

## Synthesis & Characterisation of Some Bimetallic Derivatives of Dioxouranium(VI) Dialkyldithiophosphates [UO<sub>2</sub>(dtp)<sub>2</sub>]

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Received 11 May 1987; revised 14 September 1987;  
rerevised and accepted 23 November 1987

Several new UO<sub>2</sub>(dtp)<sub>2</sub> complexes and their bimetallic derivatives with Hg(II), Cd(II) and Ag(I) acceptors have been prepared. The structures of the complexes have been determined through various physicochemical studies. In bimetallic derivatives, coordination from one of the sulphur atoms of UO<sub>2</sub>(dtp)<sub>2</sub> to the soft metal acceptors is concluded.

In recent years, metal<sup>1,2</sup> and organometal<sup>3,4</sup> dithiophosphates have attracted much attention, but only a single report has appeared on the corresponding oxometal derivatives<sup>5</sup>. This note reports the synthesis and characterisation of some new dioxouranium(VI) dithiophosphates and their adducts with some soft acceptors such as Hg(II), Cd(II) and Ag(I). This study, for the first time reports coordination from the lone pair of the sulphur atom of dithiophosphates, initially bonded to dioxouranium moiety in the parent compounds.

Dioxouranium(VI) acetate (BDH) was converted to UO<sub>2</sub>(OH)<sub>2</sub> by interaction with aqueous ammonium hydroxide. Phosphorus pentasulphide (BDH), alcohols, 2,2-dimethoxypropane/ and triethyl orthoformate (all Aldrich) were distilled/recrystallised before use. The solvents were purified by standard methods. All reactions were carried out in an atmosphere of dry nitrogen.

### Preparation of dioxouranium(VI) bis(dialkyldithiophosphates)

The title compounds were prepared by the insertion of P<sub>4</sub>S<sub>10</sub> between dioxouranium(VI) hydroxide and alcohols using 2,2-dimethoxypropane or triethyl orthoformate as the solvent according to following equation,



(R = as in Table 1)

In a representative experiment, to a mixture of freshly prepared dioxouranium(VI) hydroxide (10 mmol) and P<sub>4</sub>S<sub>10</sub> (5 mmol) suspended in 2,2-dimethoxypropane (50 ml) was added slowly methanol (40 mmol) with constant stirring, over a period of 4 hr. The mixture was refluxed when P<sub>4</sub>S<sub>10</sub> went into solution. Dioxouranium(VI) bis(dimethyldithiophosphate) was separated either by keeping in a deep freeze or by the addition of excess of hexane. The product was washed with hexane-ether mixture and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

Identical products were obtained by the reaction of dioxouranium(VI) acetate with sodium salt of dimethyldithiophosphoric acid in methanol at room temperature.

### Reaction of dioxouranium(VI) bis(dimethyldithiophosphates) with Hg(II), Cd(II) and Ag(I) salts

In a typical experiment, a mixture of a solution of dioxouranium(VI) bis(dimethyldithiophosphate) (10 mmol) in methanol and HgCl<sub>2</sub> (25 mmol) in acetone was stirred at room temperature for about 4 hr. The precipitated product was filtered, washed with acetone/methanol several times and finally with diethyl ether. The product was dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

Table 1—Analytical Data of Dioxouranium Bis(Dialkyldithiophosphates)

Dithiophosphate (m.p., °C)	Yield† (%)	Found % (Calc.)			
		U	C	H	S
UO <sub>2</sub> [S(S)P(OCH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (> 240)	88	40.6 (40.7)	8.2 (8.4)	2.0 (2.0)	21.8 (21.9)
UO <sub>2</sub> [S(S)P(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> (198(d))	86	37.1 (37.1)	15.0 (15.0)	3.1 (3.1)	19.9 (20.0)
UO <sub>2</sub> [S(S)P(OC <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ] <sub>2</sub> (196(d))	90	34.1 (34.1)	20.6 (20.7)	4.0 (4.0)	18.2 (18.4)
UO <sub>2</sub> [S(S)P(OC <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ] <sub>2</sub> (> 240)	85	34.1 (34.2)	20.6 (20.7)	3.9 (4.0)	18.3 (18.4)
UO <sub>2</sub> [S(S)P(OC <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ] <sub>2</sub> (205(d))	84	31.6 (31.6)	25.5 (25.5)	4.7 (4.8)	17.2 (17.0)

†Through insertion reaction.

Table 2—Analytical Data of Molecular Adducts of Dioxouranium Bis(Dimethyldithiophosphates)  $2M'X_2$  or  $2MX$ 

Adduct (m.p., °C)	Found % (Calc.)					
	U	Metal Hg/Ag/Cd	C	H	N	S
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2HgCl_2$ (> 240)	21.1 (21.1)	35.4 (35.5)	4.2 (4.2)	1.0 (1.0)	—	11.3 (11.4)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2Hg(SCN)_2$ (195(d))	19.5 (19.6)	32.8 (32.9)	7.8 (7.9)	0.9 (1.0)	4.5 (4.6)	21.0 (21.0)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2CdCl_2$ (> 240)	28.3 (28.3)	26.6 (26.8)	5.6 (5.7)	1.4 (1.4)	—	15.2 (15.2)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2AgSCN$ (200(d))	25.9 (26.0)	23.4 (23.6)	7.8 (7.8)	1.4 (1.5)	3.0 (3.0)	20.8 (21.0)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2Hg(OCOFC_3)_2$ (171(d))	16.5 (16.6)	27.8 (27.8)	×	×	×	8.8 (8.9)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2Hg(OClO_3)_2$ (†)	17.1 (17.2)	28.8 (28.9)	×	×	×	9.2 (9.3)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2AgOClO_3$ (†)	23.8 (28.8)	21.5 (21.6)	×	×	×	12.7 (12.8)
$UO_2[S(S)P(OCH_3)_2]_2 \cdot 2AgOCOFC_3$ (190(d))	23.1 (23.2)	21.0 (21.0)	×	×	×	12.4 (12.5)

†Explodes before melting. \*Due to explosive character or presence of fluorine, analysis of C, H, N was not possible.

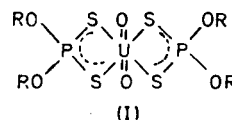
Similar adducts were prepared using  $Hg(SCN)_2$ ,  $Hg(OCOFC_3)_2$ ,  $Hg(ClO_4)_2$ ,  $CdCl_2$ ,  $AgSCN$ ,  $Ag(ClO_4)$ ,  $AgOCOFC_3$  as acceptors (Table 2).

Metal contents and sulphur were determined by the reported methods<sup>6</sup>. Semi-micro estimation of C, H and N and recording of infrared spectra in the range  $4000-200\text{ cm}^{-1}$  were carried out at CDRI, Lucknow. The molar conductance values were measured at room temperature by a Phillip's magic eye conductivity bridge model PR9500 using a diptype conductivity cell. Magnetic susceptibilities were determined at room temperature by Gouy's method.

The elemental analyses (Table 1) indicate 1:2 (metal: dithiophosphate) stoichiometry for the complexes. The compounds are yellow-green solids, soluble in common organic solvents. The conductance data in DMSO ( $10-20\text{ ohm cm mol}^{-1}$ ) and acetonitrile ( $70-90\text{ ohm cm mol}^{-1}$ ) show their non-electrolytic nature though in the latter solvent considerable dissociation seems to occur. Magnetic measurements indicate that the complexes are diamagnetic.

In the IR spectrum of dioxouranium(VI) bis-(dimethyldithiophosphate), a strong band occurring in the region  $680 \pm 2\text{ cm}^{-1}$  has been assigned to  $\nu P=S$ . It suggests chelating behaviour of dithiophosphate groups<sup>4,7</sup>. Two absorptions around  $1020 \pm 20$  and  $752 \pm 3\text{ cm}^{-1}$  are assigned to  $(P)-O-C$  and  $P-O-(C)$  stretching modes respectively<sup>8</sup>. Two absorptions assigned to  $\nu U=O$  at  $920 \pm 5$  and  $800 \pm 4\text{ cm}^{-1}$  clearly indicate the presence of a linear  $UO_2$  moiety<sup>9</sup>. Conclusive evidence of sulphur to metal bonding is provided by an ab-

sorption appearing at  $378 \pm 2\text{ cm}^{-1}$  assigned to  $\nu(U-S)$  mode<sup>10</sup>. Structure(I) may be proposed for dioxouranium(VI) bis-(dialkyldithiophosphates) in the solid state.

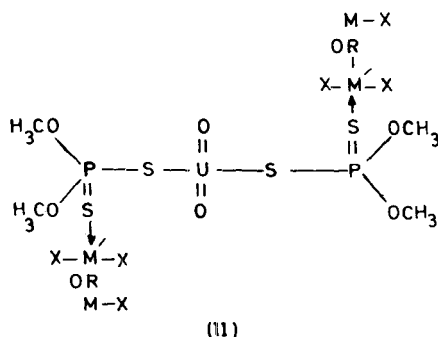


In the IR spectra of molecular adducts, dioxouranium(VI) bis(dimethyldithiophosphates). $2M'X_2$  or  $2MX$  ( $M' = Hg, Cd$ ;  $M = Ag$ ;  $X = Cl, SCN, ClO_4, OCOFC_3$ ) two strong absorptions located at  $610$  and  $530\text{ cm}^{-1}$  are assigned to  $\nu(P=S)$  and  $\nu(P-S)$ . These indicate the presence of unidentate dialkyldithiophosphate groups. This observation was supported by the shift of  $\nu(P)-O-C$  and  $\nu P-O-(C)$  to higher wavenumbers ( $1045 \pm 5$  and  $840 \pm 2\text{ cm}^{-1}$  respectively). Due to formation of a new coordination bond considerable electron drift from R takes place resulting in increase in bond orders of  $C-O$  and  $P-O$ .

The dioxouranium(VI) associated modes of vibration remain unaltered in the adducts. Stretching absorptions due to  $Hg-S$ ,  $Cd-S$ , and  $Ag-S$  could not be identified since they lie beyond the recording range of the instrument employed. The thiocyanate group is S-bonded since  $\nu C \equiv N$ ,  $\nu C=S$  and  $\delta NCS$  appear at  $2060$ ,  $730$  and  $460\text{ cm}^{-1}$  respectively<sup>11</sup>. The trifluoroacetate groups are unidentate<sup>12</sup> since  $\nu_{as}OCO$  and  $\nu_{sy}OCO$  appear at  $1690$  and  $1430\text{ cm}^{-1}$ , re-

spectively, with  $\Delta\nu_{\text{OCO}} = 260 \text{ cm}^{-1}$ . The perchlorate group is unidentately coordinated as  $\nu_{\text{Cl-O}}$ ,  $\nu_{\text{ClO}_3}$ ,  $\delta_{\text{asClO}}$ ,  $\delta_{\text{sClO}_3}$  and  $\delta_{\text{asClO}_3}$  are located at 910, 1040, 1130, 690 and  $620 \text{ cm}^{-1}$  respectively<sup>13</sup>.

It is thus concluded that one of the sulphur atoms of the dialkyldithiophosphate groups in  $\text{UO}_2(\text{dtp})_2$  is coordinated to the soft metal atom giving rising to molecular adducts. On the basis of above evidence, structure(II) may be proposed for dioxouranium(VI) bis(dimethyldithiophosphates).  $2\text{M}^+\text{X}_2$  or  $2 \text{MX}$ .



In the adducts, Hg(II) and Cd(II) are tricoordinated<sup>14</sup> and Ag(I) possesses a coordination number of two<sup>15</sup>.

The authors are thankful to Prof. T N Srivastava (Retd. Emeritus Scientist, CSIR) for valuable suggestions. Financial assistance from UGC is gratefully acknowledged.

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