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BI- AND TRINUCLEAR URANYL COMPLEXES WITH METAL SCHIFF BASE COMPLEXES

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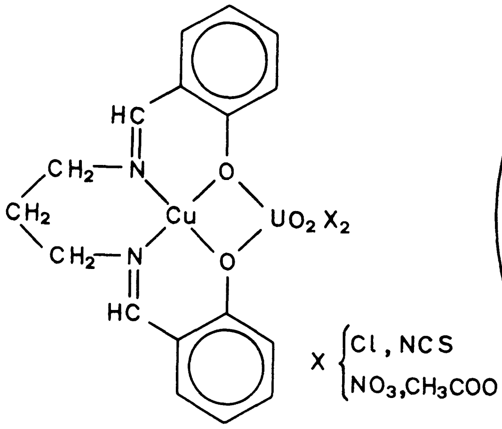
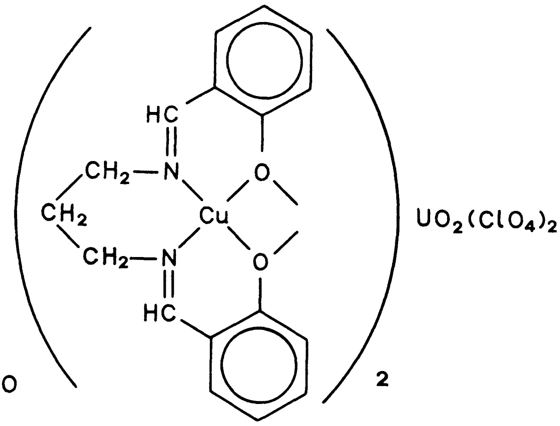
N,N'-1,3-propylene-bis(salicylideneiminato)Cu(II) reacts with some uranyl salts to form bi- and trinuclear complexes. Infrared data show that the "complex ligand" is coordinated to the uranyl ion in the equatorial plane through the phenolic oxygens. Diffuse reflectance spectra suggest a copper(II) environment more distorted from planarity in polynuclear species than the "complex ligand".

It is well known that metal complexes of tetradentate Schiff bases,such as the salicylaldimines,may act as simple bidentate ligants coordinating through the two phenolic oxygen atoms. Bi- and trinuclear compounds of various transition and non transition metals with some metal complexes as ligands,have been reported.[1-3] Nothing is known about the ability of uranyl ion to form similar compounds. On the other hand,uranyl ion is quite interesting for its peculiar coordinating mode.[4]

We report here some preliminary results of an investigation on the uranyl bi- and trinuclear complexes with N,N'-1,3-propylene-bis(salicylideneiminato)Cu(II) (abrev. Cu1,3PS),to which we attributed the oxygen-bridged structures:





Binuclear complexes were prepared by adding an ethanolic solution of Cu1,3PS to the appropriate uranyl salt in the same solvent(molar ratio 3:1). The precipitates, washed with anhydrous ethanol,were dried at 80 °C.

The trinuclear complex was obtained by reacting Cu1,3PS in chloroform solution with hexahydrate uranyl perchlorate in ethanol. The obtained complex was washed with chloroform and dried *in vacuo*.

Analytical data together with some physical properties of prepared compounds are reported in Tab.1.

Tab.1.Analytical data,conductance data and decomposition temperatures

	Analysis(%) Theoretical / (Experimental)				Λ_M ohm^{-1}cm^{2}mole^{-1} in		Decomp.
Compounds	C	N	U	Cu	CH_3CN	CH_3NO_2	temp.°C
$(Cu1{,}3PS)UO_2Cl_2$[a]	29.80 (29.54)	4.09 (4.21)	34.78 (34.22)	9.29 (9.27)		24.2	280
$(Cu1{,}3PS)UO_2(NO_3)_2$	27.66 (27.60)	7.59 (7.51)	32.27 (31.89)	8.62 (8.53)	8.5	18.5	230
$(Cu1{,}3PS)UO_2(CH_3COO)_2$	34.44 (34.02)	3.83 (3.69)	32.59 (32.21)	8.69 (8.55)	16.8	9.2	220
$(Cu1{,}3PS)UO_2(NCS)_2$	31.25 (30.75)	7.67 (7.52)	32.61 (31.25)	8.71 (8.59)	28.3	20.0	180
$(Cu1{,}3PS)_2UO_2(ClO_4)_2$[b]	35.30 (34.75)	4.84 (4.65)	20.58 (19.98)	10.99 (10.48)	240.0	170.0	280[c]

a)Theor.: Cl,10.36 Exp.: Cl,10.29. *b*)Theor.: Cl,6.13 Exp.: Cl,6.03.
c)Violent decomposition

The complexes are slightly soluble in nitromethane,acetonitrile,nitrobenzene, methanol,ethanol and rapidily decomposed by water.

Low values of the molecular conductances of the binuclear complexes in nitromethane and acetonitrile show that they are non-electrolites. The trinuclear complex behaves as 1:2 electrolite.

Information on the structure of complexes has been derived from their infrared and diffuse reflectance spectral measurements. In Table 2 i.r. data are reported. The formation of complexes leads to significant changes in the i.r. spectrum of Cu1,3PS,sufficiently specific to be diagnostic of the bi- and trinuclear compexes. The shifts to higher energies of the bands at 1533 and 1610 cm^{-1},assigned to the CO stretching vibration and to the conjugated CN stretching respectively,are compatible with the increasing constraint,introduced by the oxygen bridging.[1]

Tab.2.Selected infrared data

Compounds	ν_{CN}	ν_{CO}	ν_3UO_2	ν_2UO_2	Anions
Cu1,3PS	1610 s	1533 s			
(Cu1,3PS)UO_2Cl_2	1618 s	1560 s	934 s	268 m	
					$NO_3(C_{2v})$
(Cu1,3PS)$UO_2(NO_3)_2$	1623 s	1560 s	937 s	262 m	ν_1 1520, ν_2 1030, ν_3 815, ν_4 1295, ν_5 750, $\nu_2+\nu_5$ 1760, $\nu_2+\nu_6$ 1725
					$CH_3COO(C_{2v})$
(Cu1,3PS)$UO_2(CH_3COO)_2$	1620 s	1558 s	918 s	265 m 258	ν_3 1460, ν_5 678, ν_8 1540
					NCS
(Cu1,3PS)$UO_2(NCS)_2$	1615 s	1555 s	918 s	262 m	ν_1 2045, ν_2 477, ν_3 820
					$ClO_4(T_d)$
$(Cu1,3PS)_2UO_2(ClO_4)_2$	1620 s	1560 s	915 s	270 m	ν_3 1100, ν_4 624

Uranyl ν_3 and ν_2 vibration are not strongly influenced by ligand equatorial coordination.

Infrared data for nitrate complex suggest the NO_3 group belongs in C_{2v} symmetry. The separation observed (35 cm^{-1}) between the combinations bands,appearing in the 1700-1800 cm^{-1} region,are indicative of a bicoordination.[5]

In acetate complex,the small separation (80 cm^{-1}) between the symmetrical (ν_8) and unsymmetrical (ν_3) carboxyl stretching vibration suggests a symmetrical bidentate coordination of the acetate groups.[6,7]

In thiocyanate complex,the frequencies identified as ν_{CN}(2040 cm^{-1}), ν_{CS}(820 cm^{-1}),and δ_{NCS}(477 cm^{-1}) modes,suggest that the NCS groups are coordinated through the nitrogen.[8] The value of the integrated absorption intensity of the CN stretching band,9.5×10^4 M^{-1} cm^{-1} in acetonitrile solution,is compatible with a N-coordination.[9]

The broad band at 1100 cm^{-1} (ν_3) and the unshifted band at 625 cm^{-1} (ν_4) in the infrared spectrum of perchlorate complex indicate that the ClO_4 group retains its T_d symmetry.

Absorption spectra in nitromethane and reflectance spectra give some indication of the stereochemistry of uranyl bi- or trinuclear complexes(Tab.3).

The position of the ligand field band in Cu1,3PS, suggest that the environment around the copper atom is essentially planar. Upon complexation with the uranyl ion, this band shifts to lower energy, indicating that the environment is distorted from planarity. Theoretical[1] and experimental considerations have shown that if one of the metals in a bi- or trinuclear complex is in a planar environment, the adjacent metals will be distorted away from planarity. The distorsion found in the "ligand complex" upon coordination with UO_2^{++} confirms yet again the uranyl capacity to coordinate in the equatorial plane.

Tab.3.Ligand field spectra(cm^{-1})

Compounds	Reflectance	Nitromethane solution
Cu1,3PS	17,050	16,800
(Cu1,3PS)UO_2Cl_2	16,900	16,100
(Cu1,3PS)$UO_2(NO_3)_2$	15,650	15,900
(Cu1,3PS)$UO_2(CH_3COO)_2$	15,900	16,400
(Cu1,3PS)$UO_2(NCS)_2$	16,000	16,000
$(Cu1,3PS)_2UO_2(ClO_4)_2$	16,150	16,100

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