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PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF CIS-1,3-DIAMINOCYCLOHEXANE

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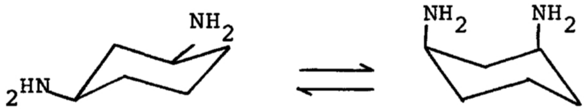
Six palladium(II) and platinum(II) complexes, $[MX_2(1,3\text{-dac})]$ and $[M(1,3\text{-dac})_2]Cl_2$ (M = Pd and Pt, X = Cl^- and Br^-) have newly been prepared (1,3-dac = cis-1,3-diaminocyclohexane). On the basis of the spectroscopic analyses, the structures of the complexes have been elucidated to be square planar. It was reasonably interpreted that interconversion of the ligand to the less stable diaxial conformer was taken place during complexation.

Although many metal complexes of trans-1,2-diaminocyclohexane have been investigated in details, no attention has been paid on the metal coordination of a cis-1,3-diaminocyclohexane(1,3-dac). We found this diamine reacted with several transition metal ions. In this paper, we wish to report the preparation and properties of palladium(II) and platinum(II) complexes of 1,3-dac. This diamine exclusively exists as the diequatorial conformer of a chair form according to cyclohexane stereochemistry. Palladium(II) and Platinum(II) ions have the strong ligand field stabilization energies which are supposed to be large enough to compensate the heat loss of the ligand on the interconversion from the diequatorial(1) to the diaxial(2) conformation. When such transformation may occur, this diamine is able to form metal complexes of six membered ring as a bidentate ligand.



(1) (2)

Ligand : 1,3-dac was prepared from cis-1,3-cyclohexanedicarboxylic acid by the procedure in the literature.$^{1)}$

Preparation of Complexes : To a solution of K_2PdCl_4(1000 mg) in water(10 ml) was added a solution of ligand(400 mg) in water(10 ml). Resultant product(1') was recrystallized from water to give $[PdCl_2(1,3\text{-dac})]$(1) as yellow crystals. Found : C, 24.53 ; H, 4.73 ; H, 9.64 %. Calcd for $C_6H_{14}N_2PdCl_2$: C, 24.72 ; H, 4.84 ; N, 9.61 %. An orange yellow complex, $[PdBr_2(1,3\text{-dac})]$ was prepared by treating an aqueous solution of (1) with KBr. Found : C, 19.25 ; H, 3.84 ; N, 7.58 %. Calcd for $C_6H_{14}N_2PdBr_2$: C, 18.94 ; H, 3.71 ; N, 7.36 %. To the filtrate of the removal of (1'), the excess amount of 1,3-dac was added and the resultant solution was evaporated, yielding nearly colorless crystals, $[Pd(1,3\text{-dac})_2]Cl_2$(3), recrystallized from water. Found : C, 35.37 ; H, 6.95 ; N, 13.70 %. Calcd for $C_{12}H_{28}N_4PdCl_2$: C, 35.13 ; H, 7.00 ; N, 13.65 %.

Crude product of $[PtCl_2(1,3\text{-dac})]$(4') was prepared by a method similar to that for (1'). The complex(4') was suspended in warm water and converted to an aqua complex by adding a $AgNO_3$ solution. Yellow crystallined products $[PtCl_2(1,3\text{-dac})]$(4) and $[PtBr_2(1,3\text{-dac})]$(5) were obtained by treating a solution containing the aqua complex with KCl and KBr, respectively. Found(4) : C, 18.93 ; H, 3.70 ; N, 7.33 %. Calcd for $C_6H_{14}N_2PtCl_2$: C, 18.96 ; H, 3.71 ; N, 7.37 %. Found(5) : C, 15.67 ; H, 3.00 ; N, 5.96 %. Calcd for $C_6H_{14}N_2PtBr_2$: C, 15.36 ; H, 3.01 ; N, 5.97 %. To a solution of the aqua complex derived from (4'), an excess amount of 1,3-dac was added and the resulting solution was passed through the anion exchange resin column in Cl^- form. $[Pt(1,3\text{-dac})_2]Cl_2$ obtained was recrystallized from water to give pale yellow crystals. Found : C, 28.87 ; H, 5.76 ; N. 11.33 %. Calcd for $C_{12}N_{28}N_4PtCl_2$: C, 29.15 ; H, 5.71 ; N, 11.60 %.

Electronic Spectra : Fig. 1 shows the electronic spectra of the $[Pd(1,3\text{-dac})_2]Cl_2$, $[Pt(1,3\text{-dac})_2]Cl_2$ and $[PdCl_2(1,3\text{-dac})]$. The complex of $[Pd(1,3\text{-dac})_2]Cl_2$ has absorption bands at 27 × 10^3 cm^{-1}(shoulder), 34.2 × 10^3 cm^{-1}(log ε = 2.54), and 47.6 × 10^3 cm^{-1}(log ε = 3.83), and $[Pt(1,3\text{-dac})_2]Cl_2$ has absorption band at 34.5 × 10^3 cm^{-1}(log ε = 1.62), and 43 × 10^3 cm^{-1}(shoulder, log ε = 2.4). These spectra resemble those of $[Pd(\ell\text{-chxn})_2]Cl_2$ and $[Pt(\ell\text{-chxn})_2]Cl_2$ (ℓ-chxn = ℓ-1,2-diaminocyclohexane), whose metal ions have D_{4h} symmetry.$^{2)}$

On the other hand, $[PdCl_2(1,3\text{-dac})]$ gives absorption bands at 27.4 × 10^3 cm^{-1}(log ε = 2.47), 37 × 10^3 cm^{-1}(shoulder), and 44.4 × 10^3 cm^{-1}(log ε = 4.22). The spectrum is also similar to that of $[PdCl_2(\ell\text{-pn})]$.$^{1)}$ The higher frequency peak having log ε larger than 3 may be considered charge transfer band. The $[MX_2(1,3\text{-dac})]$ type complexes except for $[PdCl_2(1,3\text{-dac})]$ were sparingly soluble in water, therefore, their absorption spectra could not be measured. The reflectance spectra of those complexes in the visible region exhibit a band at 25.0–26.5 × 10^3 cm^{-1}, which corresponds to the band at 27.4 × 10^3 cm^{-1} in the absorption spectrum of $[PdCl_2(1,3\text{-dac})]$. From these spectral data, we can conclude that Pd(II) and Pt(II) ions have a square planar coordination either by four nitrogen or by two nitrogen and two halogen atoms.

Infrared spectra : The infrared spectra of the present complexes were measured in the region of 200–4000 cm^{-1}. The representative peaks observed are summarized in Table 1. A conformational structure of the ligands can be identified by one or two bands located in the region between 770 to 830 cm^{-1}. They are tentatively assigned to the methylene rocking vibration in the axial position.$^{3)}$ No bands in the region of 550–840 cm^{-1} had been observed in the spectrum of 1,3-dac dihydrochloride, similarly to those of trans-1,2-dac and its metal complexes. Therefore, it is understood that the diequatorial confor-

Table 1 Main bands in the infrared spectra of the complexes

Complexes	ν_{NH}	δ_{NH_2}	ρ_{rNH_2}	ρ_{rCH_2}	ν_{MX}
$[PdCl_2(1,3\text{-dac})]$	3290, 3230, 3160	1592	755, 745	777	323
$[PdBr_2(1,3\text{-dac})]$	3280, 3220, 3150	1587	738, 705	774	239
$[Pd(1,3\text{-dac})_2]Cl_2$	3180, 3070	1592	747	812, 787	-
$[PtCl_2(1,3\text{-dac})]$	3270, 3210, 3140	1588	761, 751	780	315
$[PtBr_2(1,3\text{-dac})]$	3260, 3210, 3140	1583	759, 745	776	230sh
$[Pt(1,3\text{-dac})_2]Cl_2$	3200, 3080	1597	771	816, 806	-

mation of the ligand changed to the diaxial one during complexation.

The stretching, bending and rocking vibration of the NH_2 group were assigned by the comparison with those of ethylenediamine complexes[4)] and by deuteration studies. The δ_{NH_2} and ρ_{rNH_2} bands of $[MBr_2(1,3\text{-dac})]$ appear in the lower frequency region than those of $[MCl_2(1,3\text{-dac})]$. These shifts may occur due to the trans effect of X atoms. Assignment of the M-N stretching modes are difficult, because the spectrum of the ligand has four peaks in the region of 400–550 cm^{-1} which are assumed to shift by the axial-equatorial transformation.

PMR spectra : The 100 MHz PMR spectra of the ligand dihydrochloride and the bisdiamine complexes in D_2O were measured using DSS as an internal reference.

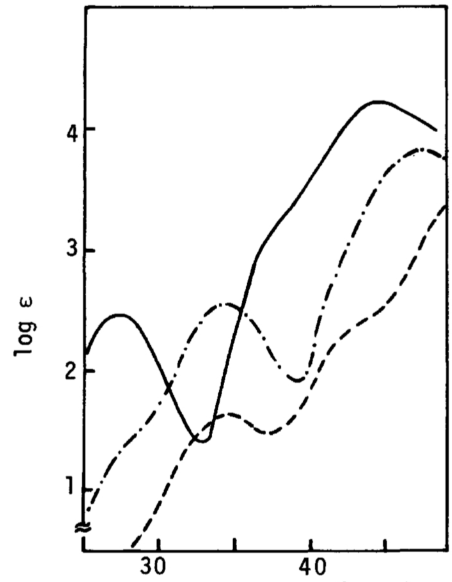


Fig. 1. The electronic spectra of
$[Pd(1,3\text{-dac})_2]Cl_2$ in 0.2 M KCl (–·–)
$[Pt(1,3\text{-dac})_2]Cl_2$ in 0.2 M KCl (– –)
$[PdCl_2(1,3\text{-dac})]$ in 0.2 M KCl (——)

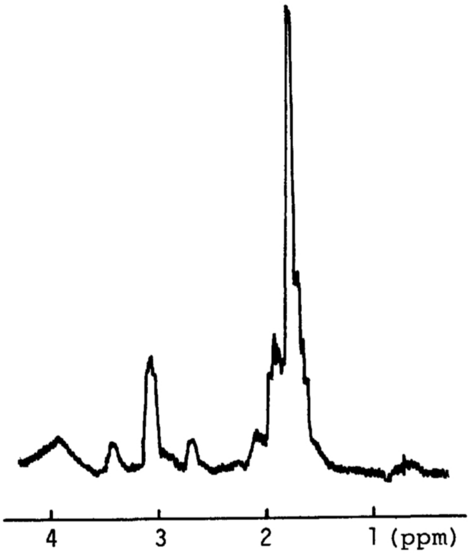


Fig. 2. The PMR spectra of $[Pt(1,3\text{-dac})_2]Cl_2$.

Fig. 2 shows the spectrum of $[Pt(1,3\text{-dac})_2]Cl_2$. This complex gives a multiplet of the methylene groups (which has a very small $W_{\frac{1}{2}}$ value relative to the 1,3-dac·2HCl), corresponding about 7 protons, and a broad methine triplet ascribable to platinum-proton coupling (J = 37 Hz), and then an additional peak corresponding about one proton. The feature of the resonance of the methylene protons suggests that the diaxial conformation of the ligand. The spectrum of $[Pd(1,3\text{-dac})_2]Cl_2$ was almost identical with that of the Pt(II) complex except for a methine proton signal without splitting. Unlike the trimethylenediamine complexes$^{5)}$, two possible forms, a chair and a boat, might be expected for the conformation of the chelate ring of these complexes. The metal ion, two nitrogen atoms and the C_2 atom can not lie coplanar on account of the steric restriction caused by the cyclohexane ring. When a chair or a boat conformation may be assumed, the molecular models show H_{5a} or H_{2e} proton exists closely to the metal ion. Although no evidence about the prefered conformation was obtained, the downfield shift of one proton might be ascribable to either H_{5a} or H_{2e}. Further details are now in progress.

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