The Crystal Structure of $Hg(SCN)_2,As(C_6H_5)_3$, a Three-co-ordinate Mercury Complex

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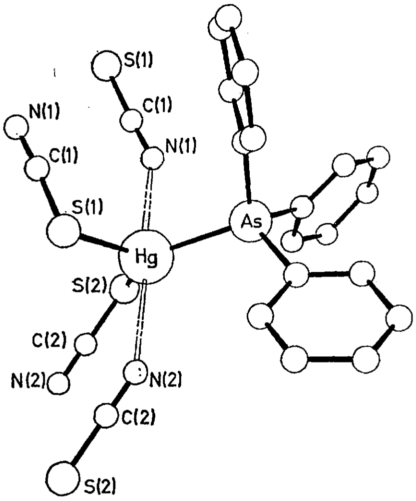
Summary Dithiocyanatotriphenylarsinemercury(II) is a three-co-ordinated monomeric molecule with a distorted trigonal bipyramid geometry around mercury.

THE 1:1 adducts of monodentate ligands with mercuric halides, like HgI_2,Et_3As, tend to form halide-bridged dimers, where the mercury atom is tetrahedrally co-ordinated.[1] A similar dimeric structure was recently suggested for the complex of $Hg(SCN)_2$ with triphenylarsine.[2] This suggestion was based on i.r.-spectroscopic evidence for the presence of both free and bridging SCN ligands in this compound. From a single-crystal X-ray study, we conclude that the *characteristic* co-ordination number[3] of mercury is not four, but three in this complex.

The crystals, grown from an acetone solution, belong to the monoclinic space group $P2_1/c$. The crystallographic data are: $a = 10{\cdot}76$, $b = 21{\cdot}24$, $c = 10{\cdot}70$ Å, $\beta = 111{\cdot}54°$, $Z = 4$, $D_m = 1{\cdot}90$ and $D_c = 1{\cdot}917$ g/cm^3. The intensity data were collected with a Picker FACS-1 automatic diffractometer, using Ni-filtered Cu-K_α radiation. A total of 2162 independent observed reflections within the range $0° < 2\theta < 120°$ were measured. The structure was solved by the conventional heavy-atom method. Refinement of the positional and isotropic thermal parameters for all non-hydrogen atoms converged to an R factor of 0·09.

The Figure shows that the mercury atom has a *characteristic* co-ordination number of three. The bond lengths are: Hg–As, 2·60, Hg–S(1), 2·53, and Hg–S(2), 2·55 Å. The trigonal geometry around mercury is significantly distorted [As–Hg–S(1) = 107°, S(1)–Hg–S(2) = 124°, As–Hg–S(2) = 128°], but the HgAsS(1)S(2) framework is practically planar, as evidenced from the sum of the angles being close to 360°. Co-ordination of the thiocyanato-group through sulphur is consistent with the i.r. spectrum and quite common for mercury. The Hg–SCN links are bent at the sulphur atom (Hg–S–C = *ca.* 101°) as commonly observed for *S*-bonded thiocyanates.[4] The expected tetrahedral geometry around arsenic is observed and the As–C bond lengths average 1·95 Å.



FIGURE

The terminal nitrogen atoms of SCN groups from two different neighbouring molecules are found above and below the co-ordination plane. When these atoms are taken into account, the overall geometry around the mercury atom can be described as a distorted trigonal bipyramid. A similar situation is found in $[(CH_3)_4N][HgBr_3]$,[5] where the mercury atom of the trigonal $[HgBr_3]^-$ ion forms a long contact with one of the bromine atoms of the neighbouring ion and achieves a higher *effective* co-ordination. In $Hg(SCN)_2$, all the thiocyanato-groups were found to interact with mercury atoms at both ends,[6] but the Hg–N interactions (2·81 Å) are relatively weak and the i.r. spectrum[7] does not show the features currently admitted as criteria for bridging SCN groups.[8] In the present compound a similar intermolecular Hg–N(1) contact of 2·80 Å is observed. The corresponding SCN group would presumably show up as a free thiocyanate ligand in the i.r. spectrum. The other Hg–N(2) contact is shorter (2·70 Å), but still longer than the sum of the covalent radii (2·28 Å). Consequently, N(1) is not considered to be closely co-ordinated to mercury, but the Hg–N(2) interaction might be sufficiently strong to give rise to the bridged SCN bands in the i.r. spectrum.

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