Existence of the Novel $Cd_2I_6^{2-}$ Anion and of the Five-co-ordinate $\{Cd[N(CH_2CH_2NMe_2)_3]I\}^+$ Cation in $Cd_2[N(CH_2CH_2NMe_2)_3]I_4$

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Summary X-Ray analysis of $Cd_2(tda)I_4$ shows the presence of a five-co-ordinate $[Cd(tda)I]^+$ cation [tda = $N[CH_2CH_2NMe_2)_3]$] and of the $Cd_2I_6^{2-}$ anion formed by two CdI_4 tetrahedra sharing one edge.

IT has been reported that the tripod-like ligand tris-(2-dimethylaminoethyl)amine (tda) forms, with first row transition metals, a series of five-co-ordinate complexes with general formula M^{II} $(tda)X_2$, where M^{II} = Cr, Mn, Fe, Co, Ni, Cu, and Zn and X = Cl, Br, I, NO_3.[1] X-Ray analysis showed the crystals of the complex bromides to be formed by regular trigonal bipyramidal $[M(tda)X]^+$ cations and Br^- anions.[2]

It seemed interesting to see whether the steric requirements of the ligand would still allow the formation of similar complexes with second and third row transition metals. Cadmium(II) and mercury(II) halides form, with tda, several complexes with different metal–ligand ratios whose preparation and properties will be reported elsewhere.[3] We report here the crystal structure of one of these complexes having formula Cd_2 $(tda)I_4$.

Crystals of the compound are monoclinic, space group $P2_1/a$ with $a = 14{\cdot}586(6)$, $b = 20{\cdot}734(12)$, $c = 8{\cdot}509(4)$ Å, $\beta = 94°36(3)'$ and $Z = 4$. 2786 independent reflections with intensity $> 2\sigma(I)$ were collected on a Hilger automatic four-circle diffractometer with Mo-K_α radiation and were corrected for Lorentz-polarization and absorption effects. The structure was solved by the usual Patterson and Fourier methods and refined by full-matrix least-squares to an R factor of 4·4%.

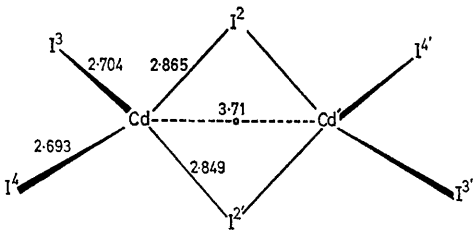

FIGURE. *The* $Cd_2I_6^{2-}$ *ion. The angles are:* I^3–Cd–I^4 = 121·6, I^3–Cd–I^2 = 107·3, I^3–Cd–$I^{2'}$ = 107·6, I^4–Cd–I^2 = 109·5, I^4–Cd–$I^{2'}$ = 109·5, I^2–Cd–$I^{2'}$ = 98·9°. *Average standard deviations on bonds are* 0·001 Å *and on angles* 0·04°.

The structure consists of $[Cd(tda)I]^+$ cations and $Cd_2I_6^{2-}$ anions. In the complex cation the cadmium atom is five-co-ordinate by the four nitrogen atoms of the ligand and by a iodine atom, arranged at the corners of a slightly distorted trigonal bipyramid. Packing forces are very likely responsible for the distortions from the trigonal symmetry, the equatorial angles being 116·6, 118·3, and 109·1°. The displacement of the metal atom from the equatorial plane is 0·53 Å towards the iodine atom and the average N_{eq}–Cd–N_{ap} angle is 76·5°. These same values were respectively 0·27 Å and 82·6° in $Zn(tda)Br_2$.[2] The greater distortion in the present case is clearly to be attributed to the increased size of the metal atom and to the steric requirements of the ligand molecule. To the authors' knowledge, [Cd(tda)I]$^+$ and $CdCl_5^{3-}$ in $Co(NH_3)_6CdCl_5$[4] are the only examples of five-co-ordinate monomeric cadmium(II) complexes so far studied by *X*-ray analysis.

The $Cd_2I_6^{2-}$ anion is formed by two CdI_4 tetrahedra sharing a common edge (Figure). The dimeric ions possess a crystallographic centre of symmetry relating the two CdI_3 moieties, but their approximate symmetry is D_{2h}. The Cd–Cd distance is 3·71 Å. Although the existence of the $Cd_2I_6^{2-}$ ion has been very recently postulated,[5] this is the first *X*-ray evidence for this anion. The known structures of the compounds $(M^I)_n(CdX_3)_n$ ($M^I = NH_4$, K, Rb, Cs and X = Cl, Br, I) show the cadmium atom in octahedron chains or in a perovskite-type lattice.[6]

The analogous mercury compound shows a similar *X*-ray powder pattern.

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