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Chelate Ethylenediamine (en) in the Tetrahedral Structure of $Hg(en)(SCN)_2$

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The great number of structures determined up to now show that in most of the octahedral and square planar structures ethylenediamine (en) acts as a chelate ligand. This happens because the value of the intrachelate angle N–M–N ($\simeq 80^\circ$) is close to that required by the mentioned symmetries; on the other hand this value, much lower than that required by a tetrahedral symmetry, makes chelation unfavourable in these structures and, to our knowledge, only those of dichloro(N,N,N′,N′-tetramethylethylenediamine)zinc(II),[1] bis-ethylenediaminelithiumbromide and bis-ethylenediaminelithium chloride[2] have been reported. In the last two compounds the tetrahedral positions are filled by the nitrogen atoms of the two en molecules, one of which is chelate while the other acts as a bridge between two cations. A bridging behaviour of the en molecule was also considered as most probable in the present compound,[3] on the analogy of $Cd(en)(SCN)_2$ studied by IR and Raman spectroscopy.[4] The present study shows on the contrary that $Hg(en)(SCN)_2$ is another example of a tetrahedral structure, with chelate ethylenediamine.

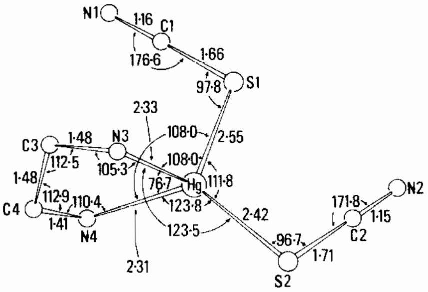

Figure. Bond distances and angles.

The molecular structure with the values of bond distances and angles is shown in the Figure. The tetrahedral geometry is highly distorted: the biggest deviation from exact symmetry is due to the amine which has an intrachelate angle of 76.7°, much lower than the tetrahedral value; the consequent increase of the remaining angles affects those involving S(2), but not those involving S(1). This last effect is most probably a consequence of hydrogen bonding between N(2) and amine nitrogen atoms, resulting from the molecular packing around two-fold screw axis.

Experimental

The crystals are orthorhombic with $a = 12.03(2)$, $b = 11.11(2)$, $c = 7.06(1)$ Å; $U = 942.8$ Å^3; $Dm = 2.61$ gcm^{-3}; $Z = 4$; $Dc = 2.65$ gcm^{-3}.

Systematic absences observed on Weissenberg photographs taken with CuKα radiation are consistent both with space group $Pna2_1$ (No. 33) and Pnma (No. 53); the first was chosen from structure analysis. The intensities of 958 reflections were measured on the Siemens AED diffractometer using Zn filtered MoKα radiation and the θ–2θ scan technique; 141 reflections having $I/\sigma(I) < 2$ were considered unobserved.

The structure was solved assuming $Pna2_1$ space group since, with four molecules per cell, Pnam would require a molecular plane of symmetry. With this assumption all the atoms but the ethylenediamine carbons were easily located in a three-dimensional Fourier map phased with the contribution of mercury and sulphur atoms determined by a Patterson synthesis. The positions of the remaining two carbon atoms were determined by fitting calculated positions to the peaks in the Fourier map. Isotropic and thermal parameters were refined by three cycles of block-diagonal least-squares method which reduced the R factor to 0.18. In the last four cycles anisotropic thermal parameters were assigned to mercury and sulphur atoms and convergence was reached at a final R factor of 0,063 for 817 refined reflections.

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