

Studies on Some Dioxouranium(VI) Dithiocarbamates

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Several new complexes of the type $O_2U(dtc)_2$ and their bimetallic derivatives with Hg(II), Cd(II) and Ag(I) acceptors have been prepared and characterised through various physicochemical techniques. In bimetallic derivatives coordination from one of the sulphur atoms of $O_2U(dtc)_2$ to the soft acceptors is concluded.

Dithiocarbamates of oxometal cations have received limited attention¹⁻³. This note describes the preparation of some dioxouranium(VI) dithiocarbamates and their donor ability towards soft acceptors.

Dioxouranium(VI) acetate (BDH) was converted to dioxouranium(VI) hydroxide, $O_2U(OH)_2$, by interaction with aqueous ammonium hydroxide. Carbon disulphide (BDH), amines, 2,2'-dimethoxypropane and triethyl orthoformate (Aldrich) were distilled/recrystallised before use. The solvents were purified by conventional methods.

Dioxouranium(VI) dithiocarbamates were prepared by insertion of carbon disulphide between dioxouranium(VI) hydroxide and amines in 2,2'-dimethoxypropane or triethyl orthoformate medium. In a representative experiment, to a mixture of freshly prepared dioxouranium(VI) hydroxide (10 mmol) and carbon disulphide (20 mmol) suspended in 2,2'-dimethoxypropane (~25 ml) was added morpholine (20 mmol) in the same solvent (~20 ml) at $-20^\circ C$ with constant stirring. The reaction mixture was further stirred for several hr. The precipitated dioxouranium(VI) bis-(morpholine dithiocarbamate) was filtered, washed with ether and dried *in vacuo* over P_4O_{10} . Identical products were also obtained by the metathetical reaction between dioxouranium(VI) acetate and ammonium morpholine dithiocarbamate.

Interaction of dioxouranium(VI) bis-(morpholine dithiocarbamate) with soft lewis acids such as Hg(II), Cd(II) and Ag(I) yielded new bimetallic dithiocarbamates. In a typical experiment, to a stirring methanolic solution of dioxouranium(VI) bis-(morpholine dithiocarbamate) (10 mmol) was added $HgCl_2$ (20 mmol) in acetone-methanol mixture. The reaction mixture was stirred for about 10 hr. The precipitated product was washed several times with acetone-methanol mixture and dried *in vacuo* over

Table 1—Analytical Data of $UO_2(dtc)_2$ Complexes

| dtc | m.p., °C (yield, %) | Found % (Calc.) | | | |
|--------------------------------|------------------------|-----------------|----------------|--------------|--------------|
| | | U | C | H | N |
| $O_2U[S(S)CN(C_2H_5)_2]_2$ | 175(d) (80) | 41.9 (42.0) | 21.1 (21.2) | 3.4 (3.5) | 4.4 (4.9) |
| $O_2U[S(S)CNHC_4H_9]_2$ | 175(d) (84) | 41.8 (42.0) | 21.1 (21.2) | 3.2 (3.5) | 4.2 (4.9) |
| $O_2U[S(S)CN(C_4H_9)_2]_2$ | 117(d) (80) | 35.0 (35.1) | 31.6 (31.8) | 5.1 (5.3) | 4.0 (4.1) |
| $O_2U[S(S)CN(C_6H_5)_2]_2$ | > 240 (88) | 31.1 (31.3) | 41.0 (44.1) | 2.6 (2.6) | 3.3 (3.6) |
| $O_2U[S(S)CN(CH_2C_6H_5)_2]_2$ | 163(d) (80) | 29.0 (29.2) | 44.0 (44.2) | 3.2 (3.4) | 3.1 (3.4) |
| $O_2U[S(S)CNHC_6H_5]_2$ | > 240 (80) | 39.1 (39.2) | 27.5 (27.7) | 1.8 (1.9) | 4.6 (4.6) |
| $O_2U[S(S)CNC_4H_8O]_2$ | 192(d) (96) | 40.0 (40.0) | 20.1 (20.2) | 2.5 (2.6) | 4.6 (4.7) |
| $O_2U[S(S)CNC_4H_8]_2$ | 194(d) (90) | 42.1 (42.3) | 21.2 (21.3) | 2.7 (2.8) | 4.7 (4.9) |
| $O_2U[S(S)CNC_5H_{10}]_2$ | 148(d) (88) | 40.1 (40.3) | 24.2 (24.4) | 3.1 (3.3) | 4.6 (4.7) |
| $O_2U[S(S)CNC_4H_8CNC_6H_5]_2$ | 147(d) (96) | 31.7 (31.9) | 35.4 (35.4) | 3.2 (3.4) | 7.4 (7.5) |

Table 2—Analytical Data of Bimetallic Complexes $UO_2[S(S)CNC_4H_8O]_2 \cdot 2M'X_2$ OR $2MX$

| Complex | m.p. °C | Found (Calc.), % | | | | |
|---|------------|------------------|----------------|----------------|--------------|--------------|
| | | U | Metal | C | H | N |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2HgCl_2$ | 208(d) | 20.8 (20.9) | 35.1 (35.2) | 10.4 (10.5) | 1.3 (1.4) | 2.4 (2.4) |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2Hg(SCN)_2$ | 177(d) | 19.3 (19.4) | 32.5 (32.6) | 13.5 (13.7) | 1.2 (1.3) | 6.8 (6.8) |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2CdCl_2$ | > 240 | 23.4 (23.4) | 22.1 (22.1) | 11.7 (11.8) | 1.5 (1.5) | 2.7 (2.7) |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2AgSCN$ | 218(d) | 25.6 (25.7) | 23.3 (23.3) | 15.4 (15.5) | 1.6 (1.7) | 6.0 (6.0) |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2Hg(OCOFCF_3)_2$ | 105(d) | 16.4 (16.4) | 27.5 (27.6) | — | — | — |
| $O_2U[S(S)CNC_4H_8O]_2 \cdot 2AgOCOFCF_3$ | 180(s) | 22.8 (22.9) | 20.7 (20.8) | — | — | — |

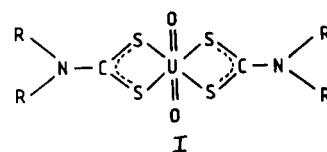
P_4O_{10} . Similar adducts were prepared using $Hg(SCN)_2$, $Hg(OCOFCF_3)_2$, $CdCl_2$, $AgSCN$ and $AgOCOFCF_3$ as acceptors.

The elemental analyses of dioxouranium(VI) dithiocarbamates indicate 1:2 (metal:dithiocarbamate) stoichiometry. The compounds are yellow to orange in colour, inert to atmospheric oxygen and moisture. They are insoluble in common organic solvents, sparingly soluble in methanol and soluble in DMSO and DMF. The molar conductance data showed their non-electrolytic nature. Magnetic measurements indicate their diamagnetic character, as expected.

The electronic spectra of the dioxouranium(VI) dithiocarbamates exhibit three bands around 24000, 34000 and 38000-38500 cm^{-1} . The two high energy bands are assigned to internal transitions in the ligand, whereas that around 24000 cm^{-1} is assigned to charge-transfer bands of the uranyl ion⁴.

The IR spectra of the dioxouranium(VI) dithiocarbamates exhibit only one strong band at 1020 \pm 5 cm^{-1} suggesting the chelating behaviour of the dithiocarbamate group⁵. The absorption at 1430 \pm 5 assigned to $\nu(C=N)$ is characteristic of thioureide bond having partial double bond character^{6,7}. Bands at 905 \pm 5 cm^{-1} and 800 cm^{-1} are assigned to $\nu(U=O)_{as}$ and $\nu(U=O)_s$ modes of vibration indicating linear⁸ character of UO_2 group. Conclusive evidence of sulphur to metal bonding is provided by a band at 378 \pm 2 assigned to $\nu(U-S)$ mode. The general structure (I) may be proposed for dioxouranium(VI) bis-dithiocarbamates.

In the IR spectra of bimetallic complexes, dioxouranium(VI) bis-(morpholine dithiocarbamate) $\cdot 2M'X_2$ or $2MX$ ($M' = Hg, Cd$; $M = Ag$; $X = Cl, SCN, OCOFCF_3$), the presence of single strong bands



at 1005 and 1470 \pm 5 cm^{-1} due to $\nu(C=S)$ and $\nu C=N$ respectively indicates coordination from both the sulphur atoms, one of which is bonded to uranium and the other to the soft metal acceptor. Due to the formation of the new coordinate bond, an electron drift from R takes place resulting in an increase in double bond character of $(C=N)$ and decrease in $(C=S)$ bond order. The former, therefore, shows a distinct positive shift, while the latter is lowered. Uranium associated modes of vibration remain unaltered in the adducts. The Hg-S stretching lies beyond the recorded range of the spectra.

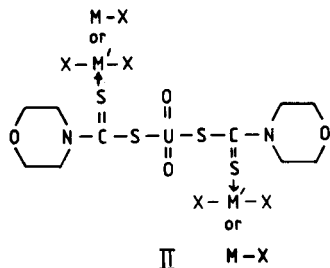
The thiocyanate group is S-bonded, since $\nu C \equiv N$, $\nu C=S$ and δNCS appear at 2110, 730 and 460 cm^{-1} respectively⁹. The trifluoroacetate groups are unidentate¹⁰ since $\nu_{as} OCO$ and $\nu_s OCO$ appear at 1690 and 1430 cm^{-1} , respectively, having $-\Delta\nu = 260 cm^{-1}$.

The ¹H NMR spectrum of morpholine shows two multiplets centered at δ 2.74 ppm and 3.52 ppm corresponding to $N-CH_2$ and $O-CH_2$ protons respectively. In the spectrum of dioxouranium(VI) bis-(morpholine dithiocarbamate) there is a slight up-field shift in both the signals which appear at δ 2.67 ppm and 3.45 ppm respectively.

In the bimetallic complex of dioxouranium(VI) bis-(morpholine dithiocarbamate) the $N-CH_2$ protons appear at δ 2.52 ppm indicating considerable drift of electrons from $-N-$ to the metal through carbon and sulphur atoms whereas the position of $O-CH_2$ protons remains more or less the same (\sim

3.52 ppm) as in morpholine, indicating little effect on the O-CH₂ protons.

On the basis of the above evidence, a bridging structure (II) is tentatively proposed for dioxouranium bis-(morpholine dithiocarbamate).2M'X₂ or 2MX.



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References

- 1 Casey A T, Mackey D J, Martin R L & White A M, *Aust J Chem*, **16** (1971) 31.
- 2 Young C C, Broomhead J A & Boreham C J, *J chem Soc Dalton*, **9** (1983) 2135.
- 3 Forghieri F, Graziosi G, Preti C & Tosi G, *Trans Met Chem*, **8** (1983) 372.
- 4 Sipio L Di, Tondello E, Pellzzi G, Ingletto G & Montenero A, *Inorg chim Acta*, **22** (1977) 23.
- 5 Wairand C G & Jaegere S De, *Spectrochim Acta*, **28A** (1972) 257.
- 6 Bonati F & Ugo R, *J organometal Chem*, **10** (1967) 257.
- 7 Dix A H, Diesveld J W & Vanderlinden J G M, *Inorg chim Acta*, **L51** (1977) 24.
- 8 Cattalini L, Croatto U, Degetto S & Tondello E, *Inorg chim Acta Rev*, **5** (1971) 19.
- 9 Norbury A H, *Adv inorg Chem Radiochem*, **17** (1975) 231.
- 10 Garner C D & Huges B, *Adv inorg Chem Radiochem*, **17** (1975) 1.