

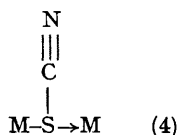
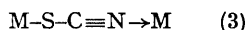
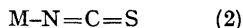
The Crystal Structure of the Complex Ion $[\text{Pd}(\text{SCN})_4]^{2-}$ in the Compound $\text{K}_2\text{Pd}(\text{SCN})_4$: a Novel Type of Thiocyanate

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Summary The complex ion $[\text{Pd}(\text{SCN})_4]^{2-}$ in the compound $\text{K}_2\text{Pd}(\text{SCN})_4$ is the first X-ray structural example of a thiocyanate linkage of the type (4).

THE thiocyanate group can co-ordinate to metal atoms in at least four ways.



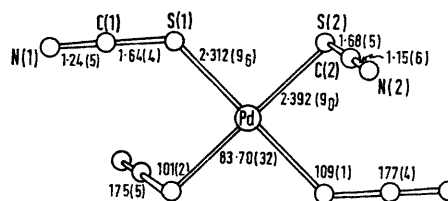
The first three types are well known but the results of an X-ray structure determination on the fourth type have not previously been reported.

Crystals of $\text{K}_2\text{Pd}(\text{SCN})_4$ are dark brownish-red, monoclinic, space group $P2_1/a$ with $a = 11.11$, $b = 12.90$, $c = 4.28$ Å, $\beta = 98.2$, $Z = 2$, $D_m = 2.37$. $D_c = 2.39$ g cm $^{-3}$. Data were collected by the equi-inclination Weissenberg technique with Cu- K_α radiation: 582 independent reflexions, from $hk0$ to $hk3$, were recorded from a needle-shaped crystal (needle thickness 0.04 mm) mounted about the needle axis. The structure was solved, from the visually estimated intensities, by Patterson and Fourier techniques. The conventional R factor from the full matrix least squares refinement with anisotropic temperature parameters for all atoms was 0.136.

The two halves of the formula unit, $\text{K}_2\text{Pd}(\text{SCN})_4$, are related by a centre of symmetry and the compound consists of K^+ ions and $[\text{Pd}(\text{SCN})_4]^{2-}$ complex ions. The thiocyanate groups are S-bonded to the palladium atom as predicted from the i.r. spectrum¹ and the palladium-thiocyanate links are bent at the sulphur atoms, as is usual for S-bonded thiocyanates.²

The planarity of the PdS_4 moiety is crystallographically exact and the lengthening of Pd-S(2) relative to Pd-S(1),

the distortion from square symmetry and the significant difference in the angles Pd-S(1)-C(1) and Pd-S(2)-C(2) are presumably due to the interaction of S(2) with the palladium atom on an adjacent complex ion as described below.



FIGURE

The complex ions are stacked in columns in the lattice so as to form distorted octahedra round Pd with axial distances to S'(2) of 3.66 Å where S'(2) is at (0, 0, z) relative to S(2). The angles S'(2)-Pd-S(2) and S'(2)-Pd-S(1) are 87.5° and 67.3° respectively. The angles between the thiocyanate groups and the square plane are 16.6° and 70.2° at S(1) and S(2) respectively. The direction of S(2)-C(2)-N(2) is away from the palladium atom on the adjacent complex ion with which S(2) interacts, and thus favours the S'(2) ··· Pd interaction. The angles Pd-S(2)-C(2), C(2)-S(2)-Pd' and Pd-S(2)-Pd' (where Pd' is at (0, 0, z) relative to Pd) are 101.2°, 142.3° and 87.5° respectively: the sum of these angles, 331°, is very close to the sum of three tetrahedral angles, 328°. This seems to imply the existence of a co-ordinate bond rather than merely a van der Waals attraction; the relative weakness of this interaction compared with the strength of the Pd-S bonds in the square plane, is attributed to the repulsion of the axial S'(2) by electrons in the full $4d_{z^2}$ orbital on palladium.

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¹ A. Sabbatini and I. Bertini, *Inorg. Chem.*, 1965, 4, 959.

² S. E. Livingstone, *Quart. Rev.*, 1965, 19, 397.