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Note

INFRARED AND THERMAL STUDIES OF URANYL(VI) COMPLEXES OF ANTIPYRINE *

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ABSTRACT

Recently, the isolation and characterisation of a large number of uranyl(VI) complexes with neutral unidentate oxygen donor ligands having X=O bonds (X=C, N, P, S or As) have been reported [1–5]. Antipyrine (1-phenyl-2,3-dimethyl-5-pyrazolone), containing a polar carbonyl group, is found to form complexes with metal ions [6–13]. This communication describes the isolation and physico-chemical properties of the complexes formed by uranyl(VI) ions.

EXPERIMENTAL

The compounds were obtained by mixing together the respective uranyl salt and antipyrine in absolute ethanol. The mixed solutions were concentrated by evaporation and the compounds crystallized out on cooling. The elemental analyses of these compounds lead to the empirical formula $UO_2X_2 \cdot 2Apy$ (Table 1). All the compounds are fairly stable at room temperature and non-hygroscopic in nature. The molar conductance of these compounds was measured in nitrobenzene. Except the uranyl iodide complex, all others are non-electrolytes, but those of the iodide compound are slightly conducting (3.2 ohm^{-1} cm^2 mol^{-1}).

Infrared studies

The infrared absorption spectra of these compounds have been recorded in the region 4000–250 cm^{-1}. The stretching frequencies for C=O, U=O and

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TABLE 1

Analytical and IR data (cm^{-1}) of $UO_2X_2 \cdot 2Apy$

Compound	Found (calcd.) (%)			IR frequencies (cm^{-1})		
	U	N	Anion	ν(C=O)	ν(U=O)	ν(U–O)
$UO_2Cl_2 \cdot 2Apy$	32.80 (33.19)	7.69 (7.81)	9.62 (9.90)	1580s	920m	400m
$UO_2Br_2 \cdot 2Apy$	29.32 (29.52)	6.72 (6.94)	19.21 (19.85)	1585s	930m	392m
$UO_2I_2 \cdot 2Apy$	26.21 (26.44)	6.06 (6.22)	27.59 (28.22)	1590s	930m	395m
$UO_2(NO_3)_2 \cdot 2Apy$	30.69 (30.90)	10.79 (10.90)	–	1580s	920m	400m
$UO_2(NCS)_2 \cdot 2Apy$	31.07 (31.23)	10.92 (11.02)	15.01 (15.22)	1580s	925m	400m
$UO_2(Ac)_2 \cdot 2Apy$	31.31 (31.15)	7.10 (7.32)	–	1585s	920m	400m

s, Strong; m, medium.

U–O (metal–ligand) bonds have been assigned and are listed in Table 1. Previous workers [6–13] have reported the C=O stretching frequency in free ligand at 1660 cm^{-1}. On complex formation, this C=O stretching frequency in all the six compounds is lowered by about 80–70 cm^{-1} as a consequence of coordination through its oxygen atom. The second notable feature is the stretching frequency of the U=O bond in uranyl(VI) compounds before and after complexation. The stretching frequency (950 cm^{-1}) falls by about 20–25 cm^{-1} after complexing with the ligand due to a lowering of the d_π–p_π interaction in the U=O bond which is supported by the observations of McGlynn et al. [14]. ν(U–O) (metal–ligand) in all the compounds has been assigned in the 400–380 cm^{-1} region. The nitrato group with C_{2v} symmetry is considered to coordinate with the metal ion, since all the six normal modes of vibration are infrared active. Further, the nitrate groups seem to be bidentate since the IR frequencies due to this group occur in almost the same frequency ranges as in $UO_2(NO_3)_2 \cdot 2H_2O$ [15]. In $UO_2(NCS)_2 \cdot 2Apy$ the C–N and C–S stretching frequencies appear at 2050 and 800 cm^{-1}, respectively. On the basis of the high relative intensity of the C–N band, it is considered that the thiocyanate group is almost certainly N-bonded [16].

Thermal studies

The thermal investigation of various antipyrine complexes of metal ions has already been reported [6–10,17,18]. In the present work, we wish to report our thermal results of antipyrine complexes of uranyl(VI) ions. Thermoanalytical results are summarised in Table 2.

When uranyl(VI) complexes are heated, there is virtually no change in weight up to 140°C, but between this temperature and ~ 220°C, a loss of 32–38% is observed because of the loss of the 1.5 moles of the ligand and from 250 to 310°C, a loss of 44–51% is observed because of the complete loss of the antipyrine molecules and reduction to the oxide, UO_3, facilitated by the antipyrine and its decomposition products. The oxide U_3O_8 is formed

TABLE 2

Thermoanalytical results obtained for the $UO_2X_2 \cdot 2Apy$ complexes

X	Sample weight (mg)	Residual mass (mg)	Ligand's mass loss (%)				Residue (%) ~ 620°C	
			140–220°C		250–310°C			
			Theor. [a]	Exp.	Theor. [b]	Exp.	Theor. [c]	Exp.
Cl	24.71	9.31	39.33	37.63	52.44	50.92	39.14	37.67
Br	27.93	8.92	34.14	32.26	45.52	43.82	33.97	31.93
NO_3	26.36	8.86	36.62	34.29	48.83	46.91	36.45	33.61
NCS	25.92	8.91	37.00	34.82	49.34	47.56	36.83	34.37
CH_3COO	26.93	9.11	36.91	34.69	49.21	47.39	36.73	33.82

[a] Calculated for loss of 1.5 ligand.

[b] Calculated for total loss of ligand.

[c] Calculated as U_3O_8.

at ~ 620°C, following which there is no sensible change in weight [19].

In the DTG curves these changes have been indicated by the presence of one sharp endothermal peak at these temperatures and a final peak due to metal oxidation [20]. In brief, these changes can be shown as

$$UO_2X_2 \cdot 2Apy \rightarrow UO_2X_2 \cdot 0.5Apy \rightarrow UO_2X_2 \rightarrow [UO_3] \rightarrow U_3O_8$$

REFERENCES

1 A.K. Majumdar and R.G. Bhattacharya, J. Inorg. Nucl. Chem., 29 (1967) 2359.
2 A.K. Majumdar and R.G. Bhattacharya, Chem. Ind., (1970) 95.
3 A.K. Majumdar and R.G. Bhattacharya, Chem. Ind., (1971) 730.
4 K.W. Bagnall, J.G.H. Du-Preeze, J. Bajorek, L. Bouner, H. Cooper and G. Segal, J. Chem. Soc., Dalton Trans., (1973) 2682.
5 A.K. Srivastava, S. Sharma and R.K. Agarwal, Inorg. Chim. Acta, 61 (1982) 235.
6 J. Gopalakrishnan, A. Ravi and C.C. Patel, Bull. Chem. Soc. Jpn., 40 (1967) 791.
7 J. Gopalakrishnan, A. Ravi and C.C. Patel, Indian J. Chem., 5 (1967) 356.
8 S.S. Krishnamurty and S. Soundararajan, J. Less-Common Met., 3 (1967) 619.
9 P. Ramamurthy, V.V. Savant and C.C. Patel, Indian J. Chem., 7 (1969) 917.
10 P. Ramamurthy, V.V. Savant and C.C. Patel, J. Less-Common Met., 22 (1970) 479.
11 S.A.A. Zaidi, T.A. Khan and N.S. Neelam, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 243.
12 R.K. Agarwal, A.K. Srivastava and T.N. Srivastava, Proc. Natl. Acad. Sci., India, Sect. A, 51 (1981) 79.
13 A.K. Srivastava, R.K. Agarwal and T.N. Srivastava, J. Indian Chem. Soc., 58 (1981) 710.
14 S.P. McGlynn, J.K. Smith and W.C. Neely, J. Chem. Phys., 35 (1961) 105.
15 G. Topping, Spectrochim. Acta, 21 (1965) 1743.
16 Z.M.S. Al-Kazaz, K.W. Begnall and D. Brown, J. Inorg. Nucl. Chem., 35 (1973) 1501.
17 Sakari Lukkari, Farm. Aikak., 60 (1971) 402.
18 A.K. Srivastava, M. Srivastava and R.K. Agarwal, Ind. Eng. Chem., Prod. Res. Dev., 21 (1982) 135.
19 W.W. Wendlandt, J. Inorg. Nucl. Chem., 5 (1957) 118; 9 (1959) 136.
20 R.K. Agarwal, J.R. Chopra and S.C. Rastogi, J. Indian Chem. Soc., in press.