

Complexes of Zirconium(III) Halides with Nitrogen-donor Ligands

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COMPLEXES of trivalent zirconium have not been reported previously although the trihalides themselves are well known. We have found that the halides ($ZrCl_3$, $ZrBr_3$, and ZrI_3) react readily at room temperature with a number of nitrogen-donor ligands to give products (*cf.* Table), which are insoluble in nonpolar organic solvents but slightly soluble in methyl cyanide. With the monodentate ligands, pyridine and methyl cyanide, the respective stoichiometries of the complexes formed differ from those of the analogous titanium(III) complexes ($TiX_3 \cdot 3L$).¹ The bipyridyl complexes have titanium(III) analogues,² but the phenanthroline complex $2ZrCl_3 \cdot 3phen$ does not.

The pyridine complexes, $ZrX_3 \cdot 2py$, which are

extremely sensitive to moist air, give conducting solutions in methyl cyanide, and in the case of $ZrI_3 \cdot 2py$ the behaviour is that of a 1:1 electrolyte. The far-infrared spectrum of $ZrCl_3 \cdot 2py$ shows Zr-Cl stretching frequencies in the same region as $ZrCl_3$, and since the latter is polymeric with six-coordinate zirconium,³ it is likely that the pyridine complex contains similarly co-ordinated zirconium atoms because of chlorine bridging.

The methyl cyanide adducts have the unusual stoichiometry $2ZrX_3 \cdot 5CH_3CN$. Their infrared spectra do not show the $C \equiv N$ stretching frequency (2250 cm.^{-1}) of the free ligand, and methyl cyanide is not released even when the adducts are heated *in vacuo* to 100° . The presence of unco-ordinated

TABLE

Complex	Colour	μ_{eff} (B.M.) at 20°	λ_M †	Gradient‡	Infrared spectra ($400-200 \text{ cm.}^{-1}$)
$ZrCl_3 \cdot 2py$	chocolate	1.29	42	247	293; 270sh
$ZrBr_3 \cdot 2py$	red-brown	1.24	24	77	§
$ZrI_3 \cdot 2py$	yellow	1.16	145.0	1308	320
$2ZrCl_3 \cdot 5CH_3CN$	red-brown	0.46	41	—	294
$2ZrBr_3 \cdot 5CH_3CN$	brown	0.29	57	98	398sh; 393; 296
$2ZrI_3 \cdot 5CH_3CN$	yellow-brown	1.10	143	—	395; 278
$2ZrCl_3 \cdot 3bipy$	chocolate	1.35	28	63	347sh; 315sh; 292; 298sh
$ZrBr_3 \cdot 2bipy$	dark-brown	1.20	65	348	—
$2ZrI_3 \cdot 3bipy$	yellow-green	0.96	199	772	—
$2ZrCl_3 \cdot 3phen$	purple-brown	1.27	122	1136	360; 302; 264; 253sh

† $10^{-3}M$ in $\underline{CH_3CN}$;

‡ From plot λ_M with \sqrt{c} ;

§ poor mull.

methyl cyanide trapped in the lattice would seem therefore to be ruled out. With the exception of $2\text{ZrCl}_3 \cdot 3\text{bipy}$, the bipyridyl and phenanthroline complexes have conductances in methyl cyanide close to that expected for 1:1 electrolytes.

The electronic spectra of the complexes show at least one weak $d-d$ transition in the 12,000—14,000 cm^{-1} region, together with much more intense charge-transfer bands between 20,000 and

25,000 cm^{-1} . The room-temperature magnetic moments of all the complexes are well below the spin-only moment, and since this is unlikely to arise entirely from spin-orbit coupling in compounds of such low symmetry, there are evidently strong Zr-Zr interactions as in the trihalides themselves.⁴ Temperature-dependence studies are being made.

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¹ G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 1963, 33.

² G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 391; T. E. Lester, unpublished observations.

³ L. F. Dahl, T. Chiang, P. W. Seabaugh, and E. M. Larsen, *Inorg. Chem.*, 1964, **3**, 1236.

⁴ J. Lewis, D. J. Machin, I. E. Newnham, and R. S. Nyholm, *J. Chem. Soc.*, 1962, 2036.