The Crystal Structure of Tris-(2,2′,6′,2″-terpyridyl)europium(III) Perchlorate

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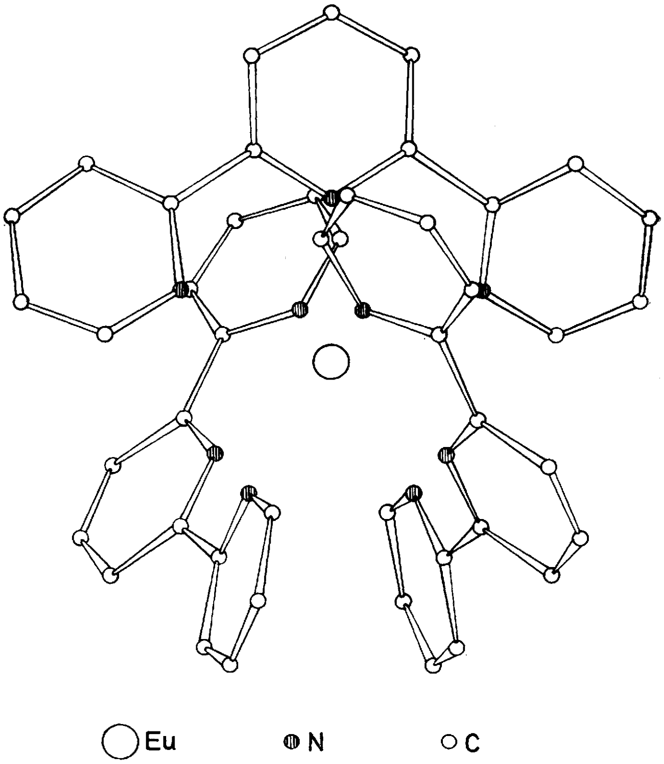
Summary An *X*-ray crystallographic analysis of tris-(2,2′,6′,2″-terpyridyleuropium(III) perchlorate has confirmed the nona-co-ordination of the metal ion, believed to be the first example of nine-co-ordination involving only nitrogen ligands.

EARLIER studies[1] on the fluorescence spectrum of tris-(2,2′,6′,2″-terpyridyl)europium(III) perchlorate suggested that the cation was a nona-co-ordinate [Eu(terpy)]$^{3+}$ species, with distorted D_3 symmetry. We have now confirmed this through an *X*-ray diffraction analysis.

Crystallisation from acetonitrile gives two distinct crystal forms, acicular and polyhedral, representing two different crystal structures. Both, however, appear to be unsolvated complexes. We report here the results of our analysis of the polyhedral crystals, powder photographs of which are identical with those of the material described previously.[1]

Crystal data: $[Eu(C_{15}N_3H_{11})_3](ClO_4)_3$; $M = 1150$. Monoclinic, $C2/c$ with $a = 17{\cdot}78$, $b = 21{\cdot}33$, $c = 12{\cdot}30$ Å, $\beta = 94{\cdot}4°$, $Z = 4$, $D_m = 1{\cdot}67$, $D_c = 1{\cdot}65$ g.cm.$^{-3}$ The structure was solved by conventional techniques using *ca.* 3800 independent reflections, visually estimated from Cu-K_α Weissenberg photographs. At the present stage of refinement, R is 0·118.

The cation, depicted in the Figure, has C_2 symmetry only. The EuN_9 co-ordination polyhedron approximates most closely to an s-tricapped trigonal prism, the distortions of the whole cation from idealised D_3 symmetry being caused mainly by the non-planarity of the ligands. The ligands are of two crystallographically distinct types, but both are distorted in a similar manner, differing only in magnitude. The distortion consists of (i) a rotation of both terminal pyridine rings about the inter-ring C–C bonds and (ii) a slight bending of these bonds. Dihedral angles between



FIGURE

neighbouring rings range from 12—26°, and are larger than values found in $[\mathrm{Me_2SnCl(terpy)}]^+$ (7 and 11°)[2] and $[\mathrm{ZnCl_2(terpy)}]$ (6 and 4°)[3] or in complexes between *d*-transition metals and 2,2′-bipyridyl. The geometries of the individual pyridine rings are quite normal and the Eu–N bond lengths, which lie in the range 2·57—2·62 Å (e.s.d. 0·012), are typical of those already observed[4,5] for lanthanide complexes.

The distortions in the ligands may be attributed to two main factors. The first is steric interaction, both between the anion and complex cation, and between ligands of one cation. The second, and, we feel, most important, is due to intra-ligand lone-pair interactions. In each ligand the distortions are such that the three nitrogen lone pairs are moved further away from each other, the closest N–N distances then being 2·71 Å (for intra-ligand) and 3·04 Å (for inter-ligand).

We consider that the results of this determination are consistent with a more ionic type of bonding both as regards the rather long Eu–N bond distances and the nature of the ligand deformation.

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