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A Novel π-Allyl Complex with the Closoborate Anion $[(h^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$

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There is quite sufficient information on closoborates of mainly alkali and alkali-earth metals [1, 2]. As far as concerns transition metal complexes and particularly of nickel, palladium and platinum data on these metals compounds are extremely sparse.

Recently we have synthesized and characterized nickel [3] and palladium [4] cationic complexes stabilized by large counterions $B_nX_n^{2-}$ (n = 10, 12; X = Cl, Br).

This paper deals with the synthesis and the results of X-ray monocrystal investigation of a new palladium complex $[(h^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$.

Experimental

Synthesis

To a solution of $Ag_2B_{10}Br_{10}$ (0.64 g, 0.55 mmol + 3% excess) in 10 ml of pure acetonitrile with vigorous stirring the solution of $[(h^3\text{-}C_3H_5)PdCl]_2$ (0.20 g, 0.55 mmol) was added. A white crowd precipitate formed immediately and the solution turned from deep to pale yellow. After leaving the solution in the dark for 2–3 hours, the white precipitate was filtered. Thus 0.16 g of the compound which was identified as AgCl was obtained.

The pale-yellow filtrate was evaporated under vacuum and then dissolved in a minimum amount of CH_2Cl_2, filtered and after addition of equal volumes of chloroform and benzene (both 5 ml) and 3 ml of acetonitrile, was left to crystallize in a Dwar flask.

The yellow crystals (0.78 g, 99% from theory) were separated and washed with chloroform and absolute ether. TLC ('Silufol', silica gel precoated sheets, 'Kavalier', C.S.S.R; eluent $(CH_3)_2CO:CCl_4$ = 3:1 v/v, visualization by iodine vapors– proved the absence of any other compounds. *Anal.* for $C_{20}H_{28}N_4B_{10}Br_{10}Pd_2$. Found: C, 16.55; H, 1.94; N, 4.09; B B, 7.60; Br, 55.10; Pd,14.45. Calcd.: C, 16.63; H, 1.95; N, 3.88; B, 7.48; Br, 55.32; Pd, 14.73%.

This complex is air stable at least for three months but in solution tends to form 'palladium mirror'. It is easily soluble in methylene chloride, acetone, acetonitrile, nitromethane and nitrobenzene but insoluble in chloroform, hydrocarbons, alcohols and ethers.

The conductivity of the complex in nitrobenzene solution (10^{-3} *M*) is 50 ohm^{-1} cm^2 mol^{-1} which corresponds to three ionic electrolites [5].

Crystal data

The orthorhombic crystals of the title compound belong to space group *Cmcm*, a = 13.786(3), b = 20.647(5), c = 14.627(3) Å; ρ_c = 2.23 g/cm^3 (calculated for $Z = 4$), μ(Mo-K$_\alpha$) = 110.3 cm^{-1}.

The intensity data of 1259 reflexions with $I \geqslant 1.96\sigma$ ($2\theta_{max}$ = 53°) were obtained on four circle automatic diffractometer "Syntex P2$_1$" (λMo-K$_\alpha$). The structure was solved by the heavy atom method and refined anisotropically by the full-matrix least-squares method to R = 0.063.

Results and Discussion

The structure is built up of the complex cations $[Pd(C_3H_5)(CH_3CN)_2]^+$ anions $B_{10}Br_{10}^{2-}$ and C_6H_6 molecules in the ratio 2:1:1. The structural units are in van der Waals distances. The complex cations lie on mirror planes *m* bisecting $CH_3CN\text{-}Pd\text{-}NCCH_3$ angle, the polyhedral borate anions are on the intersection of *m* planes.

In the complex cation each atom of palladium has been coordinated by two nitrogen atoms of acetonitrile molecules and by h^3-allyl group. The square plane coordination of palladium confirm its d^8 electronic configuration.

Palladium atom and the central carbon atom of C_3H_5 ligand lie on *m* plane. Distances: Pd–C$_{centr}$ = 2.13(2) and Pd–C$_{term}$ = 2.15(1) Å are conventional. Distances: Pd–N = 2.10(1), N–C = 1.16(2), C–CH$_3$ = 1.47(2) Å; angles; C_2PdC_2' = 70.1(6)°, C_2PdN = 96.3(5)°, NPdN' = 97.1(5)°, N–C–CH$_3$ = 177(2)°.

In the allyl ligand carbon-carbon distance – 1.44(2) Å – is longer than usual (1.36–1.38 Å) which is an evidence for a stronger π-interaction with palladium in the presence of CH_3CN molecules, effective σ-donors [6]. C–C–C angle is of 119°, the angle between the allyl and palladium coordination plane is of 113°.

Polyhedral closo borate anion is a bicapped tetragonal antiprism. Average B–B distances (B$_e$–B$_a$ = 1.85(2) Å; B$_e$–B$_e$ = 1.676(25) Å, a-apical, e-equatorial atoms) within the $B_{10}Br_{10}^{2-}$ cage agree

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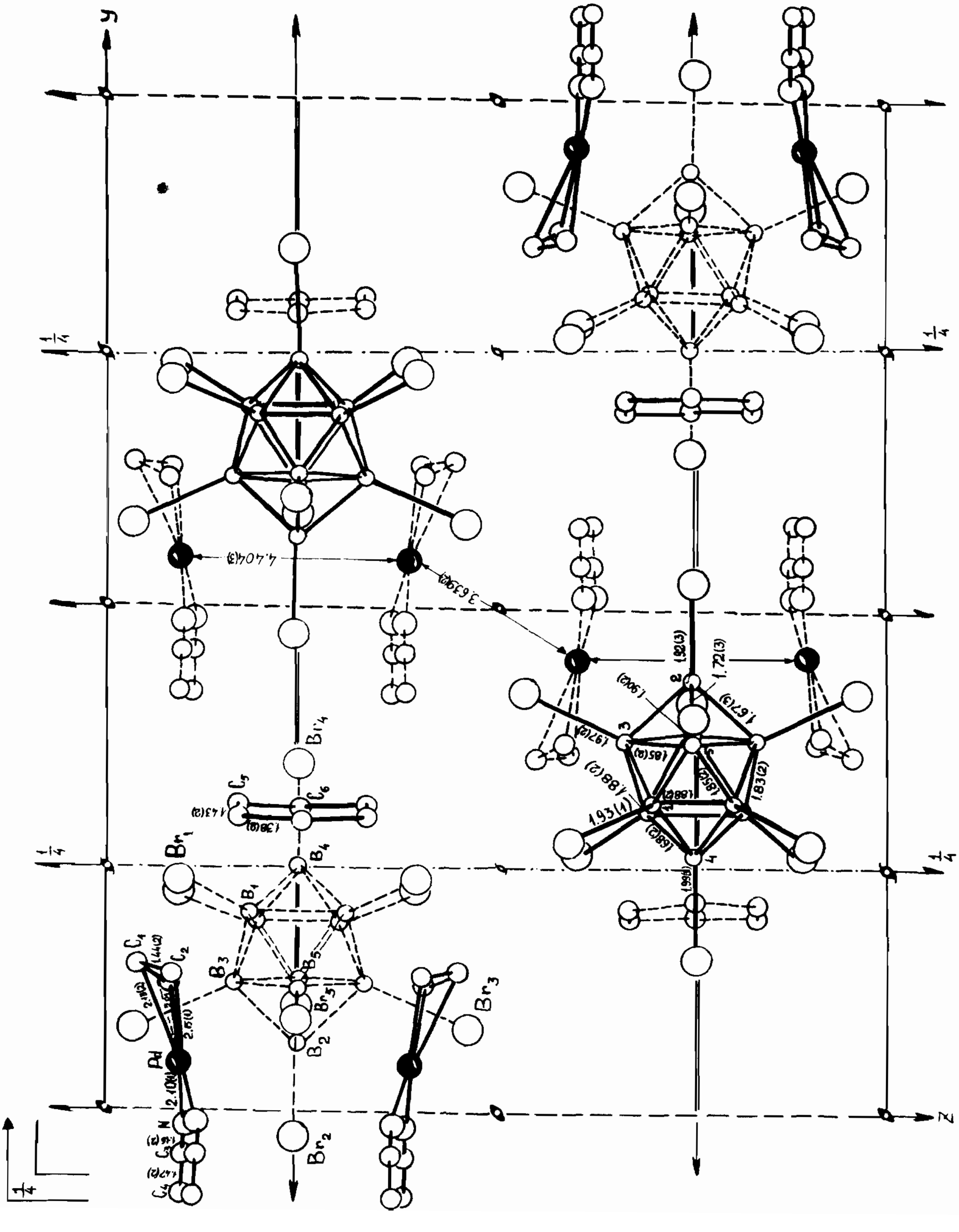

Fig. 1. The crystal structure of $[(h^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$ in projection along the *a* axis.

well with those published to $B_{10}H_{10}^{2-}$ in $[(PPh_3)_2Cu]_2$-$B_{10}H_{10}\cdot CHCl_3$ complex [7].

An unusual packing of structural units in the crystal is of a special interest (see Fig. 1). The flat complex cations are parallel. On the whole, these complex cations form zigzag columns with palladium atoms related by mirror planes (Pd–Pd = 4.404 Å) or by inversion centers (Pd–Pd = 3.639 Å).

There are no specific interactions between the metal atoms or between the allyl groups and the polyhedral cage anions (or between the benzene molecules). Bromine atoms are inserted between the complex cations related by mirror planes while the complexes related by a symmetry center are shifted with respect to each other the electric interactions $Pd^{+\delta}\cdots N^{-\delta}$, $Pd^{+\delta}\cdots\cdots Pd^{+\delta}$, $N^{-\delta}\cdots\cdots N^{-\delta}$ to be balanced.

The benzene molecules in the structure play an important role. They fill the space between the flat cations and bulky anions so different in their shape and size and lying in the planes perpendicular to the complex cations planes in order to stabilize the structure.

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