# Stereochemistry of the Octakis(pyridine *N*-oxide)lanthanum(III) Ion

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*Summary* The co-ordination polyhedron in the eight-co-ordinate complex cation $La(C_5H_5NO)_8^{3+}$ closely approximates $D_4$ symmetry and exhibits large deviations from the geometry of the square antiprism, towards that of the cube.

There are few structural studies of eight-co-ordinate complexes containing equivalent unidentate ligands and, to our knowledge, none containing the lanthanide elements has been reported to date. It now appears that the cube might be a common stereochemistry for discrete eight-co-ordinate complexes of the actinide elements,[1] in contrast to the transition elements where the square antiprism ($D_{4d}$)[2] and the dodecahedron ($D_{2d}$)[3] (or their intermediates) are judged to be the preferred polyhedra.[4] A study of a series of lanthanide $ML_8$ species might show how the varying metal ion size and the availability of valence *f* orbitals influence the geometry. The eight-co-ordinate pyridine *N*-oxide complexes, $Ln(C_5H_5NO)_8^{3+}$, form a potentially useful series for study of stereochemical and electronic properties and we here describe results obtained for the lanthanum complex in the form of its perchlorate salt.[5]

$La(C_5H_5NO)_8(ClO_4)_3$ crystallises in two monoclinic modifications that can be obtained side by side from the same ethanolic solution. On the basis of unit-cell and space-group data, these forms appear to be very closely related, the crystals of one form (**1**) belonging to space group $C2/c$ ($Z = 4$), while the crystals of the second form (**2**), which are twinned, belong to $P2_1/c$, and are isomorphous with crystals of the analogous neodymium complex.

From intensity data collected on a manual diffractometer using M-$K_\alpha$ radiation, the structure of form (**1**) has been determined using 1630 independent reflections. The residual, *R*, including anisotropic thermal parameters for the lanthanum atom and the chlorine atoms of the two perchlorate ions in general positions (one crystallographically independent) is 0·073. The third perchlorate ion, situated on the crystal two-fold axis, exhibits static disorder.

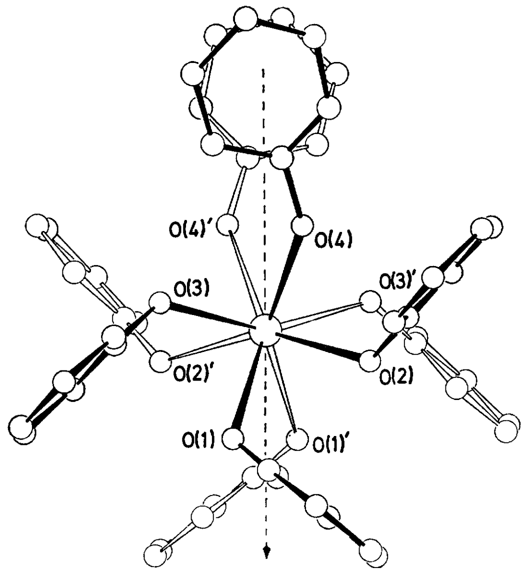

Figure. *The octakis(pyridine oxide)lanthanum*(III) *ion,* $La(C_5H_5NO)_8^{3+}$ *projected on to a plane containing the* y *crystal axis and whose normal is* ca. 4° *from the crystal* z *axis.*

The complex cation, $La(C_5H_5NO)_8^{3+}$, which possesses crystallographic $C_2$ symmetry, is illustrated in the Figure. The distances La–O(1)—La–O(4) average 2·502(8) Å, with no significant deviation from the mean. The set of oxygen atoms O(1)—O(4) are coplanar to within the estimated deviations and the average angle of inclination, $\theta$, of the La–O bonds to the normal, through this almost square face, is 55·7°. The four independent distances within this square face average 2·93(2) Å (max. 3·02 Å, min. 2·86 Å). The co-ordination polyhedron has almost perfect $D_4$ symmetry and on the basis of general shape criteria would be described as being square antiprismatic $D_{4d}$. However, the

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projected O($n$)–La–O($n$)′ angles ($n$ = 1—4) average 30·8° and 59·2° compared to 45° expected for the ideal $D_{4d}$ geometry and this is reflected in the remaining ligand O–O distances. The three distances O(1)–O(1)′, O(2)–O(3)′, and O(4)–O(4)′ average 3·13(2) Å, while O(2)–O(1)′ and O(4)–O(3)′ are 3·43(2) and 3·36(2) Å respectively. In addition, the angle of inclination, $\theta$, is less than that expected for $D_{4d}$ geometry, namely *ca.* 58°. Both this value and the retention of $D_4$ symmetry discussed above represent distortions of the polyhedron towards a cube ($\theta = 54{\cdot}75°$) rather than a dodecahedron ($D_{2d}$), and the average angular deviation from the three polyhedra computed for the sixteen angles between adjacent La–O bonds supports this description. The Figure shows that rotation of the pyridine oxide ligand co-ordinated through O(4) by *ca.* 80° would produce approximate $D_4$ symmetry for the complex cation as a whole. Preliminary indications are that this is the structure of crystalline form (**2**).

(*Received*, 28*th January* 1972; *Com.* 124.)

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[3] J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, 1968, **90**, 3177.

[4] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109; S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109, and references therein.

[5] The complexes studied were prepared by modifications of reported procedures (L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Amer. Chem. Soc.*, 1964, **86**, 5117).