The Crystal Structure of Di-μ-(bis-2-mercaptoethyl sulphide)-dinickel(II)

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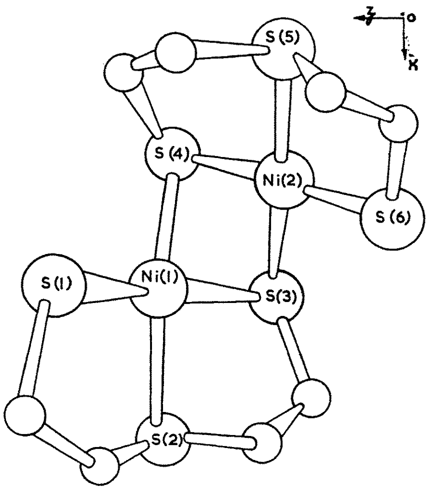
Summary Nickel–nickel distances of 2·74 Å are present in crystals of di-μ-(bis-2-mercaptoethyl sulphide)-dinickel(II).

THE red nickel complex of bis-2-mercaptoethyl sulphide reported by Harley-Mason was assigned a dimeric structure $[NiS(CH_2{\cdot}CH_2{\cdot}S)_2]_2$.[1] It was concluded that the two nickel atoms and the six sulphur atoms were coplanar. We have determined its crystal structure from Weissenberg photographs taken with Cu-K_α radiation. Crystal data: orthorhombic, $a = 9{\cdot}44$, $b = 10{\cdot}93$, $c = 28{\cdot}88$ Å, $U = 2993$ Å^3, $D_m = 1{\cdot}9$, $Z = 8$, $D_c = 2{\cdot}05$, space group *Pbca* (No. 61). The structure was solved by means of Patterson and electron-density maps and refined by several cycles of least-squares using isotropic temperature factors to R 0·114; 1705 independent reflections were used.

The eight dimeric molecules lie in general positions. The structure of the dimer (Figure) can be seen to be appreciably distorted from the planar molecule suggested by Harley-Mason.[1] Not only is the molecule folded about the bridging thiols but also the two halves of the molecule are slightly twisted relative to each other. The complex is the *cis*-isomer. Curiously, the distorted dimeric molecules have non-crystallographic two-fold axes approximately perpendicular to the plane of the Figure. The relevant angles and bond lengths of the co-ordination sphere are: Ni(1)–S(1) = 2·16, Ni(2)–S(6) = 2·17 (terminal thiols), Ni(1)–S(2) = 2·15, Ni(2)–S(5) = 2·14 (sulphides), Ni(1)–S(3) = 2·22, Ni(1)–S(4) = 2·18, Ni(2)–S(3) = 2·18, Ni(2)–S(4) = 2·21 Å (bridging thiols), Ni ⋯ Ni = 2·74 Å, Ni(1)–S(4)–Ni(2) = 77·3°, Ni(1)–S(3)–Ni(2) = 76·8°. The dihedral angle between the two halves of the molecule is 75·6°. The C–S bond-lengths are all within the range 1·80—1·87 Å, and the mean value of 1·50 Å for the C–C bond-length is typical for sp^3 hybridisation.

Both the nickel ions have, to a close approximation, a square-planar environment. However, it would appear that, in order to satisfy also the geometric limitations of the ligand, the molecule has had to fold about the bridging sulphur atoms. A model of the molecule indicated that the *trans*-configuration would be even more constrained than the *cis*-isomer. A consequence of the folding of the molecule is a shortening of the Ni ⋯ Ni distance to 2·74 Å. Short nickel–nickel distances are well known in organometallic complexes but comparatively rare in other nickel compounds. Nickel–nickel distances of 2·89 and 2·38 Å have been observed in bis(acetylacetonato)nickel(II)[2] and tetrakis(1,3-diphenyltriazenido)dinickel(II),[3] respectively. Our complex is diamagnetic over the temperature range 100—300°K which is to be expected with square-planar co-ordination about Ni^{II}. It was found impossible to obtain a mass spectrum. Therefore there is no confirmatory evidence to indicate whether our metal–metal distance of 2·74 Å constitutes an actual bond or is just due to the steric requirements of the metal ion and the ligand.



FIGURE

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