

Spectral Studies on Oxouranium(V) Compounds

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Received 14 April 1975; accepted 31 July 1975

Compounds of oxouranium(V) of the type, $(\text{BH})_2\text{UOCl}_5 \cdot \text{B}$ (B=pyridine, quinoline, isoquinoline, α -picoline or β -picoline) have been synthesized and characterized on the basis of IR, reflectance and ESR spectra and magnetic susceptibilities.

THE oxouranium(V) complex, $(\text{C}_5\text{H}_5\text{NH})_2\text{UOCl}_5$, has been shown¹ to be an equimolar mixture of complexes UCl_6^{2-} and $\text{UO}_2\text{Cl}_4^{2-}$. Oxochloro complexes of U(V) of the general formula L_2UOCl_5 have also been reported recently²⁻⁵. Only two addition compounds having the formulae, $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UOCl}_5 \cdot \text{phthalazine}$ ³ and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UOCl}_5 \cdot \text{bis}(1,10\text{-phenanthroline})$ ³ have been characterized by spectral measurements. In this paper are reported the preparation and characterization of the oxochloro complexes of U(V) of the type, $(\text{BH})_2\text{UOCl}_5 \cdot \text{B}$ (B = pyridine, quinoline, isoquinoline, α -picoline or β -picoline).

UCl_5 was prepared by refluxing UO_3 with SOCl_2 (ref. 6). Pyridine, quinoline, isoquinoline, α -picoline and β -picoline (BDH, AR) were purified as reported in literature⁶. Petroleum ether was dried and kept over sodium.

For the preparation of the compounds the undried nitrogen base, cooled in an ice-bath, was added to a solution of UCl_5 in SOCl_2 kept below 0° . The base and UCl_5 were taken in a molar ratio of 3:1. Traces of water present in these bases were sufficient to hydrolyse UCl_5 to UOCl_5^{2-} . Reddish brown solids separated out on the addition of dry petroleum ether. The compounds were washed with dry petroleum ether and dried *in vacuo*. Uranium in the compounds was estimated volumetrically⁶. Chlorine was estimated by Volhard's method and nitrogen was estimated by micro-analytical methods. The analytical results are given in Table 1.

IR, reflectance and ESR spectra were recorded as described previously⁶. Magnetic susceptibility

measurements were made at room temperature using a Gouy type balance.

The elemental analyses of the oxouranium(V) complexes conform to the molecular formula, $(\text{BH})_2\text{UOCl}_5 \cdot \text{B}$. The compounds are stable in dry atmosphere and disproportionate into U(IV) and U(VI) species in the presence of moisture. On heating to $\sim 550^\circ$, the complexes decompose to give U_3O_8 .

IR spectra (nujol) of the complexes show a very strong band at $\sim 2840 \text{ cm}^{-1}$ or a broad band in the range $2800\text{-}2900 \text{ cm}^{-1}$ which may be due to B-H^+ (ref. 5, 7). A strong band observed at $\sim 1535 \text{ cm}^{-1}$ could be due to the lowest electronic transition, $\Gamma_7 \rightarrow \Gamma_8$ (from Γ_8 in O_h) (ref. 3) but definite assignment cannot be made since pyridine ring vibrations also occur in the same region. A very strong band present in the range $910\text{-}915 \text{ cm}^{-1}$ in these complexes has been assigned to U=O stretching^{2,3}. The other IR bands in these complexes indicate that the base molecule is not loosely bound, but is in the coordination sphere of oxouranium(V).

Reflectance spectra of $(\text{C}_5\text{H}_5\text{NH})_2\text{UOCl}_5 \cdot \text{C}_5\text{H}_5\text{N}$, $(\text{C}_9\text{H}_7\text{NH})_2\text{UOCl}_5 \cdot \text{quinoline}$ and $(\text{C}_9\text{H}_7\text{NH})_2\text{UOCl}_5 \cdot \text{isoquinoline}$ show a sharp band at 600 nm. This band is due to the transition $\Gamma_7 \rightarrow \Gamma_8$ which occurs at a much higher energy in the present complexes compared to its position at 870 nm in UCl_5 . This is in agreement with the theoretical predictions³. However, some disproportionation takes place during the reflectance spectra measurements. This is shown by the appearance of bands at 640 and 760 nm which correspond to U(IV).

ESR spectra of $(\text{C}_5\text{H}_5\text{NH})_2\text{UOCl}_5 \cdot \text{C}_5\text{H}_5\text{N}$, $(\text{C}_9\text{H}_7\text{NH})_2\text{UOCl}_5 \cdot \text{quinoline}$ and $(\text{C}_9\text{H}_7\text{NH})_2\text{UOCl}_5 \cdot \text{isoquinoline}$ show a broad signal at 5930, 5915, 5880 G respectively at 80°K giving g values of 1.13, 1.13 and 1.14 ± 0.005 respectively. These g values are in agreement with the calculated and experimental values in the range 1.04-1.12 reported for oxochloro complexes³⁻⁵.

Magnetic moments of the pyridinium, quinolinium, isoquinolinium and α -picolinium complexes are 1.50, 1.53, 1.65 and 1.80 B.M. respectively at room temperature, which may be compared with the value of 1.56 B.M. expected for a $6d^1$ configuration and 1.73 B.M. for spin-only paramagnetism.

Reflectance and ESR spectra indicate that coordination number around U(V) remains the same as in UOCl_5^{2-} . Therefore, extra base molecule is in the coordination sphere probably replacing one Cl^- from UOCl_5^{2-} (ref. 3).

TABLE 1 — ANALYTICAL DATA FOR OXOURANIUM(V) COMPLEXES

Complex	Found (%)			Calc. (%)		
	U	Cl	N	U	Cl	N
$(\text{PyH})_2\text{UOCl}_5 \cdot \text{Py}$	35.00	26.21	6.15	35.50	26.47	6.26
$(\text{QH})_2\text{UOCl}_5 \cdot \text{Q}$	28.86	21.33	5.00	29.01	21.63	5.12
$(\text{IQH})_2\text{UOCl}_5 \cdot \text{IQ}$	28.75	21.42	5.05	29.01	21.63	5.12
$(\alpha\text{-picH})_2\text{UOCl}_5 \cdot \alpha\text{-pic}$	33.17	24.76	5.80	33.41	24.91	5.89
$(\beta\text{-picH})_2\text{UOCl}_5 \cdot \beta\text{-pic}$	33.07	24.63	5.85	33.41	24.91	5.89

Py=pyridine, Q=quinoline, IQ=isoquinoline.

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Complexes of Cu(II) & Hg(II) with 1,3-Diamino- & 1,4-Diamino-benzenes

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Received 6 October 1974; accepted 12 May 1975

Preparation and characterization of Cu(II) and Hg(II) complexes with *m*- and *p*-diaminobenzenes (MDAB and PDAB respectively) are reported. With MDAB, Cu(II) forms only 1:1 (metal: ligand) complexes of the type $\text{CuX}_2(\text{MDAB})$, where $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$. With PDAB, complexes of the type $\text{CuX}_2(\text{PDAB})$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$) and also $\text{CuBr}_2(\text{PDAB})$ and $\text{Cu}(\text{NO}_3)_2(\text{PDAB})_3$ are formed. Hg(II) forms the complexes $\text{HgCl}_2(\text{MDAB})_2$ and $\text{HgCl}_2(\text{PDAB})$. From the UV, magnetic moment and far IR data a polymeric octahedral structure has been proposed for the 1:1 complexes. TGA data are also reported.

IN continuation of our investigation on the complexes of *o*-, *m*-, and *p*-diaminobenzenes (ODAB, MDAB and PDAB respectively) with transition metal ions, we report in this note the results of our studies on Cu(II) and Hg(II) complexes of MDAB and PDAB which have not been reported in detail earlier.

Unlike ODAB which can function both as a chelating and a bridging ligand^{1,2}, MDAB and PDAB are not expected to form chelates. In com-

pounds were the latter ligands function as bidentate, it would be expected that the nitrogen atoms will coordinate to different metal centres, thereby facilitating the formation of polynuclear complexes.

MDAB and PDAB were purified through crystallization from abs. EtOH. All other reagents were freshly distilled before use. Anhydrous metal salts were employed for preparation of the complexes.

$\text{CuCl}_2(\text{MDAB})$ and $\text{CuCl}_2(\text{PDAB})$ — These complexes were prepared by adding a solution of the respective diamine (1.0 g) in EtOAc (30 ml) to a solution of anhyd. CuCl_2 (0.6 g) in abs. EtOH (10 ml). The precipitated complexes were $\text{CuCl}_2(\text{MDAB})$ (dark violet) and $\text{CuCl}_2(\text{PDAB})$ (dark brown). The latter complex when prepared by the method of Barvinok *et al.*³ showed partial decomposition during boiling and also showed some differences in IR spectrum.

$\text{CuBr}_2(\text{MDAB})$, $\text{CuBr}_2(\text{PDAB})$, $\text{Cu}(\text{NO}_3)_2(\text{MDAB})$ and $\text{Cu}(\text{NO}_3)_2(\text{PDAB})_3$ were also prepared by the same procedure as above except that the appropriate amounts of the respective copper salts were used in place of CuCl_2 . A molar ratio of 1:2 (copper:ligand) was used for the preparation of $\text{CuBr}_2(\text{PDAB})_2$ and $\text{Cu}(\text{NO}_3)_2(\text{PDAB})_3$ complexes.

$\text{HgCl}_2(\text{MDAB})_2$ and $\text{HgCl}_2(\text{PDAB})$ — These were prepared by a similar procedure as above. Varying the metal to ligand ratios in the reaction mixture did not affect the stoichiometry of the isolated products. The pale white compounds were washed with ethanol and dried in the oven at 80°.

The chemical analysis and physical properties of the compounds are given in Table 1. Cu(II) forms only 1:1 (metal:ligand) complexes of the type $\text{CuX}_2(\text{MDAB})$. With PDAB, complexes of the type $\text{CuX}_2(\text{PDAB})$ are formed only when stoichiometric quantity of the amine is reacted with copper salt. In the presence of excess amine, CuBr_2 and $\text{Cu}(\text{NO}_3)_2$ form $\text{CuBr}_2(\text{PDAB})_2$ and $\text{Cu}(\text{NO}_3)_2(\text{PDAB})_3$ respectively. Complexes of Cu(II) acetate, sulphate and perchlorate with MDAB and PDAB rapidly decompose yielding compounds of indefinite composition. HgCl_2 forms only 1:2 complex $[\text{HgCl}_2(\text{MDAB})_2]$ with MDAB and 1:1 complex $[\text{HgCl}_2(\text{PDAB})]$ with PDAB irrespective of the solvents

TABLE 1 — PHYSICAL DATA OF THE COMPLEXES

Complex	Colour	N (%)*		μ BM	Λ_M (ohm ⁻¹ cm ² mole ⁻¹)†
		Found	Calc.		
$\text{Cu}(\text{MDAB})\text{Cl}_2$	Dark violet	11.5	11.5	1.81	33.0
$\text{Cu}(\text{MDAB})\text{Br}_2$	Violet brown	8.7	8.5	0.78	45.0
$\text{Cu}(\text{MDAB})(\text{NO}_3)_2$	Brown	18.5	18.9	1.67	108.0
$\text{Hg}(\text{MDAB})_2\text{Cl}_2$	Pale white	11.2(a)	11.5	—	32.6
$\text{Cu}(\text{PDAB})\text{Cl}_2$	Brown	11.6	11.5	1.72	46.7
$\text{Cu}(\text{PDAB})\text{Br}_2$	Dark brown	8.3	8.5	0.67	45.5
$\text{Cu}(\text{PDAB})(\text{NO}_3)_2$	do	19.2	18.9	1.76	78.4
$\text{Cu}(\text{PDAB})_2\text{Br}_2$	Brown	12.8	12.5	1.20	48.9
$\text{Cu}(\text{PDAB})_3(\text{NO}_3)_2$	Deep violet	22.9	23.8	1.34	74.7
$\text{Hg}(\text{PDAB})\text{Cl}_2$	Pale yellow	7.8(b)	7.9	—	41.6

*Satisfactory C and H analyses were also obtained.

†Molar conductivity was measured at 10⁻³M solution in DMF at 25°C.

(a) Found: Cl, 14.2; Hg, 39.9. Calc.: Cl, 14.6; Hg, 40.5%.

(b) Found: Cl, 18.4; Hg, 52.5. Calc.: Cl, 18.7; Hg, 52.8%.

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