

Crystal Structure of an Iridium Complex Containing a Triply Bridging Nitride Ligand

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Summary The complex ion $[\text{Ir}_3\text{N}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$ has been shown by X-ray analysis of its ammonium salt to contain a coplanar Ir_3N unit with an Ir-N distance of 1.918 Å.

We have recently shown¹ by X-ray analysis that the nitride ligand can function as a bridge between two metal atoms in the complex $\text{K}_3[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]$. We now show that in the complex ion $[\text{Ir}_3\text{N}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$ in Delépine's green ammonium salt² it bridges three metal atoms, giving a

complex ion $[\text{Ir}_3\text{N}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$ which is shown in the Figure. In it the central nitrogen atom, which lies on a threefold axis, is co-ordinated to three iridium atoms, and each pair of metal atoms is joined by double sulphate bridges. The octahedral co-ordination about iridium is completed by water molecules *trans* to the nitrogen. The arrangement of the nitrogen, iridium atoms, and water molecules is essentially planar (maximum deviation *ca.* 0.01 Å). The Ir-N distance of 1.918 ($\sigma = 0.002$ Å) is

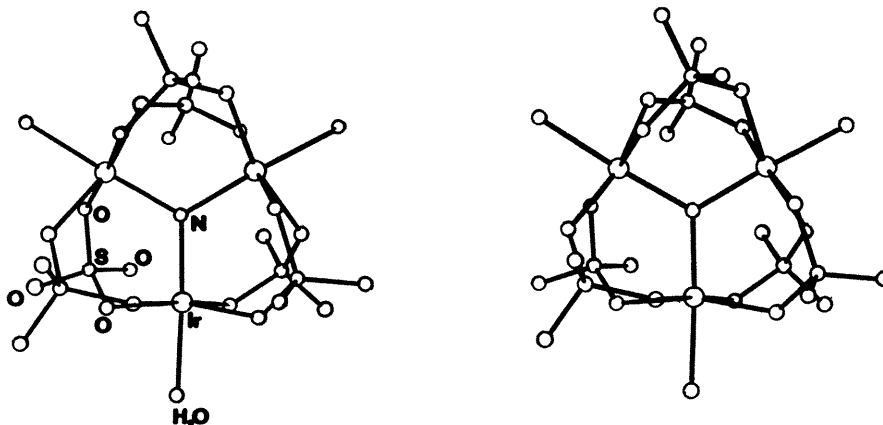


FIGURE. Stereo plot of the structure of $[\text{Ir}_3\text{N}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$.

coplanar triangular Ir_3N unit. This is the first established example of a nitrogen atom in such an environment, though a number of acetato-complexes containing coplanar M_3O units are known (*i.e.* those of trivalent iron,³ manganese,⁴ and chromium⁵). Such a structure of the iridium nitride complex has been suggested by Jørgensen and Orgel⁶ on the basis of electronic spectroscopy and magnetic data, and has also received some support from studies of the vibrational spectra of normal and ¹⁵N-enriched salts.⁷

Ammonium μ -nitrido-hexasulphatotriaquotri-iridate(IV,III) was prepared by Delépine's method² and crystallised from sulphuric acid as very dark green crystals which are cubic ($a = 22.805$ Å). Three-dimensional X-ray data were collected on a Siemens diffractometer, and the structure was solved by Patterson and Fourier methods on the basis of 562 independent reflections. Least-squares refinement in space group $\bar{I}43d$ has now reached $R = 0.035$.

A striking feature of the structure is the shape of the

somewhat shorter than would be expected for a single bond, and suggests that there is some π bonding between the $2p_z$ orbital of the nitrogen atom (perpendicular to the Ir_3N triangle) and the iridium atoms. The Ir-O distances (2.005–2.056 Å) and Ir-H₂O distance of 2.059 Å are unexceptional.

A recent preliminary study⁸ of the ¹⁹³Ir Mössbauer spectrum of the potassium salt at 4 K has been interpreted as showing that the three iridium atoms are not equivalent, because they have different oxidation states. Our results are not necessarily inconsistent with this since the apparent crystallographic equivalence of the metal atoms may well arise from the complex ion adopting three orientations with equal probability, thus satisfying the requirements of a threefold axis. An alternative explanation is that there is a time-averaging effect within any given complex ion.

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