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Dioxouranium(VI) Complexes of Monobasic Bidentate and Bibasic Tetradentate Schiff Bases

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A series of dioxouranium(VI) complexes were synthesised with the bidentate Schiff base ligands obtained by condensation of salicylaldehyde with aniline (pBH) or benzylamine (bBH), and the tetradentate Schiff base ligands derived by condensation of salicylaldehyde with ethylenediamine (SpH_2). The bidentate ligands formed complexes of the type $UO_2X_2(pBH)_n$ where $X = NO_3^-$, $n = 2$; $X = CH_3COO^-$, $n = 1$, and also the complexes $UO_2Cl_2(pBH)_2 \cdot H_2O$, $UO_2(CH_3COO)(bBH) \cdot H_2O$ and $UO_2SO_4(bBH) \cdot EtOH \cdot H_2O$. The tetradentate ligands formed the complexes $UO_2Cl_2(SBH_2) \cdot EtOH$, $UO_2SO_4(SBH)_{1/2} \cdot EtOH \cdot 2H_2O$ and also $UO_2Cl_2(SpH_2)_{1.5} \cdot 2H_2O$, $UO_2(NO_3)_2(SpH_2)_{1.5} \cdot EtOH$ and $UO_2(Sp) \cdot EtOH$.

Conductivity measurements indicate that all the complexes are non-electrolytes in $MeNO_2$ or MeCN solutions.

IR spectral data suggest that the molecules and not the anions of the Schiff base are coordinated to the central uranium atom, except for the complexes $UO_2(CH_3COO)bB \cdot H_2O$ and $UO_2(Sp) \cdot EtOH$ in which the deprotonated binegative ion is coordinated to the uranyl group. The acetato and sulphato groups are coordinated as bidentate ligands, while the nitrato group behaves as a unidentate ligand in the pBH complex and as a bidentate ligand in the SpH_2 complex.

TABLE I. Analytical Data and Conductivity Values of Dioxouranium(VI) Complexes.

Complex	Analytical Data[a]				Λ_m[a]	
	C(%)	H(%)	N(%)	U(%)	$\Omega\ cm^2\ mol^{-1}$	
					in $MeNO_2$	in MeCN
$UO_2(CH_3COO)_2(pBH)$	34.79 (34.87)	2.87 (2.90)	2.38 (2.39)	40.75 (40.68)	–	5.0
$UO_2Cl_2(pBH)_2 \cdot H_2O$	41.94 (41.43)	2.99 (3.10)	3.69 (3.71)		9.0	–
$UO_2(NO_3)_2 \cdot (pBH)_2$	39.42 (39.59)	2.77 (2.79)	7.00 (7.10)	29.93 (30.20)	–	25.0
$UO_2(CH_3COO)(bBH) \cdot H_2O$	34.33 (34.40)	3.02 (3.07)	2.36 (2.50)	43.00 (42.70)	2.42	–
$UO_2SO_4(bBH) \cdot C_2H_5OH \cdot H_2O$	18.88 (19.06)	2.24 (2.08)	1.81 (1.39)	47.56 (47.27)	–	–
$UO_2Cl_2(SBH_2) \cdot C_2H_5OH$	33.67 (32.90)	3.67 (3.38)	6.03 (4.27)	36.55 (36.35)	–	2.33
$UO_2SO_4(SBH_2)_{1/2} \cdot C_2H_5OH \cdot 2H_2O$	19.90 (20.14)	2.76 (2.56)	2.84 (2.56)	93.65 (93.58)	–	–
$UO_2(Sp) \cdot C_2H_5OH$	41.92 (41.91)	3.20 (3.19)	4.45 (4.44)	37.58 (37.70)	3.6	–
$UO_2Cl_2(SpH_2)_{1.5} \cdot 2H_2O$	42.07 (42.30)	3.01 (3.20)	4.34 (4.90)	–	–	3.7
$UO_2(NO_3)_2(SpH_2)_{1.5} \cdot C_2H_5OH$	35.47 (35.48)	2.74 (2.77)	3.71 (3.88)	43.63 (43.90)	–	2.0

[a] Theoretical values in brackets. [b] Concentration of solution 10^{-3} *M*.

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TABLE II. Infrared Absorption (cm^{-1}) of Polyatomic Anions, Uranyl Ion and Some Ligand Vibrations.[a]

Complex	Anion Vibrations	Uranyl Vibrations		Ligand Vibrations	
		$\nu_{sym}(UO_2)$	$\nu_{asym}(UO_2)$	ν_{OH} and ν_{NH}	$\nu_{C=N}$
	NO_3^{-1} ion				
$UO_2(NO_3)_2(pBH)_2$	1525s (ν_1), 1290s (ν_4)	830vw	930vs	3280–3240mb	1650vs, 1612m
$UO_2(NO_3)_2(SpH_2)_{1.5}\cdot C_2H_5OH$	1288s (ν_1), 1480s (ν_4)	832vw	920vs	3290vw	1618s
	COO^- ion				
$UO_2(CH_3COO)_2(pBH)$	1538m, 1413sh	855vw	920s	3270w, 3210vw	1640s, 1612m
$UO_2(CH_3COO)_2(bBH)\cdot H_2O$	1539m, 1410sh	830vw	900s	3140w	1650s, 1610m
	SO_4^{-2} ion				
$UO_2SO_4(bBH)\cdot C_2H_5OH\cdot H_2O$	1100m 640m 1040br 595s	845vw	920s	3560s, 3260–3140mb	1653m, 1605s
$UO_2SO_4(SBH_2)_{1/2}\cdot C_2H_5OH\cdot 2H_2O$	1100br 650s 1103sh 600s 1045br	835vw	930vs	3580w, 3200–3100mb	1642m
$UO_2Cl_2(pBH)_2\cdot H_2O$	–	830vw	922s	3680w, 3080m	1645s, 1608w
$UO_2Cl_2(SBH_2)\cdot C_2H_5OH$	–	830w	910s	3500w, 3220m	1625vs
$UO_2Cl_2(SpH_2)_{1.5}\cdot 2H_2O$	–	845vw	920vs	3620–3340mb	1618s
$UO_2(Sp)\cdot C_2H_5OH$		820vw	920s	3500–3440wb	1615s

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

Introduction

Dioxouranium(VI) complexes of monobasic bidentate [1–4] and bibasic tetradentate [5–7] Schiff bases have been reported, and it may be noted that the complexes either contain no neutral ligands and the deprotonated binegative ion is coordinated to the uranyl group [1, 5, 8, 9] or contain neutral coordinating ligands [4, 7, 10]. In the present work we report the synthesis and important properties of the Schiff base complexes with various uranium(VI) salts by analytical data, conductivities and infra-red spectra (400–4000 cm^{-1}).

Experimental

Materials and Measurements

Hydrated dioxouranium(VI) chloride, nitrate, acetate and sulphate (BDH) were used as supplied. Conductance measurements were carried out at room temperature (~300 K) in $MeNO_2$ or MeCN solutions (~10^{-3} *M*) with a bridge conductivity type MC1. The results are summarised in Table I. The infrared spectra in the region 400–4000 cm^{-1} were recorded using a Beckman IR 9 recording spectrophotometer as Nujol mulls. The assignments of some stretching frequencies of the complexes are listed in Table II.

Synthesis of the Ligands

N-phenylsalicylideneimine (pBH), N-benzylsalicylideneimine (bBH) [10]. N,N′-ethylenebissalicylideneimine (SBH_2) [11] and N,N′-phenylenebissalicylideneimine (SpH_2) [12] were prepared according to the literature. The solid ligands were characterised by their C,H,N analyses and infrared spectra. bBH could not be isolated as a solid product and was used as such in solution.

Synthesis of the Complexes

$UO_2(CH_3COO)_2(pBH)$

Uranyl acetate dihydrate (2 mol) was dissolved in a minimum volume of EtOH and added to a hot ethanolic solution of pBH (2.2 mol), the resulting solution was heated to boiling. Yellow crystals formed overnight and were washed several times with diethyl ether.

$UO_2Cl_2(pBH)_2\cdot H_2O$

Prepared as $UO_2(CH_3COOH)_2(pBH)$, but using uranyl chloride (2 mol) and 4.5 mol of the ligand. Orange crystals formed overnight and were washed several times with EtOH.

$UO_2(NO_3)_2(pBH)_2$

Prepared as $UO_2(CH_3COOH)_2(pBH)$ using 2 mol of uranyl nitrate hexahydrate and 4.2 mol of the ligand. Orange crystals formed overnight and were washed with diethyl ether.

$UO_2(CH_3COO)(bBH)\cdot H_2O$

An ethanolic solution of uranyl acetate dihydrate (1.8 mol) was added to a hot ethanolic solution of the ligand (2 mol). The solution was refluxed for twenty hours and filtered. The orange crystals were recrystallised from EtOH.

$UO_2(SO_4(bBH)\cdot EtOH\cdot H_2O$

Prepared and isolated as $UO_2(CH_3COOH)(bBH)\cdot H_2O$ but using 1.5 mol of $UO_2SO_4\cdot 3\frac{1}{2}H_2O$ with 1.7 mol of the ligand. The resulting product was washed with EtOH.

$UO_2Cl_2(SBH_2)\cdot EtOH$ and $UO_2SO_4(SBH_2)_{1/2}\cdot EtOH\cdot 2H_2O$

An ethanolic solution of uranyl salt was added to an equimolar quantity of SBH_2 in a hot ethanolic solution. The resulting orange solution was allowed to stand for ½ hour. The orange precipitate was filtered off and recrystallised from EtOH.

$UO_2(Sp)\cdot EtOH$

An ethanolic solution of $UO_2SO_4\cdot 3\frac{1}{2}H_2O$ was added to an equimolar amount of the ligand in hot ethanolic solution. The resulting solution was heated to boiling. The orange precipitate which separated overnight was filtered off and washed with EtOH.

$UO_2Cl_2(SpH_2)_{1.5}\cdot 2H_2O$ and $UO_2(NO_3)_2(SpH_2)_{1.5}\cdot EtOH$

An ethanolic solution of the uranyl salt was added to an equimolar amount of SpH_2 in hot ethanolic solution. The orange precipitate which formed was filtered off and washed several times with EtOH.

Analyses

Uranium was estimated as U_3O_8 by the ammonia method [13]. The C,H,N microanalyses were carried out by Microanalyses Laboratories, Alfred Bernhardt, West Germany. The analytical results are summarised in Table I.

Results and Discussion

Conductance Measurements

The observed molar conductivities in Table I indicate that all the complexes are non-electrolytes; also the molar conductivities show no appreciable change above 25 $cm^2\ ohm^{-1}\ mol^{-1}$.

Infrared Spectra

The infrared absorptions due to the UO_2 group are observed around 920 and 810 cm^{-1} as sharp bands corresponding to the asymmetric stretching frequency, $\nu_{asy}(U–O)$, and the symmetric stretching frequency, $\nu_{sym}(U–O)$, respectively, These observations indicate that the UO_2 moiety is virtually linear [14].

The nitrato complexes show no absorption near 1380 cm^{-1}, where the free nitrate ion is known to absorb. Thus there is no nitrate ion which is not coordinated to the uranyl ion. The ν_1 (NO_2 symmetric stretching) and ν_4 (NO_2 asymmetric stretching) vibrations [15, 16] are strong and were found to be separated by 235 cm^{-1} for the complex $UO_2(NO_3)_2(pBH)_2$ and by about 190 cm^{-1} in the complex $UO_2(NO_3)_2(SpH_2)_{1.5}\cdot EtOH$. Hence, the nitrate group appears to be bidentate in the former complex and unidentate in the latter. However, the magnitude of the splitting is not a reliable criterion for distinguishing unidentate and bidentate nitrate group [17].

In the two acetate complexes $UO_2(CH_3COO)_2(pBH)$ and $UO_2(CH_3COO)_2(bBH)\cdot H_2O$, the two COO stretching bands, ν_{asy} and ν_{sym} were observed at about 1540 and 1410 cm^{-1} respectively, indicating that the acetate group is bidentate in the two complexes [18].

The IR spectra of the uranyl sulphate complexes show that the ν_3 (asymmetric stretch) and ν_4 (symmetric bend) modes are split and the ν_1 (symmetric stretch) band (IR forbidden in uncoordinate sulphate) appears at 1000 cm^{-1} thus indicating the presence of bicoordinate (C_{2v}) sulphate [19].

In the monobasic bidentate ligands, (pBH) and (bBH), weak and broad absorption bands are observed in the 3300–3100 cm^{-1} region, which may be assigned to the hydrogen bonded ν_{OH} or ν_{NH}. An examination of the spectra (Table II) of the corresponding complexes show that broad bands are observed in the region 3200–3400 cm^{-1} and this may be assigned to the absorption of ν_{OH} or ν_{NH} group. This shows that the molecules of the Schiff base are coordinated to the central uranium atom and not their anions, except the complex $UO_2(CH_3COO)$-

(bB)·H_2O, in which no bands were observed in this region (may indicate the absence of OH stretching vibration of ligand) and thus the anion of the Schiff base is coordinated to the central uranium atom and not the molecules. The C=N stretch appears at 1625 cm^{-1} in the Schiff base ligand, while it seems to be split up into very strong bands at 1640 cm^{-1} and 1601 cm^{-1} in the complexes. It appears that the band at 1640 cm^{-1} is mainly due to –C=N stretch (which indicates that the bond order of the carbon nitrogen link is increased), whilst the lower band appears to be coupled with –C=C– stretch [20] which occurs at 1575 cm^{-1} in the Schiff base.

In the dibasic tetradentate ligands (SBH_2) and (SpH_2) which offer four possible sites of coordination, no absorption bands appear beyond 3150 cm^{-1}. Owing to strong hydrogen bonding both intermolecular (OH.....O) and intramolecular (OH.....N), the frequency of the hydrogen bonded OH is probably lowered to a considerable extent and overlaps with the ν_{OH} vibrations, thus appearing as a broad band in the region 3150–2950 cm^{-1}. In the resulting complexes of the type $UO_2X_2L_n$, where $X = Cl^- NO_3^-$, SO_4^{--} and L is the molecule of the bibasic tetradentate Schiff bases, a strong band is observed in the region 3500–3350 cm^{-1} and may be assigned to the absorption band of ν_{OH} and ν_{NH} groups. This shows that the molecules of the Schiff base rather than their anions are coordinated to the central uranium atom. In the complex UO_2(Sp)·EtOH, no bands were observed at about 3150 cm^{-1} indicating the absence of OH stretching vibration; thus this complex contains no neutral ligand and the deprotonated binegative ion is coordinated to the uranyl group.

References

1 V. G. Kulkarani, S. N. A. Taputer and N. N. Sirmokadam, *J. Indian Chem. Soc.*, *49*, 111 (1972).

2 A. K. Mukherjee and P. Ray, *J. Indian Chem. Soc.*, *32*, 633 (1955).

3 P. Teyssie and J. J. Charette, *Spectrochim. Acta*, *19*, 1407 (1963).

4 S. Yamada and A. Takeuchi, *Bull. Chem. Soc. Jap.*, *42*, 2549 (1969).

5 P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. Prakt. Chem.*, *149*, 217 (1937).

6 H. Mahanta and K. C. Dash, *J. Inorg. Nucl. Chem.*, *39*, 1345 (1977).

7 R. G. Vijay and J. P. Tandon, *Monatshefte Chemie*, *107*, 95 (1976).

8 A. Pasini, M. Gullotti and E. Cesarrotti, *J. Inorg. Nucl. Chem.*, *34*, 3821 (1972).

9 S. N. Poddar, K. Dey and S. C. Nathsarkav, *J. Indian Chem. Soc.*, *40*, 489 (1963).

10 R. G. Vijay and J. P. Tandon, *J. Inorg. Nucl. Chem.*, *39*, 1242 (1977).

11 K. L. Charda, P. Prashar and J. P. Tandon, *J. Indian Chem. Soc.*, *49*, 553 (1972).

12 S. E. Al Mukhtar and L. K. Larkworthy, (unpublished), S. E. Al Mukhtar, *Ph.D. Thesis*, Surry University (1976).

13 A. J. Vogel, 'Quantitative Inorganic Analysis', 3rd edn., Longmans, London (1962).

14 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, *Inorg. Chim. Acta Rev.*, *5*, 19 (1971).

15 E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, *81*, 3818 (1959).

16 C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

17 G. Topping, *Spectrochim. Acta*, *21*, 1743 (1965).

18 M. Vidali, P. A. Vigato and V. Casellato, *J. Inorg. Nucl. Chem.*, *37*, 955 (1975).

19 E. P. Hertzenberg and J. C. Bailar, Jr., *Inorg. Chem.*, *10*, 2371 (1971).

20 B. D. Sarma and J. C. Bailar, *J. Am. Chem. Soc.*, *77*, 5476 (1955).