vs*), 1085 (*vs*), 955 (*vs*), 650 (sh. s) and 645 (*s*) cm^{-1} suggests lowering of the T_d symmetry. This is probably due to C_{3v} symmetry as a result of distortion of the perchlorate group in the crystalline state.[21] The occurrence of many bands in the region 1500–950 cm^{-1} makes assignments of the different vibrations of the molecule more difficult.

Probable structures of the complexes

Titanium has five molecules of DMSO and one of oxygen, thus having the usual coordination with d^{2}sp^3 configuration for octahedral arrangement of the ligands. Zirconium in the heated and parent complexes is seven coordinated with six ligands of DMSO and one of oxygen. It is quite possible that the arrangement is face centred trigonal-biprism with the oxygen of zirconyl at the centre of one of the square faces, similar to (NbF$_7$)$^{2-}$ and (TaF$_7$)$^{2-}$ ions, with d^{4}sp^2 hybridization. Thorium complexes have one of the usual six coordinate structures with d^{2}sp^3 hybridization.

Acknowledgement—The authors are thankful to Prof. M. R. A. RAO for his interest in the work.

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[20] B. J. HATHAWAY and A. E. UNDERHILL, *J. Chem. Soc.* 653 and 3709 (1960).

[21] S. D. ROSS, *Spectrochim. Acta* **18**, 1055 (1961).