The Crystal and Molecular Structure of Bis(dithiobiureto)nickel(II)

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EARLIER we reported the crystal structure of bis(dithiobiureto)palladium(II),[1] and discussed the geometric possibilities for bonding of dithiobiuret with transition-metal ions.[1] The metal bisdithio-clusters are also of interest in that when the metal is Fe^{II}, they may be structural models for biological systems.[2] In the bis(dithiobiureto)nickel(II) complex one might expect shorter M–S distances than in the Pd analogue and consequently this would impose constraints on the S–S "non-bonded" interchelate distances. Further, the dithiobiureto-complexes of Ni^{II} and Pd^{II} are not isomorphous.[3] We have also prepared complexes of this ligand with Co^{II}, Zn^{II}, and Cu^{II}.

Bis(dithiobiureto)nickel(II) was prepared from nickel chloride hexahydrate and dithiobiuret in aqueous solution under controlled temperature and pH conditions. The needle crystals were monoclinic $P2_1/n$ with $a = 9{\cdot}780(4)$, $b = 11{\cdot}873(5)$, $c = 4{\cdot}660(1)$ Å, $\beta = 93{\cdot}27(1)^\circ$, $U = 541$ A^3, $M = 326{\cdot}7$, $D_m = 1{\cdot}93$, and $D_c = 2{\cdot}00$ with $Z = 2$. Intensities of 805 independent non-zero *hkl* reflections were recorded with a Picker automated diffractometer using Mo-K_α radiation. The crystal structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. All atoms, including hydrogens, having been located. The non-hydrogen atoms were refined with anisotropic temperature factors to $R = 0{\cdot}046$. The hydrogen atom position and temperature factors were not refined.

The structure consists of isolated dtb_2Ni^{II} molecules separated by normal van der Waals distances from neighbouring molecules. The molecular configuration is shown in the Figure. As in the case for the analogous Pd compound, the metal binds to the ligand *via* metal–sulphur bonds and the space group demands that the metal atom with its four sulphur neighbours must be coplanar. The Ni–S distances are *ca.* 0·1 Å shorter than the corresponding Pd–S distances and are to be compared to the 2·174, 2·156, both ±0·006 Å Ni–S, distance observed by Eisenberg and Ibers[4] in di(tetramethylammonium)bis(maleonitriledithiolate)nickel(II), $[Ni\,mnt_2{}^{2-}]$. The S–C and C–N distances in this structure do not differ significantly from those found in the related Pd compound nor in thiourea itself.[5] The S–C distances are also similar to those of $Ni\,mnt_2{}^{2-}$. There are several striking and important differences between this structure and the Pd analogue.[3] (i) the C–S–M– angle has opened up from 110° (av.) to 115°, (ii) the S–Ni–S (intrachelate) angle has increased from 92·8° to 96·1°, (iii) the S–S intrachelate distance has decreased from 3·32 to 3·22 Å while the interchelate distance has decreased from 3·16 to 2·89 Å, (iv) the molecular distortion from a completely planar molecule to the chair form (defined by the dihedral angle between the Ni, S(1), S(2), and S(1), S(2), N(2) planes has decreased from 38° to 11°. These non-bonded S–S distances are far shorter than the "normal" 3·70 Å van der Waals distance[6] and the 2·89 Å is the shortest non-bonded S–S distance observed to date. (v) In both Pd dtb$_2$ and Ni dtb$_2$ the anion deviates as much as 0·2 Å from planarity but the S(1), C(1), N(1), N(2) and the S(2), C(2), N(2), N(3) units are planar. The nitrogen and carbon atoms are much more nearly planar in Ni dtb$_2$ (max. deviation 0·06 Å compared to 0·15 Å).

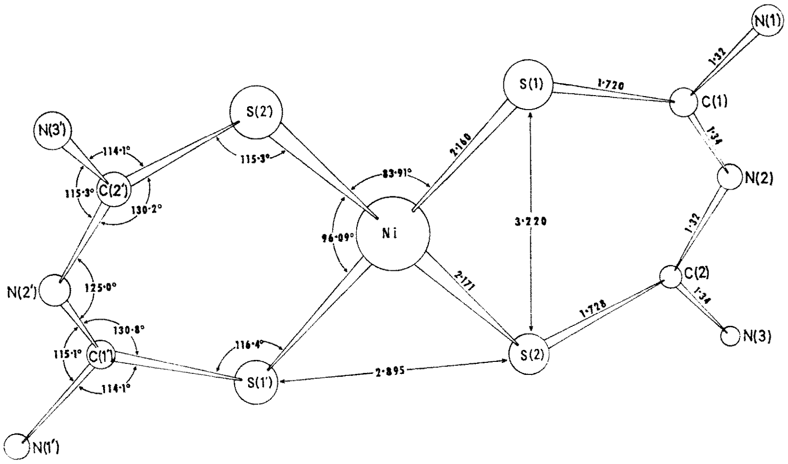

FIGURE. *Perspective view of the bis(dithiobiureto)nickel*(II) *molecule. The nickel is at a centre of symmetry and only half the molecule is crystallographically independent. Estimated errors from least-squares output are*: Ni–S ± 0·002, S–C ± 0·008, C–N ± 0·011 Å. Ni–S–C 0·2°, S–Ni–S 0·08°, S–C–N 0·7°, N–C–N 0·7°.

Gray *et al.*,[7] have postulated that S–S non-bonded intrachelate distances between 3·04—3·17 Å indicate some residual S–S bonding. The intrachelate S–S distance in both Pd dtb$_2$ and Ni dtb$_2$ is beyond this limit but the 3·16 Å and 2·89 Å, respectively, interchelate distances are well within this range. Since the Ni–S distance is shorter than the Pd–S, one would expect the repulsive non-bonded interactions to be greater between the interchelate sulphur atoms and in the absence of S–S bonding the Ni dtb should be even more distorted into the chair conformation than is the Pd dtb$_2$ to minimize non-bonded S–S repulsions. However, the angle that defines this distortion has actually decreased from 38° to 11°. Hence, we must conclude that there is some residual S–S interchelate bonding in at least Ni dtb$_2$. This is further supported by the fact that the C–S–M angle is more open in the Ni dtb$_2$ structure. These arguments lead to the interesting prediction that M dtb$_3$ complexes, where M is a tripositive ion, will either have an elongated trigonal prism structure or more likely a flattened trigonal antiprism configuration due to S–S interchelate bonding.

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[1] R. L. Girling and E. L. Amma, *Chem. Comm.*, 1968, 1487.
[2] R. Beckett and B. F. Hoskins, *Chem. Comm.*, 1967, 909; K. Knauer, P. Hemmerich, and J. D. W. van Voorst, *Angew. Chem.*, 1967, **79**, 273; *Angew. Chem. Internat. Edn.*, 1967, **6**, 262.
[3] R. L. Girling and E. L. Amma, to be published.
[4] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 605.
[5] M. R. Truter, *Acta Cryst.*, 1967, **22**, 556.
[6] L. Pauling, "Nature of the Chemical Bond," The Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 260.
[7] E. I. Steifel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3353.