Complexes of Uranium(III) with Bidentate Amides

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Summary Tervalent uranium forms air-sensitive, tetrakis-complexes with bidentate, organic amides and tetraphenylborate as the counter-anion.

Complexes of U^{III} with organic ligands are very uncommon. Apart from the cyclopentadienyl[1] $U(C_5H_5)_3$, and an adduct[2] with acetonitrile, $UCl_3{\cdot}MeCN$, the only well characterised complexes are[3] those of 1-phenyl-2,3-dimethylpyrazol-5-one (phenazone, phaz), $U(phaz)_6Cl_3$ and $[U(phaz)_6][Ph_4B]_3$, and 4-dimethylaminophenazone (dmaz), $[U(dmaz)_4][Ph_4B]_3$. All are readily oxidised by atmospheric oxygen.

Organic ligands with uncharged oxygen donor atoms are most likely[4] to give complexes of U^{III} from aqueous ethanolic solution. In preliminary experiments with lanthanoid(III) salts, we found that bidentate amides with tetraphenylborate as counter-anion gave complexes that were stable to moisture, unlike, say, those with monodentate amides and chloride. For U^{III} this would reduce the experimental difficulties.

We then found that tetrakis-(*NN'*-tetramethylmalonamide)uranium(III) tetraphenylborate (**1**), and the corresponding tetrakis-complexes with *NN'*-tetramethylsuccinamide (**2**), *NN'*-tetramethylglutaramide (**3**), *NN'*-tetramethyladipamide (**4**), and *NN'*-tetramethyl-3,3-dimethylglutaramide (**5**), are precipitated by dissolving the red[3] ammonium double chloride $NH_4UCl_4.5H_2O$ in an ethanolic solution of an amide and adding to this an ethanolic solution of sodium tetraphenylborate. All operations were performed in a nitrogen atmosphere. Satisfactory analytical figures for tetrakis-amide complexes with tetraphenylborate as the counter-anion were obtained. Chloride and water

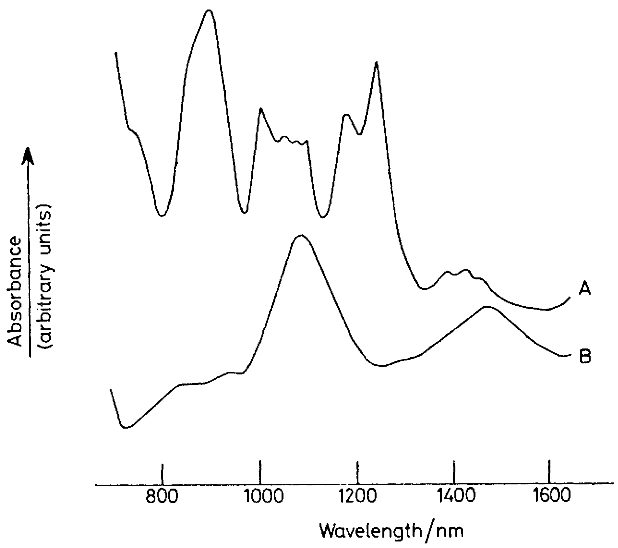

FIGURE. Powder reflectance spectra of (A), tetrakis-(*NN'*-tetramethylmalonamide)uranium(III) tetraphenylborate and (B), the U^{IV} oxidation product.

were absent. The adducts are insoluble in water, ethanol, and acetone and appear to be non-hygroscopic.

The complexes are air-sensitive; (**3**), (**4**), and (**5**) are oxidised immediately on contact with air whilst (**1**) is oxidised over 2 h and (**2**) over 48 h making this compound much more stable than any other with an organic ligand reported hitherto.

The colours of the compounds varied; (**1**) was black, (**2**) and (**5**) green, and (**3**) and (**4**) mauve-purple. The powder reflectance spectra were typical[3] for U^{III} with charge-transfer, or, more likely, *f*—*d* transitions, masking most of the *f*—*f* transitions below 800 nm. The *f*—*f* absorption spectrum above 800 nm showed that little, if any, U^{IV} was present (no significant[3] absorption at 1475 nm) but on the introduction of air, the spectrum rapidly changed to that of U^{IV} (Figure).

I.r. spectroscopy (Nujol mulls, KBr plates) indicated a fall in the amide C=O stretching frequency on comparing the spectrum of the complex with that of the free ligand, (**1**) 1618, 1575 cm^{-1}, ligand 1638 cm^{-1}; (**2**) 1595 cm^{-1}, ligand 1630 cm^{-1}; (**3**) 1600 cm^{-1}, ligand 1646 cm^{-1}; (**4**) 1585 cm^{-1}, ligand 1630 cm^{-1}; (**5**) 1588 cm^{-1}, ligand 1642 cm^{-1}. Absorption from tetraphenylborate anion (near 735 and 705 cm^{-1}) was also present.

We assume that U^{III} is eight-co-ordinate to amide oxygen atoms in the complexes. There is a dearth of crystallographic evidence, but the metal ion in tetrakis-(*NN'*-tetramethylmalonamide)lanthanum(III) perchlorate is probably[5] 8-co-ordinate since the anion has the i.r. spectrum of a regular (T_d) tetrahedral species.

We thank Dr. B. J. Gellatly and Dr. L. F. Larkworthy for useful discussions.

(*Received*, 1st *June* 1977; *Com.* 543.)

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