The *X*-Ray Crystal Structure of Trinitrato-1,2-di(pyridine-2-aldimino)ethanegadolinium(III)

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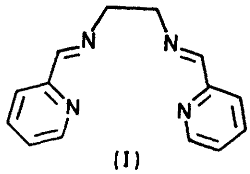
Summary The title compound is shown by *X*-ray crystallographic analysis to possess a ten-co-ordinated metal ion having an irregular co-ordination polyhedron of point group C_1.

COMPARATIVELY few instances of ten-co-ordination have apparently been established by *X*-ray analysis. Examples among monomeric metal complexes are apparently limited to $[LaH(edta)(H_2O)_4]$,[1] $(Ph_3EtP)_2[Ce(NO_3)_5]$,[2] and $[La(NO_3)_3(bipyridyl)_2]$[3] together with the similar Tb complex;[4] examples among polymeric salts, mixed oxides, and metal clusters are also recorded.[2] The lanthanide complexes $[M(NO_3)_3(C_{14}H_{14}N_4)]$,[5,6] where $(C_{14}H_{14}N_4)$ = 1,2-di(pyridine-2-aldimino)ethane (I), invited *X*-ray structural investigation (i) because of the possibility of an unusual co-ordination number and geometry and (ii) for comparison with $[M(NO_3)_3(bipyridyl)_2]$ where, in contrast to $[M(NO_3)_3(C_{14}H_{14}N_4)]$, the four ligand nitrogen atoms are not constrained into an approximately coplanar configuration.



(I)

Prepared as reported,[6] $[Gd(NO_3)_3C_{14}H_{14}N_4]$ forms colourless crystals: orthorhombic, *Pbca* with $a = 14{\cdot}774$, $b = 16{\cdot}072$, and $c = 16{\cdot}198$ Å, $Z = 8$, $D_m = 2{\cdot}03$, $D_c = 2{\cdot}01$ g cm^{-3}. Intensity data, using Mo-K_α radiation, were collected by means of a General Electric XRD-5 diffractometer equipped with a single-crystal orienter and a scintillation counter. Intensities were measured using θ–2θ scan technique, approximately 1700 reflections being above statistical fluctuations of the background. The structure was solved by means of three-dimensional Fourier syntheses subsequent to the location of the gadolinium atom from a three-dimensional Patterson function. Finally, the hydrogen atoms were located by a difference synthesis. R stands at 3·6%.

The complex, depicted in the Figure, is of C_1 symmetry. The cation is ten-co-ordinated, all three nitrate ions being bidentate and all four nitrogen atoms being co-ordinated to the metal. The two $-CH_2{\cdot}N{:}CH{\cdot}C_5H_4N$ halves of the ligand are each essentially planar but the planes of the two

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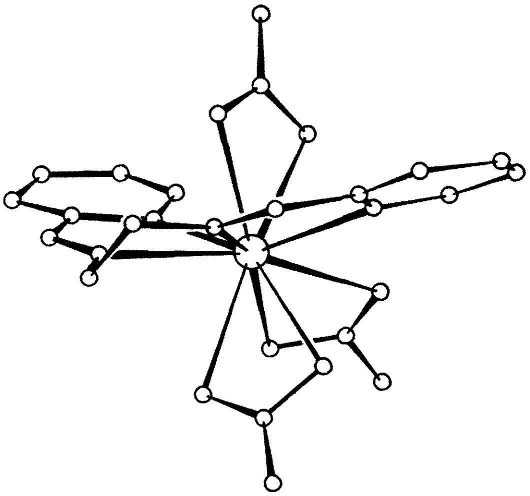
pyridine rings are mutually inclined at a dihedral angle of 16·0° thus minimising distortion at the saturated carbon atoms ($\angle$NCC = 106·5° and 108·0°) while still achieving Gd–N distances of 2·50, 2·52 Å (to imino N) and 2·54, 2·60 Å (to pyridine N). These, after correction for the lanthanide contraction, are very similar to previously-measured values;[2–4,7] the La–N distances are a little greater in the edta complex[1] where the nitrogen atoms are saturated.



FIGURE

The co-ordinated nitrate ions show Gd–O distances within the range 2·45–2·55 Å, in agreement with other lanthanide–oxygen distances.[1–4,8] The nitrate ions may be considered to be positioned in such a way that they fill the remaining three vacant positions in a very distorted pentagonal bipyramid, four of the equatorial positions being filled by the tetradentate amine. We consider, however, that this statement has mnemonic value only, and that descriptions of co-ordination polyhedra in terms of regular or semi-regular geometrical figures are usually of rather doubtful value when, as here, the polyhedron must be determined by intra-ligand constraints and inter-ligand repulsions which cannot be satisfied by any regular arrangement.

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[1] M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 1611.
[2] A. R. Al-Karaghouli and J. S. Wood, *Chem. Comm.*, 1970, 135, and references therein.
[3] A. R. Al-Karaghouli and J. S. Wood, *J. Amer. Chem. Soc.*, 1968, **90**, 6548.
[4] D. S. Moss and S. P. Sinha, *Z. phys. Chem. (Frankfurt)*, 1969, **63**, 190.
[5] E. Butter, B. Lorenz, and E. Hoyer, *J. prakt. Chem.*, 1966, **34**, 30.
[6] D. A. Durham and F. A. Hart, *J. Inorg. Nuclear Chem.*, 1969, **31**, 145.
[7] G. H. Frost, F. A. Hart, C. Heath, and M. B. Hursthouse, *Chem. Comm.*, 1969, 1421.
[8] M. Marezio, H. A. Plettinger, and W. H. Zachariasen, *Acta Cryst.*, 1961, **14**, 234.