X-Ray Structure Analysis of Iodo-[2,2′,2″-tri(dimethylamino)triethylamine]nickel Iodide, [Ni($NCH_2CH_2NMe_2)_3$I]I

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Summary In contrast to the conclusions of a previous ^{129}I Mössbauer study, the complex [Ni(Me_6tren)I]I has been found by *X*-ray crystal analysis to have a five-co-ordinate trigonal bipyramidal geometry.

On the basis of magnetic, conductimetric, and electronic absorption measurements, the metal complexes of the quadridentate ligand $N(CH_2CH_2NMe_2)_3$ (Me_6tren), having the stoicheiometric formula [M(Me_6tren)X_2] where M = Mn, Fe, Co, Ni, Cu, Zn, and X = Cl, Br, I, NCS, NO_3, ClO_4, were attributed a five-co-ordinate trigonal bipyramidal geometry, corresponding to the formula [M(Me_6tren)X]X.[1] A single crystal *X*-ray analysis on the bromide complexes confirmed the proposed structure.[2]

Recently Hendrickson *et al.*,[3] on the basis of 4·2 K ^{129}I Mössbauer spectra of the compounds [Zn(Me_6tren)I_2] and [Ni(Me_6tren)I_2], concluded that the two iodine atoms are equivalent and therefore they are bound in the same way in both complexes. On this basis they ruled out the suggested formula [M(Me_6tren)I]I (M = Zn, Ni). On the other hand preliminary measurements on [Co(Me_6tren)I_2] showed the presence of both a free iodide and a cobalt-bound iodine in agreement with the *X*-ray study on [Co(Me_6tren)Br]Br.

In order to ascertain unambiguously the structure of the zinc and nickel compounds, an *X*-ray single crystal analysis of the complex $[Ni(Me_6tren)I_2]$ has been performed. Crystals of the compound are isomorphous with those of the analogous bromide series. They are cubic, space group $P2_13$, with $a = 12{\cdot}552(3)$ Å. A total of 606 independent reflections with $I > 2\sigma(I)$, collected on a Philips automatic diffractometer were used for the structure analysis. Atomic parameters taken from $[Ni(Me_6tren)Br]Br$ gave an initial *R* factor of 0·21. Two least-squares cycles with isotropic temperature factors, followed by two cycles with anisotropic temperature factors for all the atoms gave a final *R* factor of 0·034.

As expected from the isomorphism with the bromide analogues, the structure of $[Ni(Me_6tren)I]I$ consists of $[Ni(Me_6tren)I]^+$ and I^- ions. In the complex cation the nickel atom is five-co-ordinated, the co-ordination polyhedron being a regular trigonal bipyramid with C_3 crystallographic symmetry. Bond lengths and angles around nickel are all within three standard deviations of the corresponding values for the bromide analogue,[2] with the obvious exception of the nickel–halogen distance which is 2·665(1) Å.

These results suggest:

(i) Great care must be taken in Mössbauer studies and caution used in drawing conclusions from them, especially if these are in contrast with evidence from other physical measurements.

(ii) In the present case it remains to be explained why the Mössbauer spectra of the nickel and zinc derivatives show two equivalent iodine atoms, whereas the spectrum of the cobalt complex shows both a free iodide and a metal-bound iodine.

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