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Coordination Polymers of Some Uranyl Salts Involving 4,4'-Bipyridyl, 4,4'-Bipyridyl N,N'-dioxide, 1,3-Bis (4-pyridyl) propane and Hexamethylenetetramine

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Analytical data and infrared spectral measurements down to 200 cm^{-1} on the coordination compounds formed by the interaction of uranyl chloride, thiocyanate, nitrate, sulphate and acetate with 4,4'-bipyridyl, 4,4'-bipyridyl N,N'-dioxide, 1,3-bis (4-pyridyl) propane and hexamethylenetetramine indicate that the complexes are coordination polymers having four or six coordination around the uranyl UO_2^{2+} ion with bidentate bridging organic ligand molecules and terminally bonded chloro and thiocyanato groups and bidentate chelating nitrato, sulphato and acetato groups in the solid state.

INTRODUCTION

During recent years inorganic polymers of high molecular weight have attracted much attention. Many inorganic polymers of high molecular weights exist in solid state as crystals which are either three-dimensional infinite polymers or have lattices extending into two dimensions. In addition, there are inorganic materials of high molecular weight having a large number of simple monomeric units analogous to the organic polymers. Among the inorganic compounds coordination is very often the cause of polymerization resulting in coordination polymers.[1] Structures of a number of metal halides can be explained in terms of electron pair donation from halogen to the metal atom as in palladium(II) chloride, the crystal of which has chains of double halogen bridges.[2] A number of coordination polymers have now been synthesized from organic ligands and various metal ions. Polymerization in most of such compounds is explained in terms of halogen/pseudohalogen bridges with terminally bonded organic ligands in the polymeric chain structures. The present communication describes the preparation and characterization of some coordination compounds formed by the interaction of uranyl chloride, thiocyanate, nitrate, sulphate and acetate with 4,4'-bipyridyl (Bipy), 4,4'-bipyridyl N-N'-dioxide ($BipyO_2$), hexamethylenetetramine (Hmta) and 1,3-bis (4-pyridyl) propane (DPP) (Fig. 1).

EXPERIMENTAL

Materials and Methods

4-4'-Bipyridyl (Koch-Light), hexamethylenetetramine (M/s. Ega Chemie, West Germany) and 1,3-bis (4-pyridyl) propane (Reilly Tar &

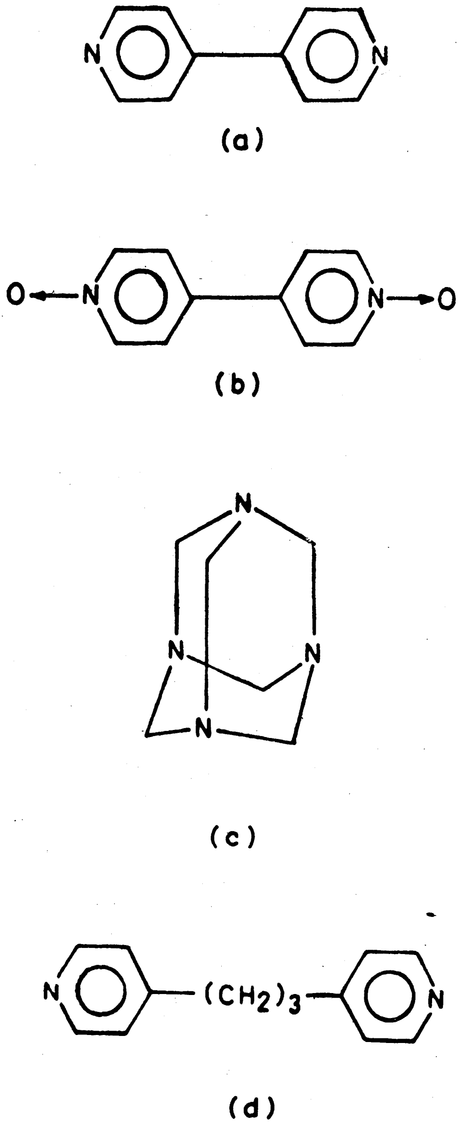


Fig. 1. (a) 4,4′-Bipyridyl,
(b) 4,4′.Bipyridyl N,N′-dioxide
(c) Hexamethylenetetramine
(d) 1,3-Di-(4-pyridyl) propane

Chemical Corporation, U.S.A.) were used without further purification. 4,4′-Bipyridyl was oxidized to its dioxide by the method of Ochiai[3] and the crude product was recrystallized from hot water by the addition of an excess of pure acetone. Purity of $BipyO_2$ was checked by its m.pt. and elemental analysis. The uranyl chloride, thiocyanate, nitrate and acetate complexes were prepared by mixing together the respective uranyl salt (10 mmole in 20 ml ethanol) and the ligand solution (20 mmole in 10 ml ethanol). The uranyl sulphate complexes were prepared by adding the ligand solution (20 mmole in 10 ml ethanol) to a hot solution of uranyl sulphate (10 mmole in 20 ml methanol). The complexes which formed were suction filtered, washed with ethanol (or methanol) and dried in an air oven at *ca* 80°C. Yield of the complexes was *ca* 80%. The uranium content was determined gravimetrically as oxinate after destroying the organic moiety with concentrated nitric acid and then with concentrated sulphuric acid. The anions were estimated gravimetrically[4]. C, H and N contents in the complexes were determined by microanalysis.

Infrared spectra of the uncoordinated ligands and of their uranyl complexes were recorded as Nujol mulls supported between sodium chloride plates (rock salt region) and thin polyethylene sheets (650–200 cm^{-1}) on a Perkin-Elmer spectrophotometer Model 783 equipped with caesium iodide optics.

RESULTS AND DISCUSSION

Analytical date (Table 1) of the compounds isolated in the present study indicate that (i) 4,4′-bipyridyl forms 1 : 1 (metal : ligand) complexes with uranyl chloride and sulphate but a 3 : 2 complex with uranyl nitrate, (ii) 4,4′-bipyridyl N,N′-dioxide gave 1 : 1 with uranyl chloride, nitrate, sulphate and acetate but 2 : 1 with uranyl thiocyanate (iii) hexamethylenetetramine gave 1 : 1 with uranyl nitrate and 2 : 1 with uranyl sulphate and thiocyanate, and (iv) 1,3-bis (4-pyridyl) propane formed 1 : 1 complexes with uranyl chloride, nitrate and sulphate. Infrared frequencies due to the uranyl group and coordinated anionic groups are listed in Table 2. Strong bands due to nitrate, sulphate and acetate groups in the range 1600–1000 cm^{-1} superimposed and masked some of the bands due to the organic moiety. No absorption bands were observed which could be attributed to water or ethanol thus establishing these compounds to be anhydrous and free from coordinated or lattice water/ethanol.

In addition to the ligand bands shifted on account of coordination (vide infra) the rock salt region infrared spectra of the complexes investigated herein show absorption bands at *ca* 900 cm^{-1} due to the ν_3 vibration of the uranyl group. The ν_1 mode of the uranyl group is infrared forbidden in the free linear uranyl ion and absence of a band assignable to this mode at *ca* 850 cm^{-1} implies that the linearity of the OUO group is maintained in all these complexes. The doubly degenerate OUO bending mode, ν_2, is observed at *ca* 260 cm^{-1} in the low frequency infrared spectra of these complexes[5].

Mode of Uranium (VI)-ligand bonding

4,4′-Bipyridyl and its dioxide: Infrared spectra of the uranyl complexes with 4,4′-bipyridyl and its dioxide indicate that both the donor atoms of these organic ligands are bonded to metal ions and that these ligands are bridged between two uranyl ions. The steric position of the donor atoms in both these ligands precludes chelation but favours coordination to different metal ions thus leading to polymer chain formation. Normal modes of 4,4′-bipyridyl N,N′-dioxide that are likely to be affected the most, upon coordination are the NO stretching and bending vibration frequencies[6]. The NO stretching vibration which appears as a strong doublet at 1249 and 1234 cm^{-1} in the uncoordinated ligand shifts to lower frequency region (Table 2) in the complexes indicating a decrease in the π-bond character of the NO bond as a result of oxygen to metal coordination and is of the magnitude expected for complexes in which N-oxide

TABLE 1
ANALYTICAL DATA OF URANYL (II) COMPOUNDS

Compound	Uranium % Found (Calc)	Anion % Found (Calc)	Carbon % Found (Calc)	Hydrogen % Found (Calc)	Nitrogen % Found (Calc)
$UO_2(Bipy)Cl_2$	48.3	14.1	24.2	1.62	5.64
	(47.8)	(14.2)	(24.1)	(1.60)	(5.63)
$UO_2(Bipy)_{1.5}(NO_3)_2$	37.1	—	27.9	2.08	10.9
	(37.8)	—	(28.6)	(1.91)	(11.1)
$UO_2(Bipy)SO_4$	46.0	18.2	23.0	1.54	5.37
	(45.5)	(18.3)	(22.9)	(1.53)	(5.36)
$UO_2(DPP)Cl_2$	44.6	13.5	29.0	2.60	5.20
	(44.1)	(13.1)	(28.9)	(2.59)	(5.19)
$UO_2(DPP)SO_4$	42.3	17.3	28.1	2.45	4.90
	(42.1)	(17.0)	(27.6)	(2.48)	(4.96)
$UO_2(DPP)(NO_3)_2$	40.4	—	26.0	2.39	9.30
	(40.2)	—	(26.3)	(2.36)	(9.45)
$UO_2(BipyO_2)Cl_2$	44.8	13.5	22.6	1.52	5.30
	(44.9)	(13.4)	(22.6)	(1.51)	(5.29)
$UO_2(BipyO_2)(NO_3)_2$	40.9	—	20.5	1.39	9.81
	(40.8)	—	(20.6)	(1.37)	(9.62)
$UO_2(BipyO_2)SO_4$	43.1	17.1	21.7	1.44	5.07
	(42.9)	(17.3)	(21.6)	(1.44)	(5.05)
$UO_2(BipyO_2)(OAc)_2$	41.0	—	29.2	2.45	4.86
	(41.3)	—	(29.1)	(2.43)	(4.86)
$UO_2(BipyO_2)_2(NCS)_2$	31.4	15.1	34.7	2.10	11.0
	(31.2)	(15.2)	(34.6)	(2.09)	(11.0)
$UO_2(HMTA)_2SO_4$	36.9	15.0	22.4	3.76	17.5
	(36.8)	(14.8)	(22.2)	(3.71)	(17.3)
$UO_2(HMTA)(NO_3)_2$	44.8	—	13.5	2.22	16.0
	(44.5)	—	(13.4)	(2.24)	(15.7)
$UO_2(HMTA)_2(NCS)_2$	34.3	17.6	25.4	3.62	21.1
	(35.7)	(17.4)	(25.2)	(3.60)	(21.0)

TABLE 2

INFRARED SPECTRAL DATA (cm^{-1}) OF URANYL (II) COMPOUNDS

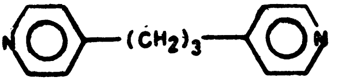
Compound	ν_{asym}UO	δOUO	Coordinated anionic modes
$UO_2(Bipy)Cl_2$	913	257	νU—Cl 249
$UO_2(Bipy)_{1.5}(NO_3)_2$	940	250	ν_1 1510 ν_2 1030 ν_3 740 ν_4 1280 ν_5 715 ν_6 m.l. (1775, 1735)
$UO_2(Bipy)SO_4$	930	257	ν_1 970 ν_2 470 ν_3 1240, 1130, 1043 ν_4 655, 602, 590
$UO_2(DPP)Cl_2$	905	252	νU—Cl 233
$UO_2(DPP)SO_4$	908	255	ν_1 998 ν_2 475 ν_3 1249, 1166, 1108, 1040 ν_4 627, 614
$UO_2(DPP)(NO_3)_2$	910	254	ν_1 1541 ν_2 1028 ν_3 748 ν_4 1290 ν_5 716 ν_6 807 (1776, 1734)
$UO_2(BipyO_2)Cl_2$	902	260	($BipyO_2$ modes: νNO 1218, 1208 δNO 838, 830) νU—Cl 230
$UO_2(BipyO_2)(NO_3)_2$	910	254	($BipyO_2$ modes: νNO 1216, 1207 δNO 842, 830) ν_1 1517 ν_2 1025 ν_3 739 ν_4 1274 ν_5 709 ν_6 800 (1750, 1713)
$UO_2(BipyO_2)SO_4$	917	260	($BipyO_2$ modes: νNO 1224, 1215 δNO 838, 830) ν_1 985 ν_2 472 ν_3 1234, 1100, 1066 ν_4 640, 632, 602
$UO_2(BipyO_2)(OAc)_2$	902	260	($BipyO_2$ modes: νNO 1225, 1216 δNO 842, 830) ν_{asym}OCO 1545 ν_{sym}OCO 1422 δOCO 666
$UO_2(HMTA)_2SO_4$	910	264	ν_1 1015 ν_2 470 ν_3 1245, 1160, 1120 ν_4 640, 613, 595
$UO_2(HMTA)(NO_3)_2$	920	260	ν_1 1520 ν_2 m.l. ν_3 745 ν_4 1310 ν_5 722 ν_6 834 (1755, 1720)
$UO_2(HMTA)_2(NCS)_2$	890	265	νCN 2058 νCS 796 δNCS 482
$UO_2(BipyO_2)_2(NCS)_2$	908	255	νCN 2064, 2040 νCS 860 δNCS 474

m.l. masked by the ligand (nitrato combination modes are given in parentheses).

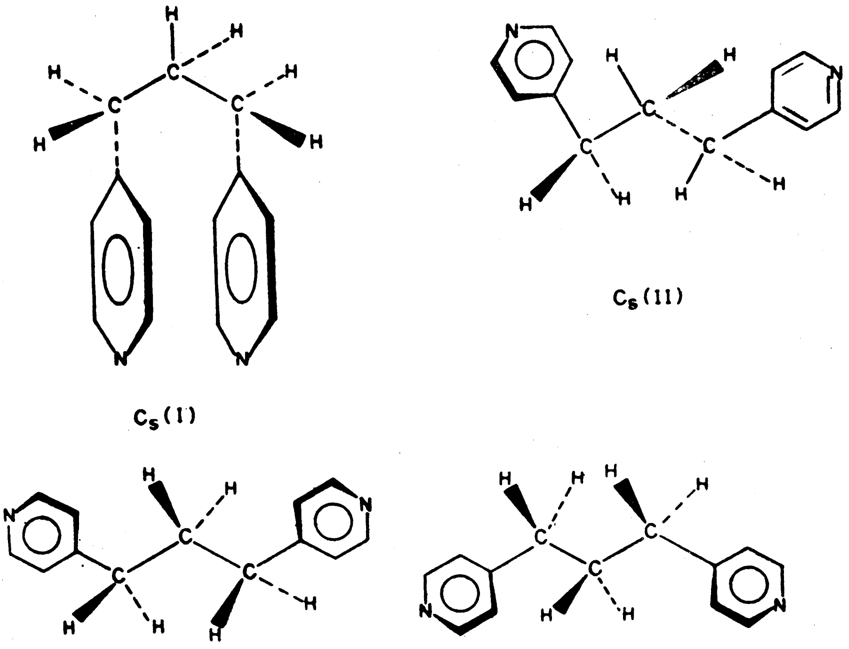
and negatively charged ligands (halides, NO_3^-, SO_4^{2-} etc.) constitute the first coordination sphere of the metal ion[7]. The NO bending vibration appearing as strong absorptions at 848 and 834 cm^{-1} in the uncoordinated ligand is observed with almost similar intensity but shifted slightly to lower frequencies in the infrared spectra of the uranyl complexes. Since the oxygen of the NO group is involved in coordination a noticeable negative shift would be expected for the δNO mode in going from the free ligand to metal complexes. The small shift observed may in fact be due to two opposing effects : (i) the effect of coordination on the NO group which would cause a vibrational shift to higher frequencies, and (ii) the decrease in NO double bond character which would tend to lower the frequency. If both these effects were roughly equal, no shift in the NO bending vibration would result[6, 7]. Coordination through only one of the oxygens of the dioxide (monodentate ligand) would have resulted in a more complex spectrum particularly in the NO stretching and bending frequency regions.

Hexamethylenetetramine: This is a potentially tetradentate ligand and the chemical and steric equivalence of the four nitrogen atoms has been demonstrated by various physico-chemical techniques[8, 9]. It may thus act as a mono-, bi-, tri- or tetradentate ligand. Framework molecular models show that it is more likely to bond to different metal ions and thus act as a bridging rather than a chelating ligand. 1300–200 cm^{-1} region infrared spectrum of the uncoordinated hexamethylenetetramine shows absorption bands at 1225s, 1180w, 1040m, 1000s, 823w, 803s, 714w, 664s, 610m and 508s. Of these, the two strong bands at 1225 and 1000 cm^{-1} are assigned to νCN modes[10]. Both these bands are split up into doublets in complexes in which this ligand acts as a bidentate bridging ligand[11] but they suffer only a very minor splitting forming closely spaced doublets or triplets in complexes where hexamethylenetetramine molecule(s) act as monodentate ligand(s)[12]. Apart from some intensity changes and the splitting of νCN bands the infrared spectra due to coordinated hexamethylenetetramine in the uranyl complexes studied herein are almost superimposable on the spectrum of the uncoordinated ligand. This may be attributed to the fact that the chair conformation[13] of the uncoordinated hexamethylenetetramine is retained in all the uranyl complexes. Although a potentially tetradentate ligand stereochemically hexamethylenetetramine seems to act only as a bidentate ligand bridging between two metal atoms retaining the chair configuration in all the uranyl complexes.

1,3-Bis (4-pyridyl) propane: This ligand consists of two pyridyl groups both bonded in γ-positions to the two terminal carbon atoms of propane. It may act as a mono- or a bidentate ligand and molecular scale models show considerable free rotation about its carbon-carbon bonds. In one of the possible configurations the two pyridyl rings may be parallel to each other (C_s symmetry) and the two nitrogens may coordinate to the same metal ion. The chelate ring thus formed would be a 12-membered one. Another possible geometry of this molecule is when the two pyridyl rings are away from each other (C_{2v} symmetry with the two rings in one and the same plane or C_s symmetry when the two rings are non-planar). Such configurations would not permit chelation as the two nitrogen atoms, being far apart from each other, would not be able to coordinate to the same metal ion. Coordination of the two pyridyl nitrogens to different metal ions would thus be favoured resulting in polymeric chain structures. Infrared spectra of the uranyl complexes studied herein show clearly the bidentate bridging nature of this ligand in these complexes. Steric position of the two nitrogen atoms in this ligand precludes chelation but favours coordination to different metal ions. Coordination through only one of the two pyridyl rings (monodentate ligand) would have given a rather complex spectrum particularly in the region which suffers splitting or shifting upon coordination. Further, infrared spectrum due to coordinated ligand in these complexes exhibits fewer absorption bands as compared with the uncoordinated ligand spectrum. This is attributed to the fact that the two pyridyl rings which are non-planar in the uncoordinated ligand become coplanar upon coordination and that the coordinated ligand achieves a higher symmetry (Fig. 2).



1, 3-Di (4-pyridyl) propane



C_s (I)

C_s (II)

C_{2v} (I)

C_{2v} (II)

Fig. 2. Possible symmetries of 1,3-di(4-pyridyl) propane

Uranyl chloride complexes: Uranyl chloride gave 1 : 1 (metal : ligand) complexes with 4,4′-bipyridyl, 4,4′-bipyridyl N,N′-dioxide and 1,3-bis (4-pyridyl) propane. Infrared spectra are consistent with the presence of bidentate bridging nature of the ligands in all these complexes. Low frequency infrared spectra of these complexes show a strong absorption band at *ca* 240 cm^{-1} which is assigned as the terminal ν(U–Cl) mode[14]. Terminal ν(U–Cl) mode occurs at *ca* 260 cm^{-1} in monomeric, six-coordinated uranium (VI) compounds $UO_2L_2Cl_2$ where L is a monodentate ligand[15,16]. The metal-halogen stretching modes absorb at much lower energies in the halogen-bridged polymeric octahedral structures as compared with the monomeric octahedral ones[17]. From a consideration that the organic ligands act as bidentate ligands bridging between two uranyl groups and that the two chlorine atoms are terminally bonded to each uranyl group the 1 : 1 uranyl chloride complexes with 4,4′-bipyridyl, 4,4′-bipyridyl N,N′-dioxide and 1,3-di-(4-pyridyl) propane are suggested to have polymeric chain structures involving six-coordinated uranium (VI) with four ligand atoms (two nitrogens or oxygens from two organic ligand molecules and two terminal chlorine atoms (Fig. 3-a) forming an equatorial ring around the linear uranyl group.

Uranyl thiocyanate complexes: Uranyl thiocyanate gave 1 : 2 complexes with 4,4′-bipyridyl N,N′-dioxide and hexamethylenetetramine but did not react with the other ligands used. In addition to the ligand bands indicating the bidentate bridging character of the organic ligands, infrared spectra of the 1 : 2 uranyl thiocyanate complexes with 4,4′-bipyridyl N,N′-dioxide and hexamethylenetetramine, new absorption bands at *ca* 2040, 860 and 470 cm^{-1} are observed in them. These new bands are identified as νCN (*ca* 2040 cm^{-1}), νCS (*ca* 860 cm^{-1}) and δ NCS (*ca* 470 cm^{-1}) due to coordinated thiocyanato groups. The frequencies of these bands are in good agreement with those associated with terminal N-bonded NCS groups[18]. Based on the considerations of (i) bidentate bridging nature of the organic ligands and terminally N-bonded NCS groups the 1 : 2 complexes of uranyl thiocyanate with 4,4′-bipyridyl N,N′-dioxide and hexamethylenetetramine are assigned polymeric chain structures involving eight-coordinated uranium (VI) with six ligand atoms—four oxygens of the bidentate bridging 4,4′-bipyridyl N,N′-dioxide molecules and two nitrogens of the N-bonded NCS groups in the former complex (Fig. 3-b), and six nitrogen atoms, four from bidentate bridging hexamethylenetetramine molecules and two from NCS groups—forming an equatorial ring around the linear OUO group.

Uranyl nitrate complexes: Uranyl nitrate gave a 2 : 3 complex with 4,4′-bipyridyl while the other ligands investigated formed 1 : 1 complexes. Infrared spectra of all these complexes indicate the presence of coordinated nitrato groups[19-21]. This is evident from the fact that the symmetrical stretching mode ν_3 at *ca* 1360 cm^{-1} and the in-plane deformation mode ν_4 at *ca* 720 cm^{-1} in the infrared spectra of ionic nitrates, both doubly degenerate, lose their degeneracies and both are split up into their components (ν_3 to ν_1 and ν_4; and ν_4 to ν_3 and ν_5) in the infrared spectra of these complexes. Moreover, the symmetric stretching mode ν_1 (i.r. inactive in ionic nitrates) becomes infrared active and the frequency of ν_2 vibration is lowered. These features clearly eliminate the presence of ionic nitrates in these complexes.

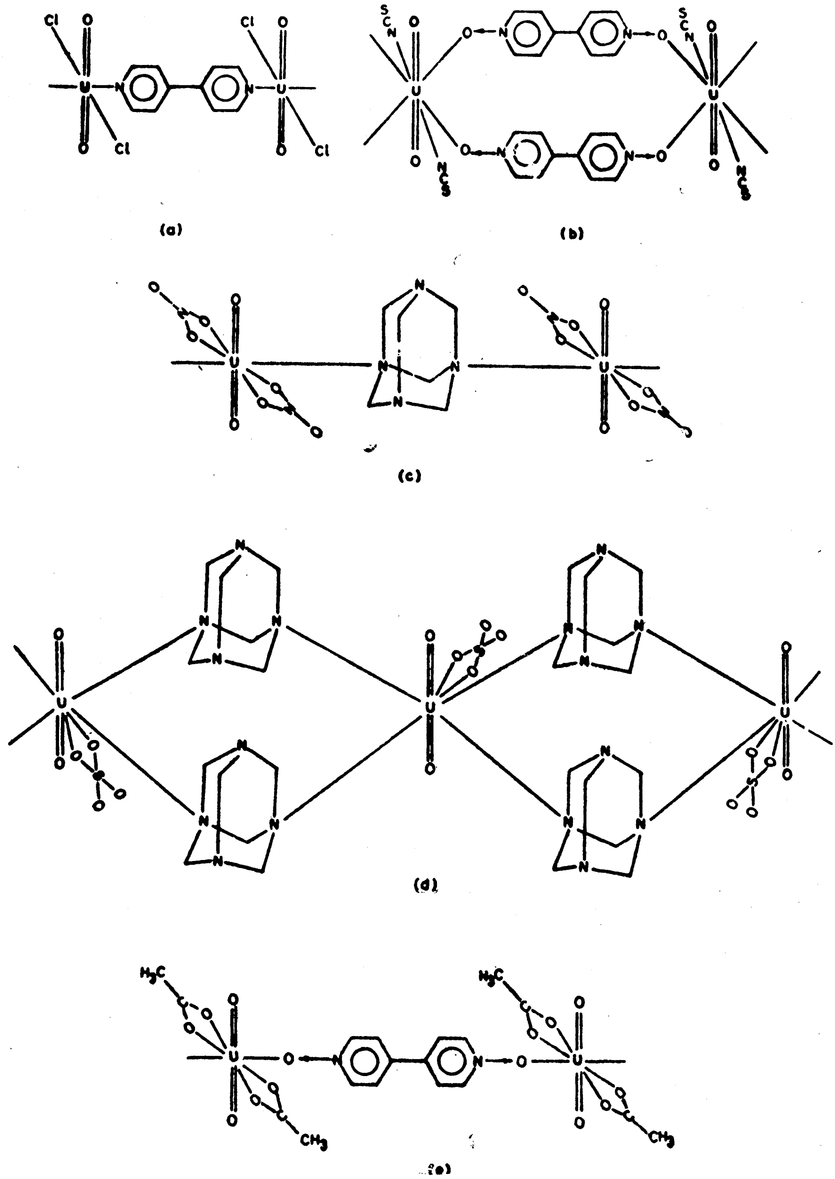


Fig. 3. Structure of (a) UO_2 (4,4′-Bipy) Cl_2
(b) UO_2 (4,4′-BipyO_2)$_2$ $(NCS)_2$
(c) UO_2 (HMTA) $(NO_3)_2$
(d) UO_2 $(HMTA)_2$ SO_4
(e) UO_2 (4,4′-BipyO_2) $(OAc)_2$

Infrared spectral studies as well as X-ray structural studies have established that in uranyl nitrate complexes the most common mode of nitrate coordination is that as a bidentate chelating ligand[22–26]. However, examples of anionic [27, 28] and monodentate[29] nitrato groups are also known. In addition to the bands due to coordinated ligand molecules (vide supra) infrared spectra of all the uranyl nitrate complexes with the ligands investigated here exhibit absorption bands at *ca* 1500, 1030, 740, 1280, 715 and 810 cm^{-1}. Such bands are neither observed in the infrared spectra of the uncoordinated ligands used nor in their complexes with metal (II) halides. These additional bands are, therefore, assigned as ν_1 (*ca* 1500 cm^{-1}), ν_2 (*ca* 1030 cm^{-1}), ν_3 (*ca* 740 cm^{-1}), ν_4 (*ca* 1280 cm^{-1}), ν_5 (*ca* 715 cm^{-1}) and ν_6 (*ca* 810 cm^{-1}) modes due to coordinated nitrato groups. Moreover, two weak bands (with a separation of *ca* 40 cm^{-1}) are also observed in the nitrato combination mode region[30–33] (1800–1700 cm^{-1}) in all these complexes. The observed magnitude of separation of ν_1 at *ca* 1500 cm^{-1} and ν_4 at *ca* 1280 cm^{-1} (*ca* 200 cm^{-1}) and of the combination modes (*ca* 40 cm^{-1}) indicate the exclusive presence of bidentate chelating nitrato groups[22–33] and clearly eliminate the presence of ionic or monodentate nitrates in these complexes. Moreover, the infrared frequencies due to coordinated nitrato groups in all these complexes occur in almost the same frequency ranges as in $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 2H_2O$, $Rb[UO_2(NO_3)_3]$ and several other uranyl nitrate complexes in which the presence of bidentate chelating nitrato ligands has been established by infrared spectroscopy and/or X-ray structural studies[22–26].

Based on the considerations of uranyl-ligand bonding modes and the bidentate chelating nature of the nitrato ligands the 1 : 1 uranyl nitrate complexes with 4,4′-bipyridyl N,N′-dioxide, hexamethylenetetramine and 1,3-bis(4-pyridyl) propane are tentatively assigned as polymeric chain structures involving eight-coordinated uranium (VI) with (a) six oxygen atoms—two from bidentate bridging 4,4′-bipyridyl N,N′-dioxide molecules and four from two bidentate chelating nitrato groups in the case of 4,4′-bipyridyl N,N′-dioxide complex, or (b) six ligand atoms—two nitrogens from bidentate bridging hexamethylenetetramine (Fig. 3-c) or 1,3-bis (4-pyridyl)-propane molecules and four oxygen atoms from two bidentate chelating nitrato ligands—forming a hexagonal equatorial ring perpendicular to the plane of the linear uranyl group. Infrared spectrum of the 2 : 3 uranyl nitrate complex with 4,4′-bipyridyl shows the presence of bidentate bipyridyl molecules bridging between two uranyl groups and bidentate chelating nitrato ligands. However, with non-integral metal : ligand ratio it is difficult to postulate the probable coordination number of uranium (VI) in this complex.

Uranyl sulphate complexes: Infrared spectra of the 1 : 1 uranyl sulphate complexes with 4,4′-bipyridyl, 4-4′-bipyridyl N,N′-dioxide, 1,3-di-(4-pyridyl) propane and the 1 : 2 complex with hexamethylenetetramine show the presence of coordinated sulphato groups[34, 35]. This is evident from the fact that the strong broad band at *ca* 1120–1080 cm^{-1} due to the triply degenerate SO stretching mode ν_3 in ionic sulphates splits up into its components at *ca* 1245, 1160 and 1120 cm^{-1} (masking the ligand bands in the region) in the infrared spectra of these complexes. The triply degenerate OSO bending mode ν_4 which occurs as a sharp well defined band at *ca* 610 cm^{-1} in sulphate with T_d symmetry also splits up into its components in this compound. In addition to these, ν_1 and ν_2 both infrared forbidden in uncoordinated sulphates, appear at *ca* 1220 and *ca* 470 cm^{-1}, respectively. The fundamental frequencies due to coordinated sulphato groups in all these complexes are consistent with those normally associated with bidentate chelating sulphato groups[34, 35]. Based on the considerations of uranium(VI)-ligand and uranium(VI)-sulphate bonding modes the tentative coordination numbers and the stereochemical environments for the uranyl sulphate complexes are suggested as follows: (i) 1 : 1 uranyl sulphate complexes with 4,4′-bipyridyl and 1,3-di(4-pyridyl)propane have polymeric chain structures involving 6-coordinated uranium(VI) with two nitrogen atoms of the bridging 4,4′-bipyridyl/1,3-di(4-pyridyl)propane molecules and two oxygens of the bidentate chelating sulphato groups forming a tetragonal ring around the linear uranyl group; (ii) UO_2(4,4′-bipyridyl N,N′-dioxide)SO_4 complex is a polymeric chain structure involving six-coordinated uranium(VI) with four oxygen atoms (two from bridging 4-4′-bipyridyl N,N′-dioxide molecules and two from bidentate chelating sulphato groups) in an equatorial plane around the linear OUO group; and (iii) the 1 : 2 uranyl sulphate-hexamethylenetetramine complex is considered to have a linear polymeric chain structure having eight-coordinated uranium(VI) with six ligand atoms—four nitrogens from two bidentate bridging hexamethylenetetramine molecules retaining the chair configuration of the uncoordinated ligand and two oxygens from bidentate chelating sulphato groups—around the linear uranyl group (Fig. 3d).

Uranyl acetate complexes: 4,4′-Bipyridyl N,N′-dioxide gave a 1 : 1 complex with uranyl acetate while the other ligands did not react under similar conditions. Infrared spectrum of the 1 : 1 uranyl acetate complex with 4,4′-bipyridyl N,N′-dioxide shows absorption bands at *ca* 1545, 1422 and 666 cm^{-1} (but not in the uncoordinated ligand) which are assigned to νOCO asymmetric, νOCO symmetric and δOCO modes, respectively, due to coordinated acetato groups[34]. The free acetate ion has a low symmetry (C_{2v}) and has fifteen fundamental vibrational modes all of which are infrared and Raman active. Although no marked differences in the infrared spectra are expected for the various ways an acetate group coordinates with metal ions, the effect and type of coordination are usually judged from the magnitude of separation of the OCO asymmetric and symmetric stretching frequency shifts caused by coordination[36]. X-ray structural[37] and infrared spectral[38] studies have shown that the acetate groups coordinate in a bidentate chelating fashion with the uranyl acetate[39]. Based on the considerations of bidentate bridging nature of 4,4′-bipyridyl N,N′-dioxide and bidentate chelating acetato groups the 1 : 1 uranyl acetate complex with 4,4′-bipyridyl N,N′-dioxide is tentatively assigned to have an overall eight-coordinated (all oxygen atoms) polymeric chain structure with six oxygens (four from two bidentate chelating acetato ligands and two from bidentate bridging organic ligandm olecules)—around the linear uranyl group (Fig. 3e).

All the uranyl compounds reported herein are considered as coordination polymers involving bridging organic ligand molecules. Molecular weights of polymers, in general, can be determined by chemical or physical methods of functional group analysis, by measurements of colligative properties, light scattering or ultracentrifugation or by measurement of dilute solution viscosity. However, with the exception of some types of end group analysis all the methods require solubility of the polymer and all involve extrapolation to infinite dilution or operation in a solvent where polymer-solvent interaction is zero. Moreover, dimeric and oligomeric compounds are generally soluble is organic solvents as well in molten camphor. Because of the insolubility of the uranyl compounds, studied herein, in suitable organic solvents and in molten camphor, molecular weight determinations could not be carried out.

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