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Metal Complexes of Phosphinic Acids: Part XIII[*]—Dithiophosphinic Acid Complexes of UO_2(VI) & In(III)

P. N. MOHAN DAS, K. DIEMERT & W. KUCHEN[†]

Institut für Anorganische Chemie, Universität Düsseldorf, Universitätsstr 1,4000 Düsseldorf, West Germany

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UO_2(VI) and In(III) complexes of dimethyldithiophosphinic acid and the In(III)-complex of *p*-methoxyphenyl-methyldithiophosphinic acid have been prepared. Their properties and structures have been studied using elemental analysis, molecular weight determinations, IR, UV, mass, nmr, magnetic studies, thermal analysis etc. It is found that these complexes having the formula InL_3 and UO_2L_2 (where L is a deprotonated bidentate ligand molecule) form neutral complexes to which octahedral structures have been assigned. The stability constants of the uranyl complex have been determined potentiometrically in 20% dioxan-water medium at an ionic strength of $0{\cdot}2M_2$ (KNO_3). Log β_2 values is found to be 5·58.

DIPHENYLDITHIOPHOSPHINIC acid has been used as a complexing agent by many workers[1-7]. Kuchen *et al.*[8-10] have reported the studies of the metal complexes of dialkyldithiophosphinic acids. Metal complexes of *p*-methoxyphenyl-methyl dithiophosphinic acid have been investigated by Diemert[11]. A survey of the literature shows that the UO_2(VI) and In(III) complexes of dimethyldithiophosphinic acid (dmdtp) and In(III) complex of *p*-methoxyphenyl-methyl dithiophophinic acid (mpmdtp) have not been studied. This prompted us to prepare and characterize UO_2(VI) and In(III) complexes of dmdtp and In(III) complex of mpmdtp. The stability constants of the UO_2-dmdtp complex have also been determined in 20% dioxan-water medium.

Materials and Methods

All the chemicals used were of AR grade. Sodium salts of the ligands, $(CH_3)_2PS_2Na.2H_2O$ (ref. 12) and (p-$CH_3OC_6H_4$) $CH_3PS_2Na.2H_2O$ (ref. 13) were prepared as described in the literature. Dimethyldithiophosphinic acid [$(CH_3)_2P(S)SH$] was prepared from the sodium salt as follows:

Dry HCl gas was bubbled for 4 hr through a suspension of the sodium salt (20 g) in absolute dioxan (200 ml) at 0°. NaCl that precipitated out was filtered off, the filtrate concentrated under reduced pressure and the acid precipitated by the addition of absolute ether. The white crystals formed were washed with ether and dried in vacuum, m.p. 48-50° (lit.[14] m.p. 47-50°).

Preparation of the complexes: *UO_2(dmdtp)$_2$* — Concentrated aqueous solutions of uranyl nitrate and the sodium salt of dmdtp were mixed in the molar ratio of 1:3 and warmed at 50° to 60°, for a few minutes. The solution which turned red was repeatedly extracted with small portions of ether. The ether extract was dried (anhyd. $MgSO_4$), concentrated under reduced pressure and allowed to crystallize. The reddish yellow crystals separated out were filtered, washed with ether and dried over P_2O_5 in high vacuum at 85°. The dry crystals were brownish yellow in colour, yield ≈60%.

In(dmdtp)$_3$ and In(mpmdtp)$_3$— Aqueous solutions of In(III) chloride and sodium salt of the ligand were mixed in the molar ratio of 1:3, with continuous stirring. White precipitate, appeared instantaneously, was filtered and washed well with water. For purification In(dmdtp)$_3$ was recrystallized from chloroform and In(mpmdtp)$_3$ was precipitated from an acetone solution by the addition of ether. Both were white crystalline powders; yield ≈75%.

Determination of stability constants — The following solutions were prepared and titrated against standard NaOH solution: (i) 0·2 ml of $0{\cdot}168M$ $HClO_4$+10 ml of $1{\cdot}0M$ KNO_3; (ii) solution (i)+25 ml of $5\times10^{-3}M$ dmdtpH; and (iii) solution (ii)+5 ml of $5\times10^{-3}M$ uranyl nitrate. The total volume in all the cases was adjusted to 50 ml with dioxan and water so that the medium contained 20% dioxan (v/v). The *p*H value corrections were done as described by Van Uitert and Haas[15].

Physical measurement — Elemental analysis were done according to the usual methods. Molecular weights were determined using a vapour pressure osmometer (Knauer, Berlin), in chloroform at different concentrations. Visible and UV spectra were recorded on a Beckman DK-2A spectrophotometer against solvent as blank. IR spectra (as KBr pellets), mass spectra and ^{1}H NMR spectra were recorded on a Perkin-Elmer model 521 IR spectrophotometer, a Varian MAT model 311 A mass spectrometer, introducing the samples through a direct inlet system, and a Bruker HX-60 spectrometer at 60 MHz (in deutero solvents containing internal tetramethylsilane as reference) respectively. Magnetic studies (Gouy method) were done using a Bruker-Physik AG magnet B-E 10 in combination with a Sartorius microbalance 4107. A Mettler thermoanalyser T A-1 was used for thermal studies. Potentiometric studies

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[*] Part XII, P. N. Mohan Das, W. Kuchen, H. Keck & G. Hägele, *J. inorg. nucl. Chem.*, **39** (1977).

[†] Author to whom all correspondence may be addressed.

TABLE 1 — VISIBLE AND UV SPECTRAL DATA OF THE COMPLEXES

Compound	Wavelength (nm)	Energy (kK)	ε
$UO_2(dmdtp)_2$	404·0	24·7525	2929·08 CT
	229·5	43·573	4193·22 CT
In $(dmdtp)_3$	270·4	36·9822	6152·13 CT
	231·0	43·290	11470·41 CT
In $(mpmdtp)_3$	328·0	30·4878	896·86
	205·0	48·7805	114991·48 CT

CT = charge transfer.

were done with a Metrohm Titriskop E 516 *p*H meter with combined electrodes.

Results and Discussion

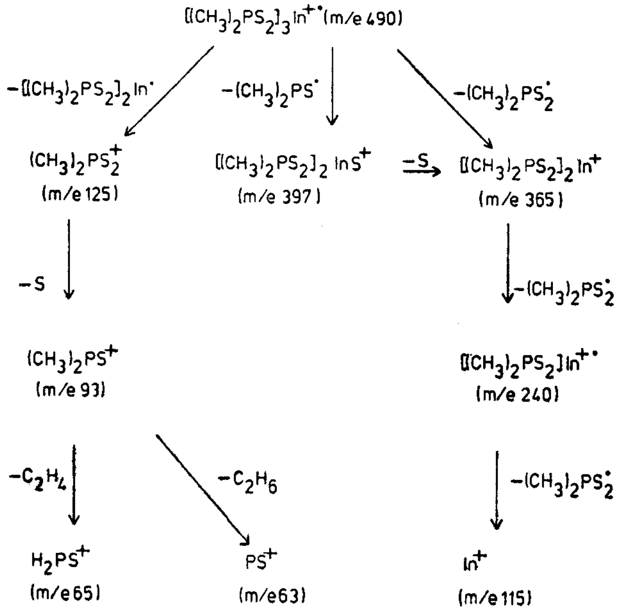
Uranyl complex is readily soluble in common organic solvents like methanol, ethanol, dioxan, chloroform, etc. Indium complexes are easily soluble in hot chloroform, dioxan, benzene, etc., but sparingly soluble in ethanol, ether, carbon tetrachloride, etc. Uranyl complex on heating changed colour slowly from yellow to red, brown and finally black and decomposed above 240°. $In(dmdtp)_3$ turned to pale yellow colour on heating and melted at 212-13°. The $In(mpmdtp)_3$ melted at 167-68°.

The elemental analysis data are given below: $UO_2(dmdtp)_2$ (Found: C, 11·58; H, 2·62; S, 24·41: P, 11·34. Required: C, 9·23; H, 2·3; S, 24·65; P, 11·91%). The analysis for carbon was always high by 1-2%. $In(dmdtp)_3$ (Found: C, 14·47; H, 3·65; S, 38·91; P, 18·40; In, 23·16. Required: C, 14·69; H, 3·67; S, 39·25; P, 18·96; In, 23·42%). $In(mpmdtp)_3$ (Found: C, 38·35; H, 4·06; S, 25·30; P, 11·66; In, 14·62. Required: C, 37·5; H, 3·92; S, 25·12; P, 12·13; In, 14·98%).

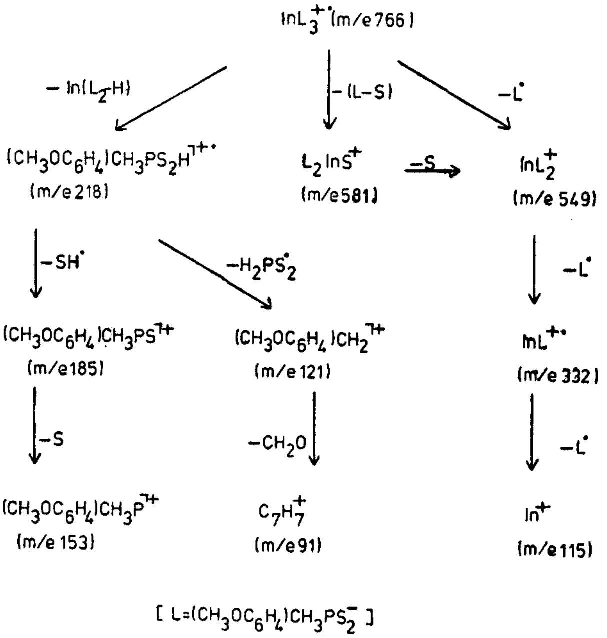
The molecular weights of $UO_2(dmdtp)_2$, $In(dmdtp)_3$ and $In(mpmdtp)_3$ were independent of the concentrations employed and were 551, 494 and 772 against theoretical values of 520·0, 490·1 and 766·0 respectively, indicating absence of molecular association or dissociation.

IR spectra — The IR spectra* of the complexes and the ligands show following significant features: The weak band at 2360 in dmdtpH and the broad medium band at 2260-2320 in mpmdtpH due to νS-H disappear in the complexes showing the absence of free S-H group. The strong bands at 450 and 580 in dmdtpH are shifted to 495 and 590 in UO_2(VI) and to 488 and 585 in In(III) complexes while those at 500 and 600 in mpmdtpH shift to 520 and 598 in In(III) complex. In the case of dmdtp complexes the νM-S are seen at 385 and 410 in UO_2 complex and at 295 in In complex. The strong band at 922 in the case of UO_2(VI)-dmdtp may be assigned to the ν_3 of the U-O group[16]. The visible and UV spectral data of the complexes are given in Table 1.

Mass spectra† — The mass spectrum of the uranium complex could not be recorded as elemental sulphur got deposited from the complex during the studies. The mass spectral data of the In complexes indicate that the base peaks in the spectra of the complexes are due to the very stable ion ML_2^+ (L=dmdtp or mpmdtp molecule) resulting from the radical elimination of one L· from the molecular ion. Other strong peaks observed are given by the fragments $(CH_3)_2PS_2^+$ and In^+ in $In(dmdtp)_3$ while by $(CH_3OC_6H_4)CH_3PS^+$ in $In(mpmdtp)_3$. The fragmentation patterns are shown in Schemes 1 and 2.



Scheme 1 — Fragmentation pattern of $In[(CH_3)_2PS_2]_3$



Scheme 2 — Fragmentation pattern of $In[(p\text{-}CH_3OC_6H_4)CH_3PS_2]_3$

Magnetic measurements — These studies show that all the complexes are diamagnetic in nature which is in agreement with the U(VI) ($5f^0$) and In(III) ($4d^{10}$)

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*νmax values in cm^{-1}.

†For detailed IR and mass spectra contact the Senior author Prof. W. Kuchen.

ions. The diamagnetism of In$(dmdtp)_3$ and In$(mpmdtp)_3$ were found to be $-199 \cdot 49 \times 10^{-6}$ cm^3 $mole^{-1}$ at 292K and $-473 \cdot 72 \times 10^{-6}$ cm^3 $mole^{-1}$ at 294·4K respectively.

NMR spectra — The ^1H NMR spectra of all these complexes showed the expected signals. For the $UO_2(dmdtp)_2$ and In$(dmdtp)_3$ complexes doublets due to proton-phosphorus coupling ($^2J_{PCH} \approx 13$ Hz) are observed. The δ values were found to be 2·25 ppm ($CHCl_3$) and 2·15 ppm (CD_3COCD_3) for UO^2 and In complexes respectively while $\delta = 2 \cdot 12$ ppm. (CD_3COCD_3) for $(CH_3)_2PS_2H$. A non-equivalence of the methyl groups could not be detected in this temperature region. The In (mpmdtp)$_3$ showed in the aromatic region the complex signals of a $[AM]_2X$ system similar to the pure ligand absorption discussed elsewhere[13]. All the absorptions $\delta_{ortho} = 7 \cdot 9$ ppm, $\delta_{OCH_3} = 3 \cdot 8$ ppm, $\delta_{meta} = 6 \cdot 9$ ppm, and $\delta_{CH_3} = 2 \cdot 4$ ppm, are only slightly shifted.

Thermal behaviour — It was observed that the dry uranium complex on keeping in contact with moisture absorbed water giving red crystals which on heating at 90° *in vacuo* gave back the brownish yellow crystals. The number of water molecules absorbed was found to be one by loss of weight (3·53%) on thoroughly drying at 95° over P_2O_5. Loss of weight on TG experiment up to 150°≈3%. The theoretical loss of weight for one water molecule is 3·46%.

On continuous exposure to highly humid atmosphere for a few weeks, these red crystals absorbed one more water molecule which was determined by TG (Loss of wt found up to 150°=6·3%. Theoretical wt for 2 water molecules =6·47%).

A combined TG/DTA experiment of the monohydrated and the water-free form of the uranyl complex established a remarkable influence of the experimental conditions on its thermal behaviour. In an atmosphere of flowing nitrogen containing traces of oxygen and at a heating rate of 2°/min the TG curve (Fig. 1B) showed a weight loss of 3% between 80° and 160° which is an endothermic process, due to the loss of one water molecule in the case of the monohydrated form. With increasing temperatures there was an increase in weight of about 4·5% with reference to the initial weight. This was a strong exothermic reaction as shown by DTA (Fig. 1). There was no further increase in weight after about 220° and then the normal thermal degradation process started (220-320°: weight loss =3·0%; 320-420°: weight loss =15·0%). The product after the exothermic reaction up to 220° showed no P-S absorption bands in the IR spectrum but a new very strong and broad band appeared at 1070-1090, possibly due to νP-O.

Experiments under high vacuum (10^{-4}-10^{-5} mm Hg) and in an atmosphere of extremely pure nitrogen showed no exothermic reaction at this range. The complex was stable up to 200° and this product showed all the IR absorption bands of the original dry complex. An exothermic reaction with increase in weight in this temperature range, similar to that mentioned above, was observed when this experiment was done under flowing air. A change from aluminium to aluminium oxide crucible did not have any effect on the nature of the reaction.

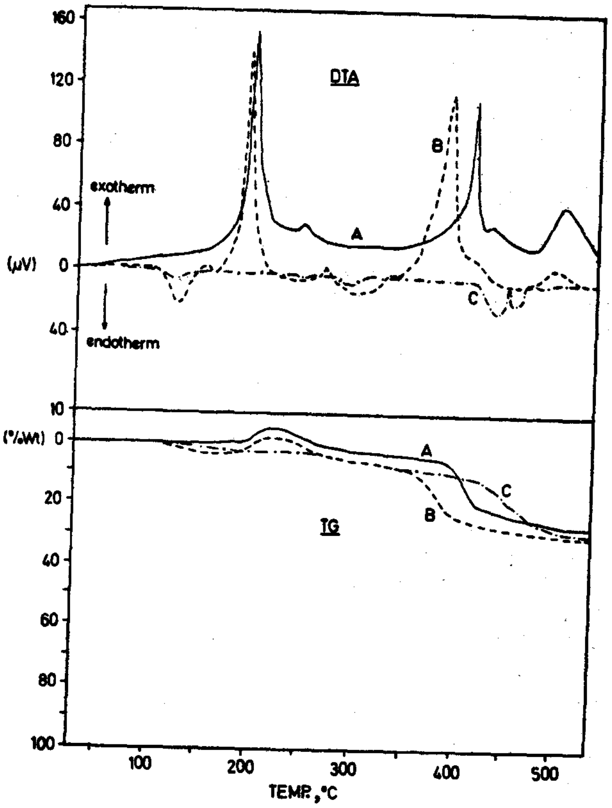


Fig. 1 — DTA and TG profiles [(A) Studies of $UO_2(dmdtp)_2$ in air; (B) studies of $UO_2(dmdtp)_2 \cdot 1\ H_2O$ in air and impure nitrogen; and (C) studies of $UO_2(dmdtp)_2$ in pure nitrogen and in high vacuum]

Obviously there is an uptake of oxygen by the uranium complex at elevated temperatures, so far as not observed in other dithiophosphinates investigated by us. The nature of the reaction in which the sulphur in the ligand seems to be exchanged for oxygen is not yet clear.

In$(dmdtp)_3$ on heating at a rate of 4°/min in nitrogen atmosphere remained constant in weight up to 213°, then melted and up to 380°, 70·0% of the weight was lost. The weight was practically constant from 380° to 500°. The complete destruction of the complex might be taking place from 213° to 380°.

TG experiment on In$(mpmdtp)_3$ showed constant weight up to 290° with a melting point of 167° and then the loss of weight took place in three stages, from 290° to 370°=23%, 370° to 440°=17% and upto 500°=7% due to the thermal decomposition of the complex.

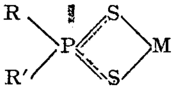
Stability constants — For stability constant determinations the ligand solutions were titrated against standard NaOH solution in the absence and presence of the metal ions at 20°±0·1°C, $\mu = 0 \cdot 2$ (KNO_3). The acid dissociation constant of the ligand $(CH_3)_2PS_2H$ (dmdtpH) was determined by the method of Irving and Rossotti[17]. Formation curve for proton-ligand system was drawn between $\bar{n}_H$ and pH, where $\bar{n}_H$ is the average number of protons attached per ligand molecule. The pK value was directly read from the formation curve. It was also calculated using the equation

$$\log\ K_1^H = \log \frac{\bar{n}_H}{\bar{n}_{H-1}} + p\mathrm{H}$$

The average pK value of dmdtpH was found to be 2·79 in 20% dioxan-water medium.

The ligand neutralizes one equivalent of the base to yield one buffer region in the potentiometric titration curve indicating its monobasic nature. A fall in pH was observed on adding the uranyl nitrate solution to the ligand, which indicated the formation of a complex. During titration the metal hydroxide got precipitated at $p\text{H} \approx 4{\cdot}7$.

The formation curve for the metal-ligand system was drawn between $\bar{n}$ and pA, the values of which were calculated by the method of Irving and Rossotti[17].



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log K_1 and log K_2 values were directly read from the formation curve at $\bar{n}=0{\cdot}5$ and 1·5. The log K_1, log K_2 and log β_2 values were found to be 2·82, 2·75 and $5{\cdot}58 \pm 0{\cdot}01$ respectively. As there was not much difference between the log K_1 and log K_2 values, no other methods were applied for the refinement of the values. As a comparative study of the stabilities was not in our present interests, we did not carry out the stability constant determinations of the In complexes.

From these data it is clear that the UO_2(VI) forms 1:2 complex $UO_2[(CH_3)_2PS_2]_2$ and In(III) forms complexes of the type ML_3 where L is a dmdtp or mpmdtp molecule. The bonding nature is shown in structure (I).

In all these cases octahedral structures can be assigned to the complexes, the O=U=O group in the uranium compound lying perpendicular to the plane containing the 4 sulphur atoms of the ligand[18].

Acknowledgement

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