

## NOTE

**Studies on Some Oxozirconium(IV) and Dioxouranium (VI) Complexes of 2,2-Dithiodianiline**

P. R. SHUKLA\* AND MINAKSHI MISRA

*Department of Chemistry  
University of Lucknow, Lucknow 226 007, India*

Eight new oxozirconium(VI) and dioxouranium(IV) complexes of the ligand 2,2-dithiodianiline have been prepared and their structures elucidated by elemental analysis, IR and  $H^1$  NMR studies. Ligand, though tetradentate in nature, behaves as tridentate in the present complexes which are all 1 : 1 electrolytes and are found to possess square pyramidal and octahedral structures respectively.

Some transition metal and organotin complexes of  $N_2S_2$  donor ligands have been prepared and reported from this laboratory<sup>1,2</sup>. The present communication deals with the synthesis and characterisation of some oxozirconium(IV) and dioxouranium(VI) complexes of the ligand 2,2-dithiodianiline. These complexes are found to be 1:1 electrolytic in nature and their square pyramidal and octahedral structures have been established on the basis of elemental analysis, molar conductance, IR, and  $H^1$  NMR measurements.

The complexes have been prepared in the two steps as follows:

**(a) Preparation of 2,2-Dithiodianiline (L)**

5 g of *o*-aminobenzothiol was added slowly to a 20% solution of sodium hydroxide (25 ml) maintained at 0°C. After the addition of thiol had been completed, the solution was heated slowly with 5 ml of 30%  $H_2O_2$  for some time. The reaction mixture was then subjected to cooling when the disulphide crystallised out, which was recrystallised from alcohol to give pure disulphide<sup>3</sup> (m.pt. 92°C).

**(b) Preparation of Complexes**

(0.001 Mole, 0.248 g) of ligand 2,2-dithiodianiline was taken in dry methanol (25 ml) and refluxed with (0.001 mole, 0.3222 g) of  $ZrOCl_2 \cdot 8H_2O$  or (0.001 mole, 0.4242 g) of  $UO_2(CH_3COO)_2 \cdot 2H_2O$  for 14-16 hrs. Distilling off the solvent resulted in complexes which were recrystallised using a mixture of petroleum ether and solvent ether, dried and analysed. For the preparation of complexes of anions other than chloride and acetate appropriate amount of  $AgNO_3/AgClO_4$  was suspended in methanol and  $AgSCN$  was taken in 1:5 acetone and DCM mixture and stirred

for about 14 hrs followed by filtration of  $\text{AgCl}/\text{AgCH}_3\text{COO}$  thus formed. The solution containing desired oxometal salt was refluxed with the ligand as mentioned above, and thereafter crystallised likewise.

The above synthetic procedure gave eight new complexes whose analytical data as summarised in Table 1 shows the molecular formula to be  $[\text{ZrO}(\text{L})\text{X}]\text{X}$  and  $[\text{UO}_2(\text{L})\text{X}]\text{X}$  where  $\text{X}=\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$  and  $\text{ClO}_4^-$ . The complexes are crystalline solids of reddish or greenish white in colour. Their molar conductances in DMF are in the range  $65\text{--}90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  corresponding to 1 : 1 electrolyte.

TABLE 1  
ANALYTICAL DATA OF  $[\text{ZrOLX}]\text{X}$  AND  $[\text{UO}_2\text{LX}]\text{X}$

Compound	m.pt. °C	(Calcd %)				Conductance $\text{ohm}^{-1} \text{ cm}^2$ $\text{mole}^{-1}$ in DMF
		%C	%H	%N	%M	
$\text{H}_2\text{S}_2\text{C}_{12}\text{H}_{12}(\text{L})$	93	58.50 (58.06)	5.00 (4.83)	11.56 (11.29)	—	—
1. $[\text{ZrOC}]\text{Cl} \cdot 8\text{H}_2\text{O}$	220	25.60 (25.25)	4.14 (4.91)	4.65 (4.91)	15.60 (15.06)	65.58
2. $[\text{ZrOLSCN}]\text{SCN}$	105d	35.40 (35.64)	2.42 (2.54)	11.69 (11.80)	18.96 (19.32)	65.90
3. $[\text{ZrOLNO}_3]\text{NO}_3$	65d	30.56 (30.04)	2.74 (2.50)	11.94 (11.68)	18.26 (18.98)	66.20
4. $[\text{ZrOLClO}_4]\text{ClO}_4$	*	*	*	*	*	65.68
5. $[\text{UO}_2\text{LCH}_3\text{COO}]\text{CH}_3\text{COO} \cdot 2\text{H}_2\text{O}$	>250	28.10 (28.56)	2.65 (2.27)	4.28 (4.16)	34.96 (35.42)	68.10
6. $[\text{UO}_2\text{LSCN}]\text{SCN}$	>250	26.08 (26.49)	2.50 (1.89)	8.54 (8.83)	36.98 (37.54)	64.98
7. $[\text{UO}_2\text{L}_3\text{NO}_3]\text{NO}_3$	>250	22.10 (22.42)	2.60 (1.68)	8.59 (8.72)	36.58 (37.07)	67.32
8. $[\text{UO}_2\text{LCLO}_4]\text{ClO}_4$	*	*	*	*	*	70.05

\* Explodes before melting.

In the IR spectra of free ligand  $\nu_{\text{NH}}$  vibrations occur at  $3310$  and  $1620 \text{ cm}^{-1}$ , aromatic ring vibrations occur at  $1590$ ,  $1528$  and  $1460 \text{ cm}^{-1}$  and  $\nu_{\text{C-S}}$  vibrations occur at  $750 \text{ cm}^{-1}$ . In the spectra of complexes  $\nu_{\text{NH}}$  vibrations shift to lower values indicating coordination through nitrogen to oxometal ions, and as a consequence the aromatic ring vibrations undergo positive shifts and are observed at  $1600$ ,  $1550$  and  $1475 \text{ cm}^{-1}$ . The

$\nu_{C-S}$  vibration in complexes undergoes splitting and also shift lower to  $735 \pm 5 \text{ cm}^{-1}$  the phenomenon being an outcome of the involvement of one sulphur atom in coordination<sup>4</sup>. The  $\nu_{O=U=O}$  and  $\nu_{Zr=O}$  stretching frequencies are observed around  $910 \pm 5$  and  $970 \pm 5 \text{ cm}^{-1}$  respectively as reported for other similar complexes and established the presence of oxo ions in complexes<sup>5,6</sup>. In addition a sharp band at  $430 \pm 10$  has been assigned to be due to  $Zr \leftarrow N$  stretch<sup>6</sup>.

In the  $^1\text{H}$  NMR spectra of ligand broad multiplets due to aromatic protons appear at  $\delta$  7.6–8.3 and NH protons appear at  $\delta$  3.1–3.2. In the spectra of complexes the phenyl protons appear at  $\delta$  7.5–8.1 and NH protons at  $\delta$  2.8–3.0 suggesting coordination of ligand to the centrally located oxometal ion.

The coordination in the present complexes is suggested to occur through two nitrogen and one sulphur atoms of the ligand, one anion while the oxygen atoms of  $ZrO^{2+}$  and  $UO_2^{2+}$  occupy axial positions and project outside the coordination plane resulting in square pyramidal and octahedral geometries for the complexes.

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#### REFERENCES

1. P. R. Shukla, B. B. Awasthi and R. Rastogi, *J. Indian Chem. Soc.*, **61**, 898–899 (1984).
2. P. R. Shukla, Nihal Ahmad and M. C. Sharma, *Asian J. Chem.*, **4**, 648 (1992).
3. S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, **26**, 1670 (1973).
4. B. K. Sinha, Rajeshwar Singh, J. P. Srivastava and L. K. Mishra, *J. Inorg. Nucl. Chem.*, **39**, 1799 (1977).
5. C. P. Prabhakaran and C. C. Patel, *J. Inorg. Nucl. Chem.*, **31**, 3316 (1969).
6. S. K. Madan and A. M. Donohue, *J. Inorg. Nucl. Chem.*, **28**, 133 (1966).

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