Crystal structure of palladium 2-methylthio-8-mercaptoquinolinate \( \{ \text{Pd}_3[C_9H_5(SCH_2)NS]_3 \} \).

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Keywords: crystal structure, palladium complexes, 8-mercaptoquinolinate.

Palladium 2-methylthio-8-mercaptoquinolinate has been synthesized in the scope of systematic comparative structure investigations of chelates of 8-hydroxy-, 8-mercapto- and 8-hydroselenoquinolines with metals.

The complex was prepared by interaction of 2-methylthio-8-mercaptoquinoline with palladium chloride in aqueous ethanol medium. The chemical formula of palladium 2-methylthio-8-mercapto-quinolinate-\( \{ \text{Pd}_3[C_9H_5(SCH_2)NS]_3 \} \) was established on the basis of X-ray diffraction analysis.

The structure is built of trimeric \( \{ \text{Pd}_3[C_9H_5(SCH_2)NS]_3 \} \) units. The thrdentatic (S,N,C) function of the ligand - 2-methylthio-8-mercaptoquinoline - has been observed for the first time. Three ligands act as divalent anions in tridentate (S,N,C-) fashion between three palladium atoms forming neutral unit. Each palladium atom forms one 5-membered metal-containing ring with one 2-methylthio-8-mercaptoquinoline ligand via covalent bonds Pd-S (2.348(6)-2.384(7)\( \text{Å} \)) and Pd-N (1.971(18)-2.015(15)\( \text{Å} \)). Palladium atom has been established to substitute the hydrogen atom in the methylthio group, and the second 5-member of metal-containing ring containing the same ligand is closed by formation of a strong covalent bond Pd-C (2.03(2)-2.05(2)\( \text{Å} \)). Each S atom bridges two palladium atoms inside the molecular units. The bond Pd-S(bridge) is always shorter than the Pd-S(chelate) bond. The ranges of the bond angle values: chelate angles SPdN 84.8(5) - 85.1(5)\( \circ \); NPdC 86.2(9) - 87.4(8)\( \circ \); interligand angles S(chelate)PdS (bridge) 92.7(2) - 96.0(2)\( \circ \); S(bridge)PdC 92.9(7) - 95.9(6)\( \circ \); S(chelate)PdC 170.4(6) - 171.1(7)\( \circ \) and NPdS (bridge) 170.6(5) - 174.6(5)\( \circ \). The three crystallographically nonequivalent palladium atoms are in distorted cis-square (2S+N+C) coordination. The central part of the complex is formed by nonplanar six-membered heterocycle 3Pd+3S consisting from the alternating palladium and mercapto group sulfur atoms. The values of the bond angles SPdS and PdSPd are in the range of 92.7(2) to 96.0(2)\( \circ \) and of 92.0(2) to 105.9(2)\( \circ \) correspondingly.

The structure of \( \{ \text{Pd}_3[C_9H_5(SCH_2)NS]_3 \} \) differs essentially from that of palladium 2-methyl-8-mercaptoquinolinate \( \{ \text{Pd}_3[C_9H_5(CH_3)NS]_3 \} \) in which a distorted cis-square surrounding (2S+2N) is characteristic of the palladium atom.

Crystal data for \( \{ \text{Pd}_3[C_9H_5(SCH_2)NS]_3 \} \); triclinic, \( a=8.256(2); b=14.706(3); c=15.638(3)\( \text{Å} \); \( \alpha=115.29(3); \beta=96.76(3); \gamma=96.35(3)\( \circ \); \( V=1677.2(6)\( \text{Å}^3 \); \( Z=2; D_{\text{c}}=1.840\text{ g/cm}^3; \text{sp.gr. P-1; CAD-4; } \lambda_{\text{MoK} \alpha}=0.0593. \)