

Notes

Complexes of UCl_5 with Methyleneanthrone, Benzalanthrone and Dioxane.

RAM CHAND PAUL, GURDEV SINGH and MANGAL SINGH*
Department of Chemistry, Panjab University, Chandigarh.

Manuscript received 10 June 1976, revised 19 May 1977,
accepted 3 October 1977

SELBIN and coworkers have synthesized and characterized UCl_5 complexes with N, P, As, Bi, O, S, Se and Te donors^{1,2}. We have reported the synthesis and characterisation of UCl_5 complexes with some N and O donors^{3,4,5}. In the present work we report the synthesis of $UCl_5 \cdot 2B$ ($B =$ methyleneanthrone, benzalanthrone and dioxane) complexes. IR, ESR and reflectance spectra and magnetic susceptibilities have been studied to characterize them.

Experimental

UCl_5 was prepared by refluxing UO_3 or UO_2Cl_2 with $SOCl_2$ ^{4,5}. Methyleneanthrone and benzalanthrone were prepared and recrystallized as reported in literature^{6,7}.

$UCl_5 \cdot 2B$ type complexes: Methyleneanthrone, benzalanthrone and dioxane were dissolved in ice cooled $SOCl_2$ and then added to an ice cooled solution of UCl_5 in $SOCl_2$ in 2 : 1 molar ratio. On the addition of petroleum ether dark brown solids in the case of methyleneanthrone and benzalanthrone and deep yellow complex in the case of dioxane got precipitated. These complexes were washed with dry petroleum ether and dried in vacuum.

The analytical results are given in Table 1.

an equimolar mixture of U(IV) and U(VI). Bagnall and coworkers⁸ report that there is a characteristic peak for U(V) in the range 600-900 nm. We have already reported the reflectance spectra of UCl_5 complexes with some nitrogen⁴ and oxygen⁵ donor ligands which record a characteristic peak in the above mentioned range. In the present paper reflectance spectra of $UCl_5 \cdot 2$ methyleneanthrone, $UCl_5 \cdot 2$ benzalanthrone and $UCl_5 \cdot 2$ dioxane have been studied which record strong absorption peaks at 855, 865 and 860 nm respectively.

ESR spectra of $UCl_5 \cdot 2$ -methyleneanthrone, $UCl_5 \cdot 2$ -benzalanthrone, $UCl_5 \cdot 2$ -dioxane and $UCl_5 \cdot 3$ dioxane produce broad signals at $\sim 5925, 5960, 6000$ and 5950 Gauss at $80^\circ K$ and 'g' values are 1.12, 1.13, 1.13 and 1.12 respectively. These 'g' values are comparable to the average 'g' value of ~ 1.1 already reported^{4,5,9} but in contrast to 'g' values of ~ 2.0 reported by Selbin et al^{1,2}. From ESR spectra of UCl_5 complexes it can be inferred that 5f electron in U(V) is not heavily delocalized into the π -antibonding molecular orbitals of the organic ligands.

In the IR spectra of $UCl_5 \cdot 2$ -methyleneanthrone and $UCl_5 \cdot 2$ -benzalanthrone $\nu(C=O)$ from 1650^5 cm^{-1} is lowered to 1590 and 1580 cm^{-1} respectively indicating that oxygen atom of these anthrones coordinates to uranium atom of UCl_5 . The probable coordination number of uranium is seven in these complexes. IR spectra of $UCl_5 \cdot 2$ -dioxane, $UCl_5 \cdot 3$ -dioxane and dioxane resemble each other very closely. Apart from some intensity changes, only noticeable differences are the slightly higher or lower frequencies of some absorption bands for the complexes than for dioxane. The similarity of the

TABLE-1 UCl_5 COMPLEXES WITH OXYGEN BASES

Complex	Analytical results					
	Uranium	Found (%) Chloride	Anthrone	Uranium	Required (%) Chloride	Anthrone
$UCl_5 \cdot 2$ -methyleneanthrone	28.61	21.20	50.25	28.78	21.43	49.80
$UCl_5 \cdot 2$ -benzalanthrone	24.52	18.00	57.15	24.30	18.10	57.60
$UCl_5 \cdot 2$ -dioxane	40.05	30.12	-	40.26	29.98	-

Results and Discussion

$UCl_5 \cdot 2B$ and $UCl_5 \cdot 3$ dioxane complexes are stable in dry and inert atmosphere and disproportionate into U(IV) and U(VI) in the presence of moisture. These complexes are insoluble in common organic solvents but disproportionate in U(IV) and (VI) in polar solvents. Reflectance and ESR spectra have been used to make the distinction of U(V) from

spectra of the complexes and the free ligand have also been previously observed for $SbCl_5 \cdot C_4H_8O_2$ and $MCl_5 \cdot C_4H_8O_2$ ($M = Hg^{2+}, Cd^{2+}, Cu^{2+}$ and Ni^{2+})¹⁰⁻¹². Since there is good evidence that dioxane consists of molecules in the chair configuration in both liquid and solid state, it is probable that the structure of dioxane in these complexes has also chair configuration. Therefore, polymeric structures with chains of metal ions linked through

*Present Address: Department of Chemistry, Guru Nanak Dev University, Amritsar.

dioxane molecules may be proposed for these complexes.

Magnetic susceptibilities of UCl_5 complexes have been studied by various workers¹⁻⁵. Magnetic susceptibilities of UCl_5 , 2-methyleneanthrone, UCl_5 , 2-benzalanthrone and UCl_5 , 2-dioxane have been measured at room temperature only giving μ_{eff} values of 1.81, 1.75, and 1.71 B.M., respectively. These values are very close to the spin value only.

References

1. J. SELBIN, N. AHMAD and M. J. PRIBBLE, *Chem. Commun.*, 1969, 759.
2. J. SELBIN, N. AHMAD and M. J. PRIBBLE, *J. Inorg. Nuclear Chem.*, 1970, 32, 3249.
3. RAM CHAND PAUL, GURDEV SINGH and MANGAL SINGH, *Proc. Chem. Symp.*, 1970, 2, 279; *Chem. Abs.*, 1971, 74, 106694X.
4. RAM CHAND PAUL, GURDEV SINGH and MANGAL SINGH, *J. Inorg. Nuclear Chem.*, 1971, 33, 713.
5. MANGAL SINGH, GURDEV SINGH and RAM CHAND PAUL, *Inorg. Chim. Acta*, 1974, 10, 225.
6. E. B. BARNETT and M. A. MATTHEW, *Ber.*, 1926, 59, 767.
7. J. W. COOK, *J. Chem. Soc.*, 1926, 2165.
8. K. W. BAGNALL, D. BROWN and J. G. H. DU PREEZ, *J. Chem. Soc.*, 1965, 5217.
9. J. SELBIN, J. D. ORTEGO and G. GRITZNER, *Inorg. Chem.*, 1968, 7, 976.
10. P. TARTE and P. A. LAURENT, *Bull. Soc. Chim. Fr.*, 1957, 403.
11. P. J. HENDRA and D. B. POWELL, *J. Chem. Soc.*, 1960, 5105.
12. L. W. DASSCH, *Spectrochim. Acta*, 1959, 726.

Preparation of 4'-Amino-3-carboxy-6-methoxy-diphenyl Sulphide and its Derivatives

H. E. MASTER AND V. V. NADKARNY

Nadkarny-Sacasa Research Laboratory, St. Xavier's College, Bombay-400001

Manuscript received 16 February 1976, revised 14 July 1977, accepted 3 October 1977

3-Mercaptoanisic acid has been obtained by the reduction of 3-chlorosulphonylanisic acid¹ by Gattermann's method² or by hydrolysis of the xanthate derivative of 3-aminoanisic acid³. We have now obtained this compound in 81% yield by reducing 3-chlorosulphonylanisic acid with stannous chloride and hydrochloric acid. It was characterised through some new derivatives, viz. disulphide, ethyl thioether and thioglycollic acid. We also record here the preparation of hitherto unreported 3-carboxy-6-methoxy-4'-nitrodiphenyl sulphide by condensation of the mercaptan with 4-chloronitrobenzene and its reduction product 4'-amino-3-carboxy-6-methoxy-diphenyl sulphide.

*Satisfactory elemental analysis have been obtained for all the compounds reported.

Experimental*

3-Mercaptoanisic acid: To a warm acetic acid solution (100 ml) of 3-chlorosulphonylanisic acid (0.02 mole), prepared in 68% yield by the chloro-sulphonation of anisic acid⁴, was gradually added with swirling $SnCl_2$ (0.05 mole) dissolved in conc. HCl (12 ml). The mixture was refluxed for an hour, cooled and poured into cold water (600 ml) containing conc. HCl (25ml). The precipitate obtained was filtered, washed with water and crystallised from acetone to give pale yellow crystals. m.p. 236° (lit. 220°³ and 317°¹). Yield 81.5%, (Found: C, 52.03; H, 4.20; S, 17.3 Calcd. for $C_8H_8O_3S$; C, 52.18; H, 4.35; S, 17.39%).

6,6'-Dimethoxy-3, 3'-dicarboxydiphenyl disulphide: The mercaptan on oxidation with Na_2CO_3 and I_2 solution gave the disulphide, $C_{16}H_{14}O_8S_2$, m.p. 339° in 67.5% yield.

Ethyl-3-carboxy-6-methoxyphenyl sulphide: Sodium (2 g) was gradually added to refluxing dry ethanol (40 ml) followed successively by 3-mercaptoanisic acid (0.01 mole) and ethyl bromide (5 ml). The reaction mixture was refluxed for 2 hr, water (10 ml) added and the excess ethyl bromide and ethanol distilled off. The aqueous solution on acidification gave the desired compound, $C_{10}H_{12}O_3S$, crystallised from ethanol (30%) in white flakes m.p. 139° in 73% yield.

3-Carboxy-6-methoxyphenylthioglycollic acid: 3-Mercaptoanisic acid (0.01 mole) was condensed with chloroacetic acid (0.01 mole) using alc. KOH⁵. The product $C_{10}H_{10}O_5S$, m.p. 214° (50% ethanol) was obtained in 68% yield.

3-Carboxy-6-methoxy-4'-nitrodiphenyl sulphide: 3-Mercaptoanisic acid (0.01 mole) was condensed⁶ with 4-chloronitrobenzene (0.01 mole) using alc. KOH. Yield 58.7%, m.p. 210° (ethanol). It analysed for $C_{14}H_{11}O_5NS$.

4'-Amino-3-carboxy-6-methoxydiphenyl sulphide: Best yield of the amine was obtained when the above nitro derivative was reduced in ethanol with Sn and HCl. After the reduction, the pH was raised to 6-7 with NaOH and the precipitated amine was extracted with ethanol. It was dissolved in 20% $NaHCO_3$, filtered and acidified with AcOH. It was crystallised from ethanol to give pale brown crystals, m.p. 250°, in 56% yield. (Found: C, 60.91; H, 5.0; N, 5.09; S, 11.91. Calcd. for $C_{14}H_{15}O_3NS$: C, 61.09; H, 4.73; N, 5.1; S, 11.63%).

The amine was characterised through its acetyl ($C_{18}H_{15}O_4NS$, m.p. 287°), tosyl ($C_{21}H_{19}O_5NS_2$, m.p. 226°), brosyl ($C_{20}H_{16}O_5BrNS_2$, m.p. 232°), N-substituted phthalimide ($C_{22}H_{15}O_5NS$, m.p. 241°), N-substituted-3-nitrophthalimide ($C_{22}H_{14}O_7N_2S$, m.p. 274°) and N-substituted succinimide ($C_{18}H_{15}O_5NS$, m.p. 216°) derivatives.