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PREPARATION, CRYSTAL STRUCTURE AND INFRARED SPECTRA OF  
*cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(CN)<sub>2</sub>]

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In an attempt to prepare the cyanide-analogue of the Vauquelin Red Salt (VRS), [Pd(NH<sub>3</sub>)<sub>4</sub>][PdCl<sub>4</sub>], freshly prepared solutions of [Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and K<sub>2</sub>[Pd(CN)<sub>4</sub>] were mixed in an equimolar ratio. After standing for several days, needle-like crystals separated from the reaction mixture and were recrystallized from hot water. They gave an infrared spectrum (Fig. 1) which clearly showed the presence of NH<sub>3</sub> and CN groups.

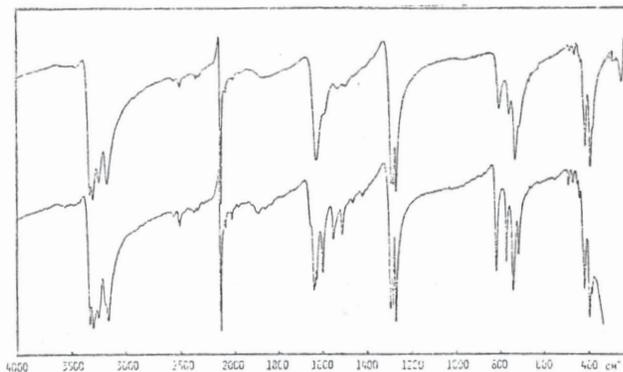


Fig. 1. Infrared spectrum of *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(CN)<sub>2</sub>]

The calculated Fourier maps were, however, in disagreement with the expected molecular geometry [Pd(NH<sub>3</sub>)<sub>4</sub>][Pd(CN)<sub>4</sub>] and indicated, instead, that the reaction product was, in fact, *cis*-[Pd(NH<sub>3</sub>)<sub>2</sub>(CN)<sub>2</sub>]. The successful refinement of the structure (to a final *R* value of 0.031) proved that this, indeed, was the true molecular structure. It should be noted that VRS itself undergoes isomerization to *trans*-[Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and, thus, the outcome of our preparation is not entirely unexpected.

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## СОБРАНИ ТРУДОВИ

The crystals of the title compound are monoclinic, space group  $F2_1/m$ ,  $a = 6.825(2)$ ,  $b = 12.733(3)$ ,  $c = 6.779(2)$  Å,  $\beta = 111.02(2)^\circ$ ,  $V = 546.9$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 2.34$ ,  $d_m = 2.41$  g/cm<sup>3</sup>,  $F(000) = 368$ .

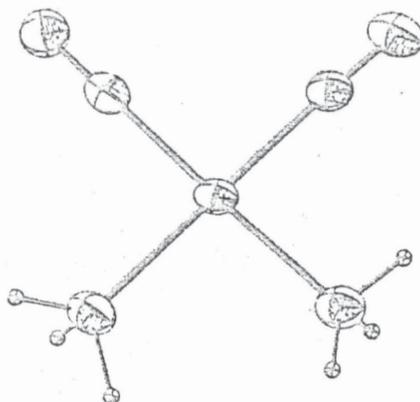
The intensity data were collected on a Philips PW 1100 computer-controlled diffractometer in the range  $0.1 < \sin \frac{\theta}{\lambda} < 0.7$  Å<sup>-1</sup>, with  $\omega$ -2 $\theta$  scan and MoK $\alpha$  radiation. A total of 1384 reflections were measured, of which 1354 had  $I > 3\sigma(I)$  and were considered as observed. No correction for absorption was applied.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedure, with anisotropic thermal parameters for all atoms except hydrogens to which an anisotropic parameter  $B = 3.0$  Å<sup>2</sup> was assigned (the hydrogen atoms were located in difference Fourier maps).

The infrared spectra were recorded on a Perkin-Elmer Model 580 infrared spectrophotometer, both at room temperature (upper curve on Fig. 1) and at liquid-nitrogen temperature (lower curve on that figure). A VLT-2 (RIIC) cell was used for the low-temperature measurements.

The structure consists of discrete  $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$  units. The two  $\text{NH}_3$  and the two cyanide ligands form the expected square-planar coordination sphere of the Pd atoms, the two ligands of each pair being *cis* to each other. The coordination is not ideal, however, and slight distortions are observed. Thus, two of the angles around Pd [C(1)-Pd-C(2) and C(2)-Pd-N(1)] deviate for about  $-2.3$  and  $+1.6^\circ$  from the ideal  $90^\circ$  value, the other two having values of  $90.2$  and  $90.5^\circ$ . The two Pd-C distances have values of  $1.962(5)$  and  $1.942(6)$  Å and the two Pd-N bonds are  $2.073(5)$  and  $2.092(5)$  Å long. The cyanide C $\equiv$ N distances [ $1.136(8)$  and  $1.147(9)$  Å] are as expected. One of the two Pd-C $\equiv$ N groups is practically linear [the Pd-C(2)-N(21) angle is  $179.8(5)^\circ$ ], whereas the other one is slightly bent, the corresponding angle [Pd-C(1)-N(11)] being  $178.0(5)^\circ$ . The six N-H distances range from  $0.876$  to  $1.173$  Å and the N-H $\cdots$ N contacts from  $3.049$  to  $3.421$  Å, all N-H $\cdots$ N angles being between  $149.5$  and  $157.4^\circ$ , except for one which has a value of almost  $173^\circ$ .

The structure is shown in Fig. 2.

Fig. 2. View of the  $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$  unit

The room-temperature infrared spectrum consists of the following main bands (the wavenumbers, in  $\text{cm}^{-1}$ , are followed by assignments given in brackets) : 3340, 3315, 3255, 3185 [ $\nu(\text{NH})$ ], 2145, 2135 [ $\nu(\text{CN})$ ], 1630, 1600sh [ $\delta_{\text{as}}(\text{NH}_3)$ ], 1395, 1385, 1375 [ $\delta_{\text{g}}(\text{NH}_3)$ ], 810, 765, 735, 715 [ $\rho(\text{NH}_3)$ ], 420, 395, 385sh [ $\nu(\text{PdN})$  and  $\nu(\text{PdC})$ ]. Judging from these frequencies, the product obtained by us is certainly not identical with that formulated as  $\text{Pd}(\text{CN})_2 \cdot 2\text{NH}_3$  [R. Nast, W. Hörl, *Ber.* **95**, 1470 (1962)] and probably not identical with that formulated [R. D. Gillard, *J. Inorg. Nucl. Chem.* **21**, 1321 (1965)] as *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$  : only one CN frequency is, namely, reported in Gillard's paper and the bands around  $800 \text{ cm}^{-1}$  are not mentioned at all.

The lowering of the temperature produces significant changes in the IR spectrum, some of which are expected (narrowing of the bands, shift to higher frequencies of the  $\text{NH}_3$  rocking bands and increase in their intensity), while others, especially the appearance of clearly separated bands around  $1600 \text{ cm}^{-1}$ , are more difficult to explain. The new bands in the  $\text{NH}_3$  bending region (they can not be due to fundamentals) may be explained as originating from overtones reinforced by interaction with the neighboring fundamentals, but their appearance and temperature behaviour are so similar to those of the bands observed by us [B. Šoptrajanov *et al.* *Horizons in Hydrogen Bond Research 1980, Poster Abstracts 23*, Sānga-Sūby, Sweden, 1980] in the HOH bending region of some crystallohydrates that a common origin can be suspected.