

Dinitrile Complexes of Uranium(IV) Halides

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Coordination compounds of the type $(UX_4 \cdot L-L)$ or $(UX_4 \cdot 2L-L)$ [where $X = Cl$, or Br and $L-L =$ dinitrile] have been prepared and characterized by chemical analysis and molar conductance measurements. The IR results suggest that both the nitrile groups are σ -bonded, probably bridging two metal atoms forming coordination polymers.

By virtue of their bridging or chelating potential, the dinitriles with varying chain length, $NC-(CH_2)_n-CN$ ($n = 2$ to 4), form an interesting group of ligands where cyano groups can coordinate to metal atoms through either σ -electrons^{1,2} or π -electrons³. In the present note we report the results of our studies on the reactions of uranium(IV) chloride and bromide with succinonitrile (SN), glutaronitrile (GN), adiponitrile (AN) and dicyanobenzene (DCB). The compounds have been synthesized in dry CH_2Cl_2 medium by reacting UX_4 and the ligand in 1:2 stoichiometry under inert and anhydrous conditions². Infrared spectra of the compounds ($200-4000\text{ cm}^{-1}$) have been recorded in nujol mull on a Perkin Elmer grating spectrophotometer model 577 using CsI plates. Molar conductances

of the complexes were measured at room temperature in purified acetonitrile using a conductivity bridge with a cell constant of unity. The analytical and physical data of the compounds prepared are presented in Table 1.

It is seen from Table 1 that under similar experimental conditions, both the halides form 1:1 adducts with SN and 1:2 adducts with GN and AN. However, DCB forms 1:1 adduct with UCl_4 and 1:2 adduct with UBr_4 . The compounds obtained are powders which do not melt or sublime but decompose between 110° and $180^\circ C$ when heated in sealed capillaries.

Irrespective of the nature of the adduct, the $\nu(CN)$ mode in the complex shows a positive shift of $20-40\text{ cm}^{-1}$ as compared to the band position in the ligand indicating bonding through the free electron pair on nitrogen^{1,2}. The magnitude of the shift, $\Delta\nu(CN)$, is lower in the present case as compared to that observed for group (IV) and (V) halide complexes [$\Delta\nu(CN)$ $40-50\text{ cm}^{-1}$]^{1,2}.

It is well known that a particular rotational isomer of the nitrile gets established on complex formation and each isomer has a definite number of IR active bands^{2,6}. The presence of a large number of absorption bands in the spectra of the complexes under study indicates that the nitrile in the complexes is present in the form of more than one rotational isomer. In the far infrared region, bands observed near 260 cm^{-1} are assigned to $\nu(U-Cl)$ bands⁵.

Table 1—Analytical Data of the Complexes

Compound	Colour	m.p. ($^\circ C$)	Found (Calc) %		Molar conductance ^{6,7} ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)
			U	Cl or Br	
$UCl_4 \cdot CN(CH_2)_2CN^*$	Green	110 D	53.98 (51.87)	30.65 (30.90)	—
$UBr_4 \cdot CN(CH_2)_2CN^*$	Gray	150 D	39.03 (37.33)	—	160
$UCl_4 \cdot 2CN(CH_2)_3CN$	Light green	160 D	43.90 (41.90)	25.33 (24.99)	130
$UBr_4 \cdot 2CN(CH_2)_3CN^\dagger$	Gray	210 D	30.96 (31.91)	40.73 (42.85)	130
$UCl_4 \cdot 2CN(CH_2)_4CN$	Light green	135 D	39.67 (39.93)	22.93 (23.78)	—
$UBr_4 \cdot 2CN(CH_2)_4CN$	Reddish brown	180 D	29.96 (30.76)	41.40 (41.35)	—
$UCl_4 \cdot CN(C_6H_4)CN^*$	Light green	300 D	46.77 (46.85)	26.27 (27.91)	150
$UBr_4 \cdot 2CN(C_6H_4)CN^*$	Yellowish green	140 D	28.13 (29.15)	38.46 (39.27)	100

*Satisfactory N analysis was also obtained; † satisfactory C and H analyses were obtained.

The IR spectra of these complexes have shown that both the nitrile groups are σ -bonded. Moreover, the insoluble nature of the compounds in inert solvents and lack of definite melting points suggest that these complexes in solid state are probably polymers with bridging ligands.

The adducts are, however, sparingly soluble in acetonitrile which itself is a coordinating ligand and when present in large excess can dissociate the adduct. This may result in an equilibrium between the adduct and its oligomers and polymers. The conductivity data^{6,7} on dilute solutions of the adducts are reported

in Table 1.

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