

INFRARED SPECTRA OF *c/s*-[Pd(CN)₂(NH₃)₂]

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ABSTRACT

The infrared spectrum of the title compound was recorded at room and liquid-nitrogen temperature and correlated with the available crystallographic data. In order to clarify the origin of some of the low-frequency bands an approximate normal-coordinate analysis was carried out. The appearance of multiple bands in the NH₃ bending region was tentatively explained by taking into account the details about the environment of the ammonia ligands.

INTRODUCTION

Compounds with composition analogous to that of the title one have been reported [1-2], but judging from the comparison of the reported frequencies with those found in our infrared spectra, neither of them is identical with the presently reported one.

EXPERIMENTAL

The title compound was inadvertently obtained in the course of our attempts to prepare a double complex containing tetraamminepalladium(II) cation and tetracyanopalladate anion by mixing equimolar, very diluted, solutions of the corresponding chloride and potassium salts and letting the resulting mixture to crystallize slowly. The successful solution and refinement of the crystal structure of the product of this reaction [3] showed, however, that *c/s*-dicyanodiamminepalladium(II) was obtained instead.

The infrared spectra were recorded, at room and liquid-nitrogen temperature, on a Perkin-Elmer Model 580 infrared spectrophotometer.

The calculations were performed on a PDP 11/70 computer, using a set of programs written by Dr. Anders Eriksson from the Institute of Chemistry at the University of Uppsala, Sweden.

RESULTS AND DISCUSSION

The infrared spectra are shown in Fig. 1. It is a rather straightforward task to assign the bands centered around 3200 cm⁻¹ to ammonia stretching vibrations, the sharp ones around 2100 cm⁻¹ to cyanide stretchings and those around 1600 and 1300 cm⁻¹ to antisymmetric and symmetric NH₃

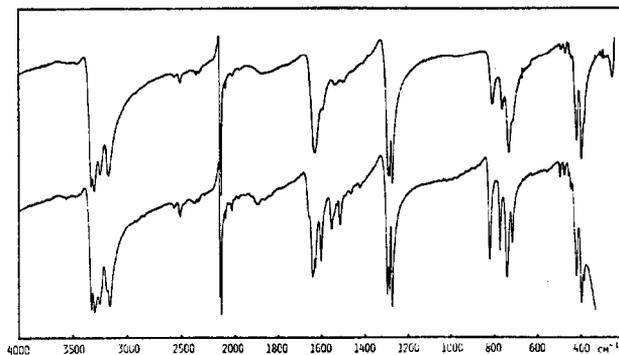


Fig. 1. Infrared spectra (RT and LNT) of $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$

should undoubtedly be attributed to rocking vibrations of the ammonia ligands. More difficult, on the other hand, is the precise assignment of the bands (some of them quite weak) around 400 cm^{-1} , although one would intuitively expect that all bands found at such low frequencies would originate from mixed modes.

In order to confirm these expectations, an approximate normal-coordinate analysis was carried out. The geometrical values (atomic positions in Cartesian coordinates) were derived from our crystal-structure determination [3], whereas the force constants were transferred from similar molecules [4,5]. The geometry was somewhat simplified and made closer to the idealized one and the force constants were slightly adjusted in order to obtain an approximate fit between the majority of the calculated and observed frequencies. No attempt was made to refine the force constants by iterative methods.

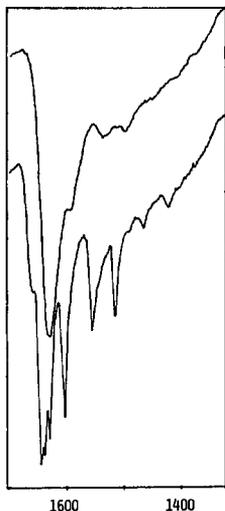


Fig. 2. The antisymmetric NH_3 bending region (RT and LNT)

The calculation showed that the bands above 1200 cm^{-1} were due to almost pure modes (NH and CN stretching and NH_3 bending respectively), whereas the low-frequency ones (those appearing around 400 cm^{-1}) had mixed character with Pd-N and Pd-C coordinates playing the major role (in fact, the vibration with somewhat more Pd-N character is that giving rise to the weak band around 490 cm^{-1}).

The problem which could not be solved by the normal-coordinate analysis was related to the existence of multiple bands in the NH_3 antisymmetric bending region. As can be seen in Fig. 2, namely, several shoulders and ill-defined bands visible in the room-temperature spectrum develop, in the low-temperature one, into bands whose intensity can not be neglected (this being especially true for the bands appear-

ring slightly above 1500 cm^{-1}). Somewhat weaker bands are found as low as 1400 cm^{-1} , their total number (including shoulders) amounting to over a dozen - appreciably more than expected on group-theoretical grounds. The main problem, however, does not lie in the *number* of bands in this region but in their *spread* over more than two hundred reciprocal centimeters (if all the bands, including the weak ones, are taken into account).

It is not likely that in this case one is dealing with an example of exceptionally large correlation-field splitting. The whole spectral picture instead corresponds so closely to that observed in the HOH bending region of the spectra of various crystallohydrates [6] (this being particularly true for the temperature behaviour of the bands) that it is natural to assume a common origin of the whole effect in both cases. In the latter one the tentative explanation has been [6] that the multiple bands arise from vibrational couplings, possibly with some low-lying fundamental. It was further proposed that such couplings would be possible as a consequence of the pronounced anharmonicity of the bending HOH vibration, either because of the asymmetric character of the water molecule environment (see also [7]) or because of other reasons (bifurcated hydrogen bonds including).

In the case of the studied compound, as the crystallographic data clearly show, the environment of the ammonia ligands is such as to indeed imply a high degree of anharmonicity of their vibrations. Thus the Pd-N-H angles are 111.5 , 121 and 126.4° for one of the ammonia ligands and 104.2 , 110.8 and 123.5° for the other one, whereas the corresponding palladium-nitrogen-acceptor (Pd-N-A) angles are 95 , 100.7 and 105.4° for the first, and 89.3 , 106 and 112.9° for the second NH_3 ligand. As a consequence, practically all hydrogen bonds except one are appreciably bent, and the conditions are favorable for the existence of bifurcated hydrogen bonds as well. Namely, in the vicinity of the hydrogens participating in the H-bonds for which the Pd-N-A angles are smallest (95 and 89°) there is an additional cyanide nitrogen, the Pd-N-A angles being, this time, rather large (137.8 and 150.8°).

Under such circumstances, as mentioned above, all kinds of vibrational interactions - with second-order transitions and/or low-frequency fundamentals become possible, leading either to intensity enhancement (in the former case) or to the appearance of band progressions (in the latter).

The spectra of the presently studied compound are not exceptional as far as the appearance of multiple bands in the ammonia bending region is concerned since we have observed the same general picture in a number of other palladium(II) ammine complexes as well [8].

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REFERENCES

1. R. Nast and W. Horl, *Ber.*, 95 (1962) 1470.
2. R.D. Gillard, *J. Inorg. Nucl. Chem.*, 21 (1965) 1321.
3. M. Penayić, B. Kamenar, L. Šoptrajanova, G. Jovanovski and B. Šoptrajanov, *Ann. Yugosl. Center Crystallogr.*, 17 (1982) S59.
4. U.P. Verma, V.K. Rastogi, A.N. Pandey and D.K. Sharma, *Indian J. Phys.* 51B (1977) 293.
5. G.J. Kubas and L.H. Jones, *Inorg. Chem.* 13 (1974) 2816.
6. B. Šoptrajanov, V. Petruševski, M. Ristova and M. Trpkovska, *Horizons in Hydrogen Bond Research, Poster Abstracts*, Sanga-Saby, Sweden, 1980.
7. B. Šoptrajanov and V. Petruševski, *J. Mol. Struct.* (in press).
8. L. Šoptrajanova, L. Andreevska and B. Šoptrajanov, *IV Jugoslavenski simpozij o analitickoj kemiji, Sinopsisi radova*, 129, Split, 1985.