¹H n.m.r. Studies of Palladium(II) Complexes of 2,9-Dimethyl-1,10-Phenanthroline and 8-Hydroxyquinoline

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Summary

The structures in solution of a series of palladium(II) complexes have been determined by ¹H n.m.r. and i.r. spectroscopy. Dicyanobis-(8-hydroxyquinoline)palladium(II) has a *cis*-square-planar configuration, the unidentate 8-hydroxyquinoline molecules bonding to Pd through the nitrogen atoms. Dicyanobis-(2,9-dimethyl-1,10-phenanthroline)-palladium(II) has a *cis*-square planar arrangement about Pd with respect to the nitrogen atoms of the two heterocyclic ligands. The cyanide groups bond to the two apical positions apparently giving rise to a six-coordinate Pd^{II} atom. Dihalo-2,9-dimethyl-1,10-phenanthrolinepalladium(II) (X = Cl, Br, I) exhibits the usual *cis*-square-planar arrangement of Pd^{II}, whereas the halobis-(2,9-dimethyl-1,10-phenanthroline)-palladium(II) ion (X = Cl, Br) has a trigonal bipyramidal structure with the halogen atom in the trigonal plane.

Introduction

Much attention has been focussed[1-6] on the possibility of strong interactions between the hydrogen atoms in the 6- and 6'-positions of 2,2'-bipyridyl and in the 2- and 9-positions of 1,10-phenanthroline in bis-complexes of these di-imine ligands. Plowman and Power[7, 8] have synthesized several Pt^{II} and Pd^{II} complexes of 2,9-dimethyl-1,10-phenanthroline (dmp) in order to study deviations from the normal square-planar geometry of these complexes and the effect of steric overcrowding enforced with coordinated polyatomic anions. Gillard[9] has drawn attention to one of these compounds, Pd(dmp)₂(CN)₂ · 2 H₂O, and suggested that it may be formulated as the covalent hydrate [1]. In the same paper it was also proposed that such a Reissert-type formulation could explain the apparently unusual stoichiometry and stereochemistry of the compound Pd(oxine)₂(CN)₂ · 2 H₂O (oxine = 8-hydroxyquinoline) as shown in [2].

[1]   [2]
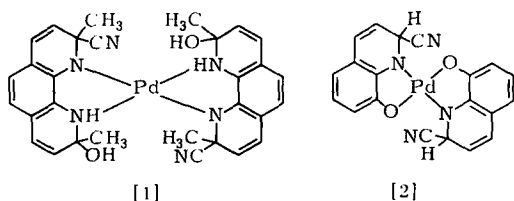
We therefore studied, using ¹H n.m.r., these two compounds together with the Pd^{II} complexes of dmp with halide anions in order to see if it was possible to deduce their stereochemistry.

Experimental

The Pd(dmp)X₂ (X = Cl, Br, I) and Pd(dmp)₂X₂ (X = Cl, Br, I) complexes were all made according to the directions of Plowman and Power[7]. Pd(dmp)₂(CN)₂ (H₂O)₂ was also made according to the method of Plowman and Power[8] except that it was found necessary to heat the reaction mixture on a water bath for some time. Following the directions given, a white crystalline compound separated after a few min. This was filtered off and dried *in vacuo* over silica gel, during which the crystals broke down to a powdery mass. The i.r. spectra indicated that this white powder was in fact *pure* dmp. A fresh crop of crystals dried in air to give the same product, gave off the characteristic "almond-like" smell of HCN. It is apparent that the initial product is the hydrocyanide salt of dmp, but the exact nature of this compound is unknown.

The Pd(oxine)₂(CN)₂(H₂O)₂ complex was prepared according to the method of Feigl and Heisig[10]. All compounds were characterized by their u.v. spectra, where known, and by elemental analysis.

¹H n.m.r. spectra were measured using a Perkin-Elmer R 32 spectrometer (with a digital signal analyser in some instances) using deuteriated solvents with TMS or DSS as internal standards. The i.r. spectra were measured in KBr discs or in solution using a Perkin-Elmer 257 grating spectrophotometer. Thermogravimetric analyses were obtained with a Stanton Redcroft TG-750 temperature-programmed thermogravimetric balance using samples weighing between 10 and 50 mg. The results of the n.m.r. studies are given in the Table.

Results and Discussion

a) Pd(oxine)₂(CN)₂(H₂O)₂

In KBr disc, the i.r. spectrum of this compound exhibits two cyanide stretching frequencies at 2155 and 2128 cm⁻¹ which suggests[11, 12] that both cyanide groups are coordinated to the Pd atom in a *cis*-configuration. There is no nitrile (*i.e.* $\geq$C—CN) absorption such as has been observed[13] in Reissert-type coordination complexes with cyanide. This fact coupled with the normal 4-coordination of Pd^{II} and the strong hydrogen bonding apparent from the i.r. spectrum suggests that the two oxine molecules are unidentate. In addition, the n.m.r. spectrum of the compound shows that they are equivalent. This was confirmed by the reaction of Pd(oxine)₂(CN)₂(H₂O)₂ with base. The nature of the deprotonation and chelation (1) was confirmed by n.m.r. studies, the oxinate ion [3] being liberated quantitatively.

$$Pd(oxine)_2(CN)_2 + 2\ HO^- \rightarrow [Pd(oxinate)(CN)_2]^- +$$
$$oxinate + 2\ H_2O \qquad (1)$$

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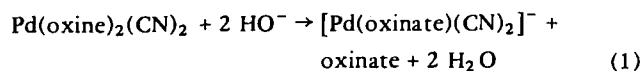
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[Pd(oxinate)(CN)₂]⁻ may be precipitated as its tetra-N-butylammonium salt from the basic solution, with the expected loss of hydrogen bonding due to the free phenolic


[3]

hydroxyl group as shown in the i.r. spectrum. The cyanide stretching frequencies in this complex are at 2138 and 2123 cm⁻¹. The ¹H n.m.r. spectrum of the alkaline reaction mixture is identical with a superimposition of the spectrum of this compound with that of the oxinate anion. Pd(oxine)₂(CN)₂(H₂O)₂, shown in [4], is thus the analogue of Fehling's compound[14]. The molecule has the *cis*-configuration and it has so far proved impossible to synthesise the *trans*-analogue. No evidence of covalent hydration, such as has been shown[15] for Pd(bipy)(CN)₂, in this compound or in [n-Bu₄N] [Pd(oxinate)(CN)₂] could be obtained from the n.m.r. studies.

b) *Pd(dmp)₂(CN)₂(H₂O)₂*

From the n.m.r. spectrum of this compound it is evident that there is no covalent hydration or Reissert-type behaviour present. Only one set of signals is observed for the compound

and this is compatible with the two ligands being in the same environment and also with the two halves of each ligand being chemically and magnetically equivalent.
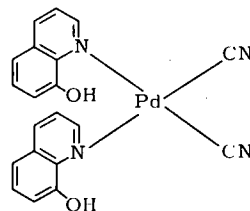
[4]

Plowman and Power[8] have proposed a six-coordinate structure for this compound which is a nonelectrolyte. The CN stretching frequency[8] (2140 cm⁻¹) is not split in the solid state and in MeOH solution the frequency is almost the same, (2130 cm⁻¹), indicating that the cyanide ions are still bonded. Furthermore, there is no evidence for a *cis*-arrangement of the cyanide moieties in the i.r. There will be some steric repulsion in the square plane involving the methyl groups of the ligand and it therefore seems likely that there will be some distortion in the square plane containing the bonding nitrogen atoms. In addition, the two *trans*-Pd-CN bonds must be of the same length in order to maintain the equivalence of the ligand halves.

The fact that water is lost from the molecule only at elevated temperatures with accompanying decomposition[8]

Table 1. ¹H n.m.r data for the palladium(II) complexes

Compound	Solvent	Chemical Shifts[a]
dmp	CDCl₃	H³:d, 7.46; H⁴:d, 8.10; H⁵:s, 7.69; Me:s, 2.92; $J_{3,4}$ = 8.0
dmp	CD₃COCD₃	H³:d, 7.56; H⁴:d, 8.25; H⁵:s, 7.80; Me:s, 2.77; $J_{3,4}$ = 8.6
Pd(dmp)Cl₂	CDCl₃	H³:d, 7.55; H⁴:d, 8.34; H⁵:s, 7.86; Me:s, 3.25; $J_{3,4}$ = 8.4
Pd(dmp)Br₂	CDCl₃	H³:d, 7.62; H⁴:d, 8.37; H⁵:s, 7.90; Me:s, 3.37; $J_{3,4}$ = 9.8
Pd(dmp)I₂	CDCl₃	H³:d, 7.58; H⁴:d, 8.22; H⁵:s, 7.79; Me:s, 3.01; $J_{3,4}$ = 8.0
Pd(dmp)₂Cl₂	CDCl₃	H³:d, 7.57; H⁴:d, 8.38; H⁵:s, 7.91; H⁶:s, 7.79; H⁷:d, 8.22; H⁸:d, 7.63; 2-Me:s, 3.34; 9-Me:s, 3.01; $J_{3,4}$ = 8.0, $J_{7,8}$ = 8.2, $J_{5,6}$ ca. 0
Pd(dmp)₂Br₂	CDCl₃	H³:d, 7.58; H⁴:d, 8.37; H⁵:s, 7.90; H⁶:s, 7.79; H⁷:d, 8.22; H⁸:d, 7.63; 2-Me:s, 3.35; 9-Me:s, 3.01; $J_{3,4}$ = 8.0, $J_{7,8}$ = 8.4, $J_{5,6}$ ca. 0
Pd(dmp)₂(CN)₂(H₂O)₂	CD₃OD	H³:d, 7.98; H⁴:d, 8.76; H⁵:s, 8.14; Me:s, 3.03; $J_{3,4}$ = 8.5
Pd(oxine)₂(CN)₂(H₂O)₂	CD₃OD	H²:d, 8.87; H³:t, 7.73[b]; H⁴:d, 8.55; H⁵:m, 7.23[b]; H⁶:m, 7.58[b]; H⁷:m, 7.16[b]; $J_{2,3}$ = 5.2; $J_{3,4}$ = 9.2; $J_{2,4}$ = 2.0
[n-Bu₄N][Pd(oxinate)(CN)₂]	CDCl₃	H²:d, 8.87; H³:t, 7.38; H⁴:d, 8.24; H⁵:d, 6.94[b]; H⁶:m, 7.31[b], H⁷:m, 6.94[b]; α-CH₂:t, 3.33; β, γ-CH₂:m, 1.52; CH₃:t, 0.94; $J_{2,3}$ = 4.6, $J_{3,4}$ = 8.8, $J_{2,4}$ = 1.8
Oxine	D₂O/NaOD pD = 12	H²:d, 8.66; H³:t, 7.48; H⁴:d, 8.21; H⁵:d, 7.02; H⁶:t, 7.42; H⁷:d, 6.86; $J_{2,3}$ = 4.0; $J_{3,4}$ = 8.0, $J_{2,4}$ = 1.6; $J_{5,6}$ = 8.1; $J_{6,7}$ = 7.6; $J_{5,7}$ ca. 0.5

a) Chemical shift results are given in the order:proton number, splitting pattern and chemical shift (ppm) thus: H⁵:s, 8.14. Coupling constants (Hz), where measured, follow the chemical shifts.

b) Determined from spin decoupling experiments. The ABX spectrum of benzene ring was not analysed further.

(which we have verified by thermogravimetry) and that the water molecules are not covalently bonded to the ligands or to the Pd atom can therefore only be explained by their being involved in a strong hydrogen bond network in the solid state.

c) Pd(dmp)X₂ (X = Cl, Br, I)

The ^{1}H n.m.r. spectra of these compounds gave no unexpected results. For X = Br, I the complexes are fairly insoluble in CDCl₃ so a digital signal analyser was employed to facilitate the recording of their spectra.

For all halide anions, signals corresponding to only one half of a ligand could be observed so that either a mirror plane or a twofold axis is present perpendicular to the long axis of the ligand molecule, for the equilibrium configuration of the molecule in solution. In the solid state, the structure of dinitro(2,9-dimethyl-1,10-phenanthroline)palladium(II)[16] has been determined, showing the expected cis-planar arrangement of the ligand atoms about palladium. However in the solid state, there are some deviations observed from the expected bond lengths and angles which help to accommodate the steric crowding between the methyl groups of the dmp ligand and the nitro groups. The most notable of these distortions are the buckling of the nitrogen-containing rings and the relationship of the least-squares plane containing the palladium and the four bonding nitrogen atoms, and that containing the dmp molecule. These two planes are inclined at an angle of 13°, giving rise to a distortion towards tetrahedral geometry.

However, the net result of the small bond length changes and distortions is to essentially preserve the square-planar arrangement. While for the Pd(dmp)X₂ compounds, the equilibrium position of the molecule in solution gives rise to a chemically and magnetically symmetric ligand, it might also be expected that in the solid state such small distortions would also be evident. It would not be expected however that there would be a significant departure from the normal square-planar configuration either in the solid state or in solution.

d) Pd(dmp)₂X₂ (X = Cl, Br)

It was unfortunately impossible to measure the n.m.r. spectra of Pd(dmp)₂I₂, even with the use of a digital signal analyser, because of the compound's extreme insolubility in nonpolar solvents.

The three possible geometries proposed[7] for these five-coordinate compounds are shown in [5]—[7]. It should be noticed that [5] imposes the most steric strain of the three structures. In [5], none of the four ligand halves are equivalent, and in [6] there are three distinct chemical and magnetic environments for the halves of each ligand. The proposed structure [7] with the halide atom in the trigonal plane gives rise to two environments and indeed there are only two sets of signals observed in the n.m.r. spectra of the compounds.

It has been observed by Plowman and Power[7] that complexes of the type Pd(dmp)₂X₂ are extensively dissociated in solution. Reference to the Table however shows that under the conditions for the n.m.r. measurements of these compounds, no significant dissociation occurs. No signals were observed corresponding to free dmp in CHCl₃ solution, and neither

set of chemical shifts and coupling constants corresponds to the spectra of the compounds Pd(dmp)X₂. The spectra also rule out dissociative equilibria fast on the n.m.r. time scale, and further show no variation with temperature over a range from 0 to 50°.

[5]   [6]   [7]
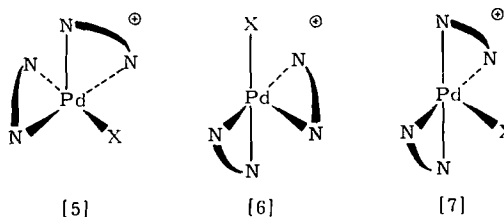
It has been pointed out[17] that because the $d_{x^2-y^2}$ orbital is highly destabilized in Pd^{II} and Pt^{II} complexes having a d⁸ electronic configuration, penta- or hexa-coordination is much less frequent than is the case with Ni(II). These unusual compounds containing two coordinated dmp molecules are however analogous to the trigonalbipyramidal complexes[18,19] of Pd^{II} with phosphorus or arsenic and halide ligands. One notable feature for the chloro- and bromo-compounds of Pd(dmp)₂X₂ is that their n.m.r. spectra are very nearly identical. It should be possible to resolve the compounds into their optical isomers. We are continuing our studies on these compounds with this aim and also to study the reaction ki-kinetics of the halide substitution processes.

Acknowledgement

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