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A New Type of Linkage Isomerism: Bis(acetylacetonato-O)bis(piperidine)platinum(II) and (Acetylacetonato-O,O′)bis(piperidine)platinum(II) Acetylacetonate

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The palladium(II) chelates of β-dicarbonyl compounds (β-dikH) such as acetylacetone(acacH) [1] and ethyl acetoacetate [2] react with various kinds of Lewis bases (L) to afford [Pd(β-dik-O,O′)(β-dik-C)L] and [Pd(β-dik-C)$_2$L$_2$] which contain the central-carbon bonded β-dicarbonyl ligand. Similar reactions have also been extended to [Pt(acac)$_2$] [3]. If an excess amount of amine is employed, however, the β-dik ligand is displaced to form [Pd(β-dik)L$_2$](β-dik) or [PdL$_4$](β-dik)$_2$ depending upon whether L is a secondary or a primary amine, respectively [4]. As an extension of these studies the reaction of [Pt(acac)$_2$] with piperidine (pip) has been examined and two isomeric products with the composition of Pt(acac)$_2$(pip)$_2$ have been isolated.

[Pt(acac)$_2$] (306 mg, 0.78 mmol) was placed in piperidine (519 mg, 6.1 mmol) and stirred at 70 °C for 15 min. The complex was dissolved gradually to produce a new white precipitate (**1**), which was filtered off and washed with benzene followed by dichloromethane. The yield was 86 mg (20%). Compound **1** is hardly soluble in usual solvents such as benzene, chloroform, methanol and dimethylsulfoxide, but can be recrystallized from a mixture (1:1 by volume) of chloroform and methanol. *Anal.* Found: C, 42.45; H, 6.53; N, 4.70%. M.p. 150 °C (dec). Calcd for Pt(acac)$_2$(pip)$_2$, $C_{20}H_{36}N_2O_4Pt$: C, 42.62; H, 6.44; N, 4.97%.

The filtrate was concentrated by evaporating at 50–60 °C under reduced pressure to result in a pale yellow oil, which, on standing in the atmosphere, crystallized in plates. The solid mass was washed several times with small portions of n-hexane to obtain a white powder (329 mg) in a 75% yield, which is soluble in various solvents such as benzene, dichloromethane, diethyl ether and acetone. Although recrystallization from n-hexane gave the monohydrate as white needles, an acetone solution produced anhydrous crystals **2**. *Anal.* Found for the monohydrate: C, 41.32; H, 6.49; N, 4.56%. M.p. 69–70 °C. Calcd for Pt(acac)$_2$(pip)$_2$·H$_2$O, $C_{20}H_{38}N_2O_5Pt$: C, 41.30; H, 6.50; N, 4.82%. Found for **2**: C, 42.68; H, 6.50; N, 4.92%. M.p. 169 °C (dec).

The ^{1}H NMR spectrum of compound **1** shown in Fig. 1. is quite similar to that of *trans*-[Pt(acac-O)$_2$(PEt$_3$)$_2$] which was prepared by Ito, *et al.* [5], and is reasonably interpreted by the proposed structure, [Pt(acac-O)$_2$(pip)$_2$]. Although the methine protons resonate as a single peak at 6.90 ppm flanked by the ^{195}Pt satellites (^{4}J(Pt-H) = 12 Hz), the methyl protons exhibit two signals at 2.32 ppm (^{4}J(Pt-H) = *ca.* 5 Hz) and 2.13 ppm. The lower-field signal carrying satellites is assigned to the CH$_3$(a) near the metal and

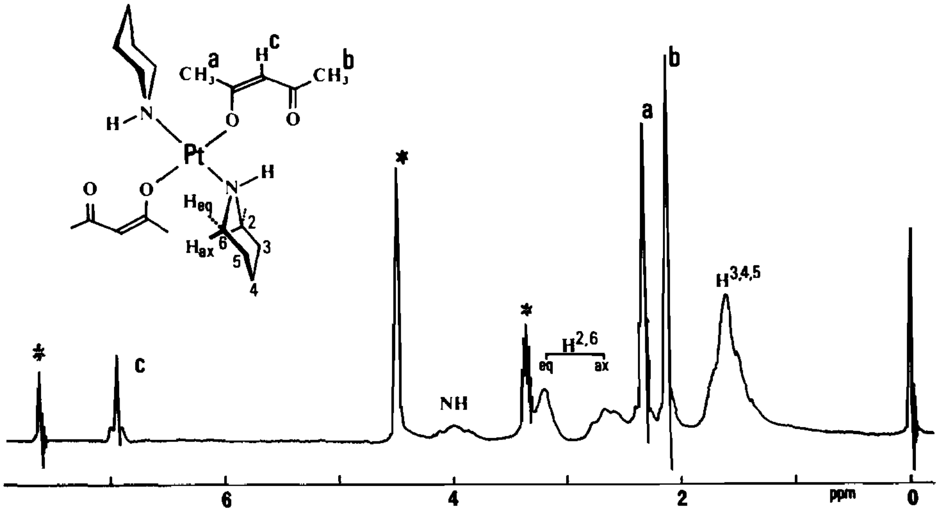

Figure 1. The proposed structure and the ^{1}H NMR spectrum of [Pt(acac-O)$_2$(pip)$_2$] (**1**) in CDCl$_3$ + CD$_3$OD (1:1 by volume) at 100 MHz with internal TMS. The asterisks denote the peaks due to solvent impurities.

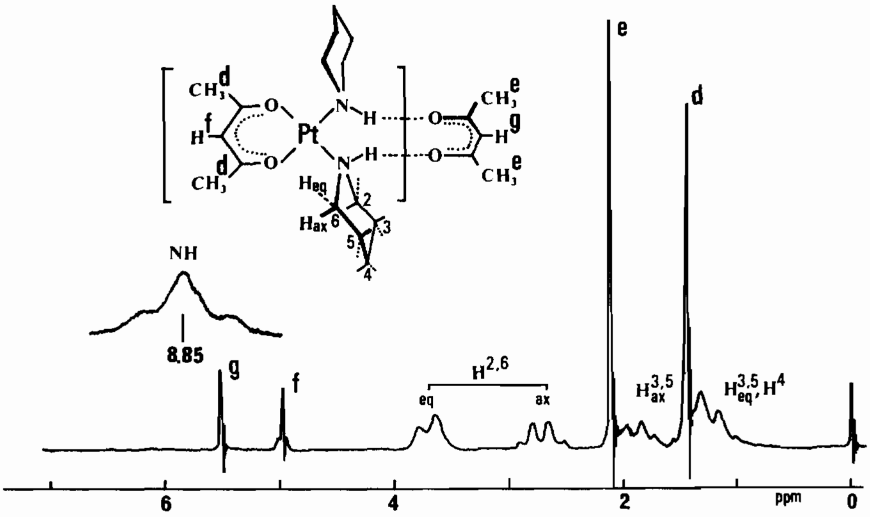

Figure 2. The proposed structure and the ^{1}H NMR spectrum of [Pt(acac-O,O')(pip)$_2$](acac) (2) in C_6D_6 at 100 MHz with internal TMS. The NH signal is magnified ten times in intensity.

the higher-field one to the remote CH$_3$(b). In the present case it is certain that the compound exists exclusively as one geometrical isomer in solution and the *trans* configuration around the metal atom as shown in Fig. 1 is presumed in analogy with the phosphine complex [5]. As to the geometrical structure of the unidentate acac ligand, absence of coupling between CH$_3$(a) and CH suggests the *cis* configuration around the C=C bond [6]).

The IR spectrum of 1 in Nujol exhibits the following characteristic bands: ν(N–H), 3170vs; ν(C=O), 1621vs; ν(C=C), 1583w; ν(C–O), 1165vs cm^{-1}. The frequency of the ν(C=O) band is *ca.* 30 cm^{-1} lower than that for [Pt(acac-O)$_2$(PEt$_3$)$_2$] [5], and might be caused by hydrogen-bonding with the piperidine NH,

In the ^{1}H NMR spectrum of compound 2 (Fig. 2) both the methyl and methine protons exhibit two signals, one set accompanying ^{195}Pt satellites and the other not. Thus the peaks at 1.44 ppm (6 H, ^{4}J(Pt-H) = *ca.* 3 Hz) and at 4.97 ppm (1 H, J(Pt-H) = 8 Hz) are assigned to the methyls and methine of the coordinated acac anion, respectively, and the peaks at 2.12 ppm (6 H) and 5.52 ppm (1 H) without satellites to those of acac in the outer-sphere. The assignment of the piperidine protons was made by reference to the literature [7].

The IR spectrum of 2 shows five bands in the ν(C=O) region, three at 1570vs, 1550s and 1525vs cm^{-1} being ascribed to the chelated acac and the other two at 1610vs and 1503vs cm^{-1} to the acac in the outer sphere. The frequency of the broad ν(N–H) band is remarkably low (3057 cm^{-1}), probably because of the positive charge of the complex and strong hydrogen-bonding with the carbonyl oxygens. In fact X-ray analysis of [Pd(acac-O,O'(Et$_2$NH)$_2$](acac) now in progress [8] confirms the interaction between the NH group and the carbonyl oxygen in the outer sphere. The large chemical shift (8.85 ppm) of the amine proton in 2 may suggest retention of the hydrogen bond even in solution.

Complex 2 is very stable and shows no change on heating in benzene under reflux for 10 h, whereas compound 1 decomposes gradually when heated in a CHCl$_3$–CH$_3$OH solution. Thus compounds 1 and 2 constitute a couple of isomers although the interconversion between each other has not been realized. In a previous paper we reported couples of linkage isomers containing O,O'-chelated and tri*hapto* acac ligands [9]. The present couple demonstrates another novel type of linkage isomerism concerning the acetylacetonate ligand.

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