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

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DITHIOBIURET (dtb) is an interesting ligand for the formation of complexes with metal ions. It has an abundance of delocalized lone-pair electrons (3 pairs per ligand) that make it suitable for the stabilization of unusual oxidation states. Moreover, it could possibly chelate: (a) *via* two sulphur atoms, (*b*) *via* two nitrogen atoms, (c) *via* a sulphur and a nitrogen atom, in each case to form a six-membered ring. This ligand can chelate either as a neutral donor or an uninegative ion, depending upon conditions.[1] It could also behave as a unidentate ligand. On the other hand, biuret[2] chelates only through the oxygen atoms as a neutral ligand or through the nitrogen atoms as a dinegative anion and through oxygen as a unidentate ligand. We have prepared $Pd(dtb)_2$ in neutral solution from dithiobiuret and palladium chloride[3] and report the results of the crystal structure analysis.

$Pd(dtb)_2$ crystallizes in the orthorhombic space group *Pbca* with $a = 8{\cdot}805 \pm 0{\cdot}004$, $b = 12{\cdot}171 \pm 0{\cdot}008$, $c = 10{\cdot}461 \pm 0{\cdot}007$ Å, $U = 1121$ Å^3, $M = 374$, $D_m = 2{\cdot}27$, $D_c = 2{\cdot}21$, $Z = 4$. Intensities of 828 independent non-zero reflections were recorded with a Picker automatic diffractometer using Mo-K_α radiation ($\lambda = 0{\cdot}71068$ Å). The crystal structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. All atoms, including hydrogens, have been located. The non-hydrogen atoms were refined with anisotropic temperature factors to a conventional *R* of 0·046. The hydrogen atom position and temperature factors were not refined.

The structure consists of discrete $Pd(dtb)_2$ molecules separated by normal van der Waals distances from other molecules. The molecular configuration of an isolated molecule is shown in the Figure. It is to be noted that: (1) the palladium is solely sulphur-bonded, (2) the proton was

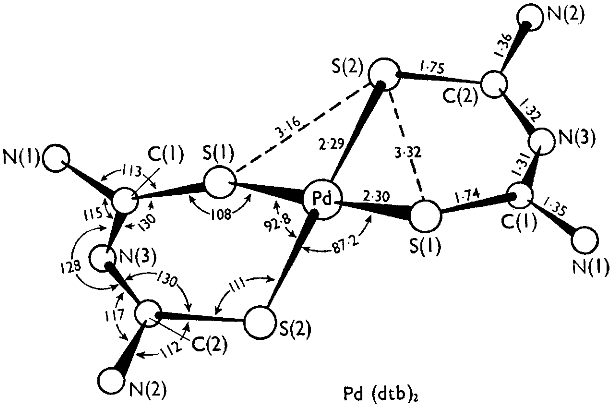

FIGURE. *Perspective view of the bis(dithiobiureto)-palladium*(II) *molecule. The palladium is at a centre of symmetry and only half the molecule is crystallographically independent.* E.s.d.'s are: Pd–S, 0·004; S–C, 0·011—0·013; C–N, 0·018—0·0020 Å; Pd–S–C, 0·4; S–Pd–S, 0·1; S–C–N, 0·8; N–C–N, 1·0°.

removed from the ligand from the central nitrogen and not from the terminal nitrogen atoms, as shown by the location of the hydrogen atoms and also by the symmetrical nature of the ligand geometry. Both of these points contrast the behaviour of biuret as a chelating agent in which it nitrogen-bonds as an anion and the protons are removed from the terminal nitrogen atoms. (3) Space-group requirements demand that the palladium atom lie on a centre of symmetry, which requires that palladium and its four sulphur neighbours must be planar. However, the remainder of the molecular complex does not lie in this plane and if viewed end-on the complex is in an approximate chair arrangement with an angle of 38° bend from the linear. This is somewhat simiiar to the 21° bend in bis(biuret)copper(II) chloride found by Freeman and Smith.[4]

Striking differences in geometry between this structure and bis(dibiuret)copper(II) chloride are the X-C-N interior angles 131° and 122° (av.) respectively and the C-X-Metal angle of 110° (av.) and 124°.

The S(1)-C(1)-N(1)-N(3) and S(2)-C(2)-N(2)-N(3) units are each planar, within the statistical errors, with the greatest deviation being $<0{\cdot}04$ Å. However, the entire dithiobiuret anion is not planar, having deviations as large as 0·2 Å from the best least-squares plane defined by the dithiobiuret anion. The nature of this distortion may be described as a folding of the S(1)-C(1)-N(3) plane down about the S(1)-N(3) line such that the angle between this plane and the S(1)-S(2)-N(3) plane is 20·6°. The S(2)-C(2)-N(2)-N(3) plane is correspondingly bent up about the S(2)-N(3) line (5·6°). The Pd–S distances are somewhat shorter than the sum of the covalent radii (2·36 Å) but not significantly different from those observed in a recent accurate structure determination of tetrakis-(thiourea)palladium(II) chloride.[5]

The C–S distances are probably not significantly different from the C–S distances in free thiourea[6] [1·720(9)] nor from C–S distances in complexed thiourea.[7] The external C–N distances are essentially those of the free ligand [1·340(6)].[6] The internal C–N distances are uniformly 0·04 Å less than the external distances but this is only marginally significant.

The intramolecular S–S distances of 3·32 Å (intrachelate) and 3·16 Å (interchelate) are short when compared to the accepted van der Waals distance of 3·70 Å.[8] The 3·32 Å is long compared to 3·04—3·17 Å observed by Gray *et al.*[9] in which S–S residual bonding is postulated, but the 3·16 Å interchelate distance falls into this range. We have also observed S–S non-bonded distances as short as 3·08 Å[10] in Pt tu_4Cl_2 (tu = thiourea). Hence, we feel that S–S distances *ca* 3·1 Å do not necessarily imply sulphur–sulphur bonding and such interpretations should be treated with caution.

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