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Dioxouranium(VI) Thiocyanate Complexes of Schiff Bases of *p*-Nitro, Chloro, Bromo, Hydroxy and Methoxy Aniline and Salicylaldehyde

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Abstract

A series of dioxouranium(VI) complexes was synthesised with some Schiff base ligands containing substituent groups at *para* positions to –CH=N– groups. These molecules were obtained by the condensation of *para*-nitro, chloro, bromo, hydroxy, methyl and methoxy aniline with salicylaldehyde. The bidentate ligands formed complexes of the type $UO_2(NCS)_2$ $(X\text{-N-Sal})_n \cdot mH_2O$, where n = 2, m = 3, x = NO_2, Cl, Br and OH; n = 3, m = 2, x = CH_3 and OCH_3.

Conductivity measurements indicate that all the complexes are non-electrolytes in nitromethane solution, whereas in DMF they correspond to 1:1 electrolytes.

IR spectral data suggest that the molecules and not the anions of the Schiff base are coordinated to the central uranium atom. IR and Raman spectra suggest that the complexes $UO_2(NCS)_2(X\text{-N-Sal})_2 \cdot 3H_2O$ (X = NO_2, Cl, Br) have C_{2h} molecular symmetry, whereas $UO_2(NCS)_2(X\text{-N-Sal})_3 \cdot 2H_2O$ (X = OCH_3, CH_3) have C_{2v} symmetry.

The frequencies of $UO_{2(asym)}$ (IR) and $UO_{2(sym)}$ (R) in the complexes seem to vary with the various substituents of the Schiff base ligand, in the order:

$NO_2 > Cl > Br > OH > CH_3 > OCH_3$

Introduction

Dioxouranium(VI) thiocyanate complexes with monobasic bidentate Schiff bases [1] have been reported and the coordination and symmetry effects, based on the IR and Raman spectral data, have been discussed. In the present work we report the synthesis and the important properties of a series of thiocyanate complexes with Schiff base derivatives which have substituted groups at *para* positions to –CH=N– groups. The coordination and symmetry effects based on the observed IR and Raman frequencies, and also the effect of the nature of the Schiff base ligand on the frequencies of $UO_{2(asym)}$ (IR) and $UO_{2(sym)}$ (R), are discussed.

Experimental

Materials and Measurements

Hydrated dioxouranium(VI) chloride (BDH) was used as supplied.

Ethanol solutions of dioxouranium(VI) thiocyanate were obtained by reaction of hydrated UO_2Cl_2 with calculated amount of KSCN and filtering off the precipitated KCl.

Conductance measurements were carried out at room temperature (~300 K) in nitrobenzene and DMF solutions (~10^{-3} M) with a bridge conductivity type MCl.

The IR spectra in the region 400–4000 cm^{-1} were recorded using a Pye Unicam Sp3 2000 recording spectrophotometer as Nujol mulls. Raman spectra were recorded in solution over the range 2400–200 cm^{-1} and were carried out by the Chemistry Department of Manchester University, U.K.

Synthesis of the Ligands

Para-X-aniline-N-salicylidene [2, 3] (X = NO_2, Cl, Br, OH, CH_3, OCH_3) was prepared as described previously.

Synthesis of the Complexes

UO_2Cl_2 and KSCN were mixed in 1:2 molar ratio in EtOH. KCl was immediately precipitated by centrifugation. To the remaining solution an excess of a warm solution of the ligand (~2 mol in EtOH) was slowly added and the resulting solution was heated to boiling. The mixture was then brought to room temperature and filtered to remove the excess of KCl. Yellow–orange crystals formed after several hours and were crystallised from absolute ethanol.

Analyses

Uranium was determined as previously described [4]. C, H and N microanalyses were carried out by the Alfred Bernhardt Microanalytical Laboratory, F.R.G. The analytical results are summarised in Table I.

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TABLE I. Analytical Results and Molar Conductance Data.

Complex	Analytical data[a]				Λ_m[b]	
	C (%)	H (%)	N (%)	U (%)	Ω cm^2 in $C_6H_5NO_2$	mol^{-1} in DMF
$UO_2(NCS)_2(NO_2\text{-N-Sal})_2 \cdot 3H_2O$	36.37	2.83	9.08	25.74	5.6	116
	(36.01)	(2.70)	(8.98)	(25.42)		
$UO_2(NCS)_2(Cl\text{-N-Sal})_2 \cdot 3H_2O$	37.21	2.66	6.20	26.38	4.2	115
	(37.00)	(2.25)	(6.31)	(26.38)		
$UO_2(NCS)_2(Br\text{-N-Sal})_2 \cdot 3H_2O$	33.84	2.62	5.64	24.00	2.0	105
	(33.53)	(2.52)	(5.72)	(24.56)		
$UO_2(NCS)_2(OH\text{-N-Sal})_2 \cdot 3H_2O$	38.79	3.00	6.46	39.22	1.6	110
	(38.67)	(3.12)	(6.39)	(38.98)		
$UO_2(NCS)_2(CH_3\text{-N-Sal})_3 \cdot 2H_2O$	50.04	4.67	6.63	22.56	2.4	120
	(50.09)	(3.81)	(6.70)	(22.47)		
$UO_2(NCS)_2(OCH_3\text{-N-Sal})_3 \cdot 2H_2O$	47.86	3.89	6.43	21.57	3.3	102
	(47.83)	(3.85)	(6.55)	(21.10)		

[a] Calculated/(found). [b] Concentration 10^{-3} M.

Results and Discussion

Conductance Measurements

The molar conductance values in Table I indicate that all the complexes in nitrobenzene (10^{-3} M) are below 5 Ω^{-1} cm^2 mol^{-1}, indicating non-electrolytic behaviour [5] in this medium. However, molar conductance values of these complexes in DMF (10^{-3} M) fall in the range 100–120 Ω^{-1} cm^2 mol^{-1}, which correspond nearly to a 1:1 electrolyte. This shows that a coordinating solvent such as DMF is able to displace the weakly-coordinated thiocyanate group to a considerable extent in sufficiently dilute solutions, as reported earlier [1, 6].

Infrared and Raman Spectra

In these reactions the Schiff base coordinates to the uranium(VI) atom as a monobasic bidentate ligand, using its oxygen and nitrogen atoms. Weak and broad absorption bands are observed in the 3100–3250 cm^{-1} region, which may be assigned to the hydrogen-bonded ν_{OH} or ν_{NH} regions. However, in these complexes this shift by 100–150 cm^{-1} towards higher wavenumber is as expected of the coordinated O–H or N–H group. This shows that the molecules of the Schiff base are coordinated to the central uranium atom and not to the anion. The latter case should occur when no bands are observed in the region 3300–3600 cm^{-1}, indicating the absence of OH stretching vibration of the ligand. No evidence for H_2O coordination was found in any of these cases.

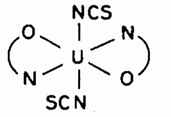
A strong band in the 1620–1632 cm^{-1} region is characteristic of the azomethine group (C=N–). In the complexes a shift of $\nu_{C=N}$ frequency towards higher wavenumber (8–20 cm^{-1}) takes place in the complex, and this may be ascribed to the increase in the bond order of the carbon to nitrogen link [8, 9]. The lower band appears to be coupled with –C=C– [10] which occurs at 1575 cm^{-1} in the Schiff base.

All the thiocyanate complexes exhibit a very strong band between 2045–2080 cm^{-1} and 795–820 cm^{-1}, corresponding to $\nu_{C=N}$ and ν_{C-S} respectively. This suggests that the thiocyanate group is coordinated through the nitrogen [11] and thus the 'hard' character of uranyl ion [12] is emphasized. These observed frequencies of the ν_1 thiocyanate mode are below the usually accepted range [13] for coordinated isothiocyanate groups, but the latter must almost certainly be coordinated in the present complexes: the coordination number of two for the UO_2 group entity, especially when in the presence of available thiocyanate ions, is most unlikely. Such low values of ν_1 for coordinated NCS have occasionally been reported [14, 15]. The bond type based on the position of ν_1 alone must be drawn with caution, especially where the metal ion is of a rather weakly polarizing nature.

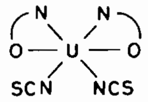
A strong band in the region 910–925 cm^{-1} and a weak band in the region 855–870 cm^{-1} are attributed to ν_{as} and ν_{sym} respectively. The Raman spectra of these compounds in absolute ethanol show a very strong polarised band occurring between 822–860 cm^{-1}, assigned to the symmetric stretch. Therefore the activities of these modes agree with that predicted for the linear model [16], with the exception of the possible weak activity of ν_{sym} in the IR.

Assuming the linear UO_2 grouping the configuration of the remaining ligands is considered in the light of C–N stretching vibration. It follows that the type of symmetry may be deduced from the activity of ν_{C-N} in the IR and Raman spectra. This is often more reliable than ν_{C-S}, because it is often obscured by other adjacent bands in the IR.

The likely symmetry for $UO_2(NCS)_2(p\text{-X-NSal})_2 \cdot 3H_2O$, where X = OH, Cl, Br, is either C_{2v} or C_{2h} with NCS^- groups situated in the equatorial plane. Two arrangements would be possible (viewed down the O–U–O axis):



(C_{2h} symmetry)



(C_{2v} symmetry)

The calculated C–N stretching modes in each case are given in Table II.

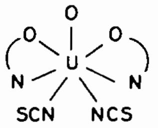
The data given in Table III show that these compounds seem to have one IR active and one R active mode, so that it is possible to suggest that these three complexes have C_{2h} symmetry.

TABLE II. Calculated C–N Stretching Modes of C_{2v} and C_{2h} Symmetries.[a]

Mode C_{2v}	A_1	B_1	N	R	P	IR	C
Activity	R(p), IR	R, IR	2	2	1	2	2
Mode C_{2h}	A_g	B_4	N	R	P	IR	C
Activity	R(p)	IR	2	1	1	1	0

[a] N = number of normal modes, R = number of Raman active modes, P = polarised Raman active modes, IR = number of infrared active modes, C = number of co-incidences.

For the complexes $UO_2(p\text{-X-N-Sal})_3 \cdot 2H_2O$ where X = CH_3 and OCH_3, C_{2v} symmetry is possible if only one of the three Schiff base ligands is coordinated as monodentate to uranium atom. Accordingly, the following arrangement would be possible:



(C_{2v} symmetry)

The calculated C–N stretching modes in this case for C_{2v} symmetry are shown in Table II. In the compounds two IR and two R active bands were observed. It may thus be possible to suggest that these compounds have C_{2v} symmetry.

The frequencies of $UO_{2(asym)}$ (IR) and $UO_{2(sym)}$ (R) seem to vary with the nature of Schiff base. With the various substituents in the *para* position, the frequencies are in the order:

$$NO_2 > Cl > Br > OH > CH_3 > OCH_3$$

This trend can be correlated with the electron-withdrawing or electron-donating nature of the substituents of the Schiff base. More powerful electron-withdrawing would tend to increase the O–U–O stretching frequencies, due to the decreased formal negative charge around the uranium atom which is expected to decrease the repulsion forces with the non-bonding or weakly π-bonding uranyl oxygen atoms [17]. Thus the lowest stretching frequency is expected for complexes with the Schiff base having strongly donating groups.

TABLE III. Vibrational Frequencies (cm^{-1}) of NCS Ions, Uranyl Ions and some Ligand Vibrations.[a]

Complex	CN and CS Vibrational modes	UO2 Vibration		Ligand Vibration	
		IR (ν_3, ν_1)	R (ν_1)	ν_{OH} and ν_{NH}	$\nu_{C=N}$
$UO_2(NCS)_2(NO_2\text{-N-Sal})_2 \cdot 3H_2O$	2080(s) 815(m)	932(s) 860(m)	860(m)	3460(m)	1610(w) 1630(vs)
$UO_2(NCS)_2(Cl\text{-N-Sal})_2 \cdot 3H_2O$	2080(s) 820(s)	925(s) 870(vw)	853(s)	3440(w)	1608(w) 1640(s)
$UO_2(NCS)_2(Br\text{-N-Sal})_2 \cdot 3H_2O$	2075(s) 820(m)	925(s) 858(vw)	845(vs)	3425(m) 3100(w)	1610(w) 1638(s)
$UO_2(NCS)_2(OH\text{-N-Sal})_2 \cdot 3H_2O$	2080(s) 815(m)	915(s) 860(w)	830(s)	3435(m) 3240(w)	1610(w) 1640(s)
$UO_2(NCS)_2(CH_3\text{-N-Sal})_3 \cdot 2H_2O$	2078(s) 2045(sh) 795(m)	912(vs) 855(w)	822(vs)	3420(w)	1608(w) 1642(s)
$UO_2(NCS)_2(OCH_3\text{-N-Sal})_3 \cdot 2H_2O$	2075(s) 2020(sh) 800(m)	912(s) 860(s)	824(vs)	3445(w) 3110(w)	1605(w) 1640(s)

[a] s = strong, vs = very strong, w = weak, vw = very weak, m = medium, sh = shoulder.

References

1 W. I. Azeez and A. F. Kazzer, *A. Anorg. Allg. Chem., 465,* 221 (1980).
2 C. Donald, J. Freeman and C. E. White, *J. Am. Chem. Soc., 78,* 2678 (1956).
3 T. J. Lane, C. S. C. and A. J. Kandathil, *J. Am. Chem. Soc., 83,* 3782 (1961).
4 K. W. Bagnall, D. Brown, P. J. Jones and J. G. H. Du Preez, *J. Chem. Soc.,* 3594 (1965).
5 J. A. Walmsley and S. V. Tyree, *Inorg. Chem., 2,* 312 (1963).
6 R. G. Vijay and J. P. Tandon, *J. Inorg. Nucl. Chem., 37,* 2326 (1975).
7 S. S. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem., 28,* 1689 (1966).
8 D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc., 78,* 1137 (1956).
9 M. Vidali, P. A. Vigato, G. Bandoli, D. A. Clemente and V. Casellato, *Inorg. Chim. Acta, 6,* 671 (1972).
10 B. D. Sarma and J. C. Bailar, *J. Am. Chem. Soc., 77,* 5476 (1955).
11 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev., 6,* 407 (1971).
12 A. K. Majumdar and R. G. Bhattacharya, *J. Indian Chem. Soc., 51,* 235 (1974).
13 M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.,* 6412 (1959);
P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.,* 1912 (1960);
J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.,* 4590 (1961).
14 D. Forster and D. M. L. Goodgame, *J. Chem. Soc.,* 268 (1965).
15 F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem., 27,* 1825 (1965).
16 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, *Inorg. Chim. Acta Rev., 5,* 19 (1971).
17 J. P. Day and L. M. Venanzi, *J. Chem. Soc. A,* 1363 (1966).