The Crystal and Molecular Structure of Arsenic(III) *NN*-Diethyldithiocarbamate

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ARSENIC(III) *NN*-DIALKYLDITHIOCARBAMATES, $[As(S_2CNR_2)_3]$, were described by Malatesta, who found[1] values for the dipole moments (4·5–5·0 D) which were greater than those (~1·5 D) found in the symmetrically chelated *NN*-dialkyldithiocarbamates of tervalent metals. He suggested that this might be indicative of a non-chelated pyramidal structure, like that of the arsenic(III) halides. Chatt, Duncanson, and Venanzi reported[2] the infrared spectra of arsenic(III) *NN*-dialkyldithiocarbamates and suggested that the high dipole moments might arise not from an unsymmetrical disposition of the sulphur atoms alone, but from the dipolar character of the carbon–nitrogen bonds. In order to establish whether these compounds have chelate structures we have studied one of them (R = Et) by single crystal *X*-ray diffraction analysis.

$[As(S_2CNEt_2)_3]$ crystallizes out from acetone as pale yellow monoclinic prisms; $a = 15{\cdot}873 \pm 0{\cdot}010$, $b = 8{\cdot}387 \pm 0{\cdot}005$, $c = 18{\cdot}548 \pm 0{\cdot}010$ Å, $\beta = 101° \; 5' \pm 5'$; $U = 2423{\cdot}2$ Å^3; $D_m = 1{\cdot}427 \pm 0{\cdot}002$ g.cm.$^{-3}$ (by flotation); $Z = 4$, $D_c = 1{\cdot}425$ g.cm.$^{-3}$; $F(000) = 1082{\cdot}8$. Space group: $P2_1/c$ from systematic absences. Data from Weissenberg photographs, Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation.

The structure was solved by Patterson and Fourier methods, using 2964 independent reflections from photographic records. Co-ordinates and anisotropic temperature factors were refined by 9 × 9 block diagonal least-squares techniques to the present set of values, corresponding to $R = 0{\cdot}088$.

The co-ordination sphere of the arsenic atom in the complex is shown in the Figure. The three *NN*-diethyldithiocarbamate groups act as bidentate chelating ligands; the two arsenic–sulphur contacts of each chelate ring, however, are quite different, one of them being practically covalent (~2·35 Å, the sum of Pauling's covalent radii[3] being 2·25 Å), the other one being indicative of an ionic interaction (2·8 to 2·9 Å). The co-ordination polyhedron around the arsenic atom is close to a distorted trigonal antiprism. The three covalent arsenic–sulphur bonds are nearly at right angles to one another, thus forming a trigonal pyramid, with the unshared electron pair orbital at the apex.

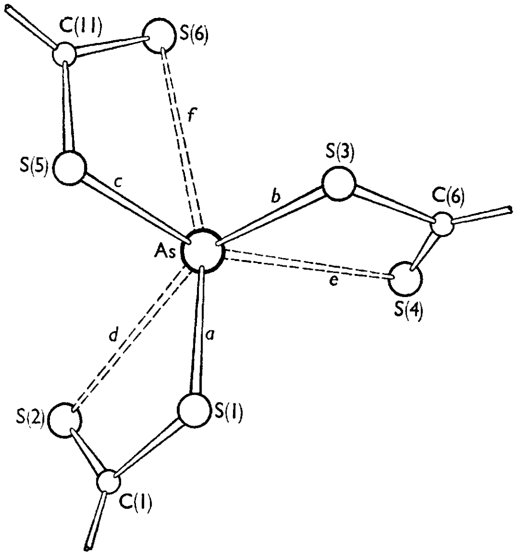
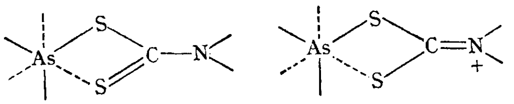


FIGURE. *The co-ordination sphere of arsenic*(III) NN-*diethyldithiocarbamate. Bond lengths are*: a = 2·351(3), b = 2·336(2), c = 2·358(3), d = 2·903(4), e = 2·820(3), f = 2·810(3) Å. *The angles* S(1)-As-S(3), S(1)-As-S(5), S(3)-As-S(5) *are* 88·53(0·08), 90·50(0·12), 91·15(0·11)° *respectively. Values in parentheses are estimated standard deviations.*

The two sulphur–carbon bond distances of each ligand molecule in the complex are quite different: 1·760 ± 0·005 Å (av.) when the related arsenic–sulphur interaction is covalent, 1·678 ± 0·006 (av.) in the other case. The latter bond has undoubtedly a high double bond character, as the carbon(sp^2)–nitrogen bond, which is 1·338 ± 0·007 Å (av.) long. It may therefore be concluded, as in the case of phenylarsine-bis-(*NN*-diethyldithiocarbamate), which was recently shown[4] to have similar bond distances, that the canonical forms:



give the most important contributions to the structure of the complex.

The arsenic co-ordination polyhedron found by two-dimensional techniques for arsenic(III) *O*-ethylxanthate[5] is very similar to that found in the present case; no comparison of the ligand geometry is however possible because of the very high e.s.d.'s affecting the bond lengths and angles of the *O*-ethylxanthate molecule.

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[3] L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, 3rd edn., 1960, p. 225.

[4] R. Bally, *Acta Cryst.*, 1967, **23**, 295.

[5] G. Carrai and G. Gottardi, *Z. Krist.*, 1960, **113**, 373.