Structures of Metal Dithiocarboxylates: the Crystal Structure of Bis(dithiobenzoato)palladium

By M. BONAMICO and G. DESSY

(*Centro di Chimica dei Composti di Coordinazione del C.N.R. Istituto di Chimica Generale e Inorganica, Università di Roma, Roma, Italy*)

FURLANI, *et al.*[1] have synthesized certain new dithiocarboxylate complexes of the type $M^{II}L_2$ and $M^{III}L_3$ where M^{II} = Ni, Pd, Pt; M^{III} = Cr, Fe, Co, Rh, In, Ir, and L^- = $PhC{\cdot}S{\cdot}S{\cdot}^-$ or $PhCH_2{\cdot}{\cdot}C{\cdot}S{\cdot}S{\cdot}^-$.

We have undertaken the *X*-ray analysis of some of these complexes which are of special interest because of their similarity to the diethyldithiocarbamates. We report the crystal structure of bis(dithiobenzoato)palladium.

Crystals of $(PhCS_2)_2Pd$ are dark red-violet monoclinic prisms; $a = 5{\cdot}943 \pm 0{\cdot}01$, $b = 12{\cdot}662 \pm 0{\cdot}005$, $c = 28{\cdot}707 \pm 0{\cdot}01$ Å; $\beta = 93°36' \pm 10'$; $U = 2156$ Å^3; $D_m = 1{\cdot}88$ g.cm.$^{-3}$ (by flotation); $Z = 6$; $D_c = 1{\cdot}909$ g.cm.$^{-3}$; F (000) = 1229·3. Space group, $P2_1/c$ from systematic absences. Data are taken from Weissenberg and precession photographs, using Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation.

We recorded the *X*-ray intensities of 2442 independent reflections, visually estimated from equi-inclination Weissenberg photographs taken about the *a*-axis and precession photographs taken about the *b*-axis.

Since there are six molecules per cell, two at least (type A in the Figure) must be centrosymmetric. A three-dimensional Patterson synthesis showed

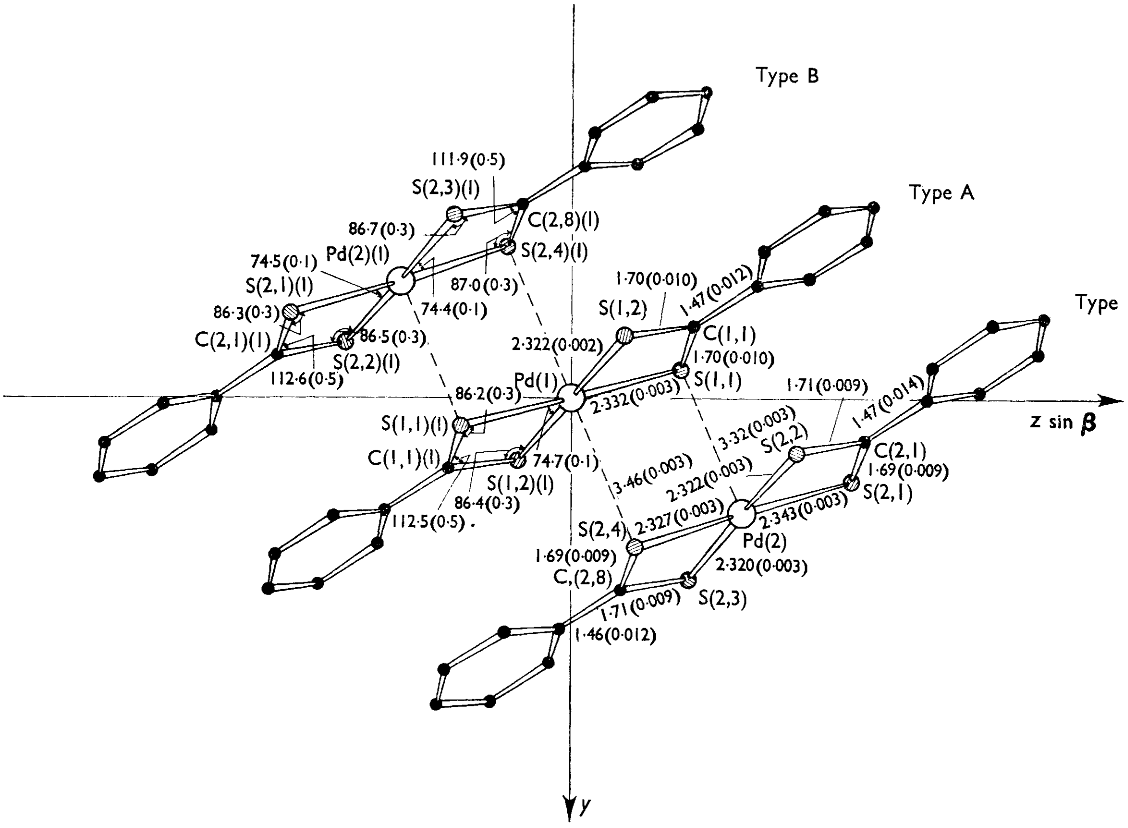

FIGURE. [100] *projection of the molecules with bond lengths (in Å) and angles (in degrees) (standard deviations in parentheses).*

the other four to be crystallographically equivalent (type B). From a succession of Fourier syntheses the positions of the sulphur atoms were determined, followed by those of the carbon and hydrogen atoms. Co-ordinates and anisotropic temperature factors were refined by least-squares. Present values ($R = 5{\cdot}1\%$) define the bond lengths and angles given in the Figure.

The two crystallographically independent molecules (types A and B) are very similar. In both molecules there is virtual planarity of all atoms (the mean deviations from planarity being 0·05 Å): the molecular planes are practically parallel and are separated by 3·5 Å. The palladium atom co-ordination is a distorted tetragonal. The Pd–S distances lie in the range 2·32—2·34 Å (with mean standard deviation $\sigma = 0{\cdot}003$ Å), whilst the S–C bond lengths do not have significantly different values (1·69—1·71 Å, $\sigma = 0{\cdot}01$ Å). The C–C distances between C(1,1), C(2,1), C(2,8), and the corresponding phenyl groups (1·46—1·47 Å with $\sigma = 0{\cdot}015$ Å) show a partial double-bond character consistent with the planarity of the molecules.

The interatomic distances between Pd(1) and S(2,4) [and the centrosymmetrically located S(2,4) (I)] of 3·46 Å, and between Pd(2) and S(1,1) of 3·32 Å suggest interesting interactions between these atoms. The centre of these molecules is similar to that found for nickel diethyldithiocarbamate.[2]

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[1] C. Furlani and M. L. Luciani, unpublished work.

[2] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 619.