NN-Diethyldithiocarbamate Complexes of Certain Tervalent Lanthanide and Actinide Elements

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IT is claimed[1] that, in general, sulphur donors coordinate only weakly with tervalent lanthanide elements in solution. Delépine reported[2] a blue tervalent neodymium complex of undetermined composition with di-isobutyldithiocarbamate and more recently Jørgensen[3] studied the reaction between tervalent lanthanide elements and sodium diethyldithiocarbamate (Na dtc) in ethanol but was unable to isolate solid compounds. We have recently characterised quadrivalent actinide diethyldithiocarbamates[4,5] of the type M(dtc)$_4$, M = Th, U, Np, and Pu, and consideration of the ionic radii of the tervalent lanthanides (1·061 Å for La^{3+} decreasing to 0·848 Å for Lu^{3+}) and actinides (1·03 Å for U^{3+} decreasing to 0·99 Å for Am^{3+}) indicated that, on size considerations alone, it should be possible to prepare tervalent complexes of the type M^{I}M^{III}(dtc)$_4$ (M^{I} = a monovalent cation, M^{III} = a lanthanide or actinide element) at least for the majority of the actinides and lanthanides.

Neutral chelates of the type M(dtc)$_3$ (M = Np, Pu, and La—Lu except Pm) are conveniently prepared by the reaction between the appropriate anhydrous tribromide[6] and the stoicheiometric amount of sodium diethyldithiocarbamate in anhydrous ethanol. After vacuum evaporation of the solvent at room temperature the pure product is recrystallised from methyl cyanide–ether mixtures. Of the tervalent actinides, the bright green, air-sensitive Pu(dtc)$_3$ has been isolated, but dark brown solutions of Np(dtc)$_3$ are rapidly oxidised and deposit red crystals of Np(dtc)$_4$ whilst the less stable uranium(III) is oxidised to the yellow quadrivalent compound U(dtc)$_4$. The products have been characterised by C, H, N, and metal analyses.

I.r.-spectral studies (4000—220 cm.$^{-1}$) suggest that the diethyldithiocarbamate groups are chelated in the usual manner. A structural change occurs within the lanthanide series of complexes, those of La—Nd inclusive being isostructural whilst those of Sm—Lu inclusive form a second isostructural series. Despite the close similarity between the ionic radii of Pu^{3+} (1·00 Å) and Nd^{3+} (0·995 Å), Pu(dtc)$_3$ possesses a different structure from either of the two exhibited by its lanthanide analogues. Unit-cell dimensions, obtained from single-crystal precession and Weissenberg studies, are listed in the Table. It is interesting to note that the results for the lanthanide complexes are quite different from those reported for analogous compounds formed by the smaller tervalent ions of arsenic,[7] cobalt,[8] and ruthenium.[9]

Crystallographic properties for certain tervalent diethyldithiocarbamate complexes

		Lattice parameters			
Compound	Space group	a_0 (Å)	b_0(Å)	c_0 (Å)	β°
As(dtc)$_3$	*P*2$_1$/*c*	15·873	8·387	18·548	101·08
Co(dtc)$_3$	*C*2/*c*	14·10	10·26	17·02	110·13
Ru(dtc)$_3$	*P*2$_1$/*c*	14·23	10·45	17·95	116·75
Nd(dtc)$_3$	*C*2/*c* or *Cc*	20·29	10·20	20·49	118·75
Eu(dtc)$_3$	*C*2/*c* or *Cc*	28·86	11·15	21·97	102·0
NEt$_4$Eu(dtc)$_4$	*P*2$_1$/*c*	11·78	20·86	19·40	117·5

By reaction of the tris(diethyldithiocarbamato)-complexes with sodium diethyldithiocarbamate and tetraethylammonium bromide (1 : 1 : 1 ratios) in alcohol, the complexes of the type $NEt_4M(dtc)_4$ (M = Np, Pu, and La—Lu excepting Pm) are obtained. These complexes, which are recrystallised from methyl cyanide–ether mixtures are all isostructural. Unit-cell dimensions for the europium(III) complex are listed in the Table. The products were characterised analytically.

The structure of one complex from each of the four isostructural series mentioned above is currently being investigated. Particularly important is the possibility that these may be the first examples of tervalent metal ions showing eight-co-ordination with sulphur chelates. We have recently shown that all eight sulphur atoms are indeed co-ordinated in $Th(dtc)_4$.[10]

Preliminary results indicate that *S*-co-ordination to lanthanide and actinide ions is not restricted to 1,1-dithiolates and work is now being carried out to characterise complexes of these metals with 1,2-dicyanoethylene-1,2-dithiolate.

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