Infrared Spectra and Structure of Acetylacetonatoplatinum(II) Complexes. III.   Infrared Spectra of Acetylacetonatoplatinum(II) Complexes Containing O-Bonded (Chelated) and C-Bonded Acetylacetones[1,2]

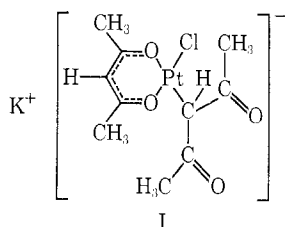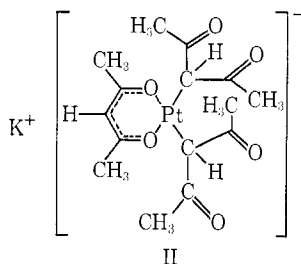By GEORGE T. BEHNKE[3] and KAZUO NAKAMOTO

Two acetylacetonatoplatinum(II) complexes containing both the O-bonded (chelated) and C-bonded acetylacetones have been prepared, and their infrared spectra (4000–200 cm^{-1}) have been interpreted based on the results of previous normal coordinate analyses on the O-chelated and C-bonded acetylacetonatoplatinum(II) complexes. It has been found that the spectra of these mixed-ligand complexes can be interpreted as a superposition of the spectra of the O-chelated and the C-bonded acetylacetonatoplatinum(II) complexes. Possible configurations of acetylacetonate ligands in these complexes have been discussed.

Introduction

In the previous papers of this series, we have reported the infrared spectra of acetylacetonatoplatinum(II) complexes containing oxygen-bonded (chelated) acetylacetone[4] and carbon-bonded acetylacetone[5] and have carried out normal coordinate analyses on these structures in order to make theoretical band assignments as well as to determine their force constants. Several acetylacetonatoplatinum(II) complexes are known in which both types of metal–ligand bonding are found. A complex of the composition K[Pt(acac)$_2$Cl] originally described by Werner[6] was the subject of a recent X-ray analysis[7] which reported the structure

I

A complex of the composition K[Pt(acac)$_3$] was recently described by Lewis, *et al.*,[8] who suggested the following structure on the basis of nmr and infrared spectroscopic evidence.

II

No detailed discussion of the infrared spectra of these structures is yet available.

The purpose of this paper is to suggest a method of interpretation of these spectra based on the results obtained in our previous normal coordinate analyses and the band shifts caused by deuterium substitution of the ligand hydrogens. Using this technique the band assignments are transferred in detail from the simpler moieties including the contributions due to vibrational coupling. Shifts in frequency of some bands are noted and the presence of new bands is used to discuss the configuration of the ligands in these two mixed-ligand complexes. Of particular importance is the assignment of symmetric and antisymmetric platinum–carbon stretching frequencies for the *cis* structure of compound II, as an added confirmation of our previous assignment. The shifts of coordinate bond stretching frequencies among the series of compounds may be interpreted in terms of the relative *trans* effects and again serves to confirm the assignments of these bands.

Experimental Section

Preparation of Compounds.—Potassium chloro(acetylacetonato)(γ-acetylacetonato)platinum(II) was isolated from the mother liquor of the preparation of potassium dichloro(acetylacetonato)platinate(II) which when allowed to stand for 8–16 hr in a desiccator under nitrogen over P$_2$O$_5$ gave canary yellow crystals of indeterminate crystalline form. A somewhat improved yield of more highly purified product was obtained by a slight modification of this procedure in which the dichloro complex separation is avoided. Potassium chloroplatinate (1.0 g, 2.4 mmol) was dissolved in 3.0 ml of water and the solution was heated to 80°. Acetylacetone (2.25 ml) and 3.6 ml of potassium hydroxide (1:3 by weight) were added in that order. The solution was placed in a desiccator over P$_2$O$_5$ and allowed to crystallize slowly. The product was isolated by filtration at hourly intervals, with the first product being highest in purity. Succeeding crops of the canary yellow product became successively darker as presumably polymeric acetylacetone condensation products became important contaminants. The crystals were washed in a very small volume of ether and dried under vacuum. The yield varied somewhat under these conditions but was not lower than 50% based on the potassium chloroplatinate used. Recrystallization was done from water. *Anal.* Calcd for C$_{10}$H$_{14}$O$_4$ClPtK: C, 25.67; H, 3.02; Cl, 7.57. Found: C, 25.52; H, 3.05; Cl, 7.38.

Potassium chloro(acetylacetonato-*d$_1$*)(γ-acetylacetonato-*d$_1$*)-

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(2) Submitted by G. T. B. to the faculty of Illinois Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Supported by a NASA fellowship during this investigation.

(4) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(5) G. T. Behnke and K. Nakamoto, *ibid.*, **6**, 440 (1967).

(6) A. Werner, *Ber.*, **34**, 2584 (1901).

(7) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, **195**, 1278 (1962).

(8) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

platinum(II) was prepared using the second technique described previously and substituting D_2O for the solvent. Acetylacetone deuterated at the γ-carbon was used as the ligand. Crystal formation was induced by evacuating the desiccator and by more rapid cooling of the solution in order to prevent deuteration of the ligand from occurring. Only the first crop of canary yellow product was adjudged suitable for use for this reason.

Potassium chloro(acetylacetonato-d_7)(γ-acetylacetonato-d_7)-platinum(II) was prepared as described previously using D_2O as the solvent and completely deuterated acetylacetone.[4] In this case, all of the several subsequent crops of crystals were used.

The degree of deuteration of the ligands was confirmed by nmr spectra.

Potassium acetylacetonatobis(γ-acetylacetonato)platinum(II) was prepared by dissolving 2.0 g (3.35 mmole) of potassium tetrabromoplatinate in 3.0 ml of water. Acetylacetone (5.0 ml) and 5.0 ml of potassium hydroxide (1:3 by weight) were added and the reaction mixture was heated and shaken for 2 hr at 70°. A green crystalline mass began to form in the course of the reaction and the large excess of acetylacetone was maintained by small additions over the course of this time. After cooling, the crystalline material was separated by filtration and washed with a small volume of alcohol and several large volumes of ether. Recrystallization was from water. A portion of the product was ignited, and a solution of the residue tested for bromide ion gave a negative test.

Spectral Measurements.—A Beckman IR-12 double-beam infrared spectrophotometer was used to obtain the spectra from 4000 to 650 cm^{-1}. The KBr-disk method was employed in this region. The spectra between 700 and 200 cm^{-1} were measured with a Beckman Model IR-7 infrared spectrophotometer equipped with CsI optics. For these spectra the Nujol-mull technique and CsI plates were used, as well as polyethylene pellets. The spectra between 300 and 70 cm^{-1} were measured with a Beckman IR-11 far-infrared spectrophotometer. For these spectra polyethylene pellets[4] were used. Calibration of frequency readings was made with polystyrene film, 1,2,4-trichlorobenzene, and water vapor.

Results and Discussion

Potassium Chloroacetylacetonato(γ-acetylacetonato)-platinum(II), K[Pt(acac)$_2$Cl] (I).—Figure 1 illustrates the infrared spectra of K[Pt(acac)$_2$Cl] (I) together with those of K[Pt(acac)Cl$_2$] and Na$_2$[Pt(acac)$_2$Cl$_2$]·2H$_2$O which have been shown[4,5] to have structures III and IV, respectively. For convenience, the O-bonded
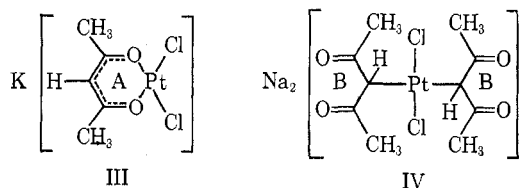
(chelated) acetylacetonato ring in III and the C-bonded acetylacetonate skeleton in IV are called A and B, respectively. Since compound I contains one A and one B, it is anticipated that its spectrum is approximately the superposition of the spectra of compounds III and IV. In fact, Figure 1 and Table I show this to be the case; namely, most bands observed for I can be attributed to the characteristic bands of either A or B on an empirical basis. In some cases, it is rather difficult to assign the bands unequivocally since the bands due to A and B are too closely located. We have, therefore, prepared the deuterio analogs of I: d_2 (both of the γ hydrogens are deuterated) and d_{14} (all of the hydrogens are deuterated). Figure 2 illustrates the infrared spec-
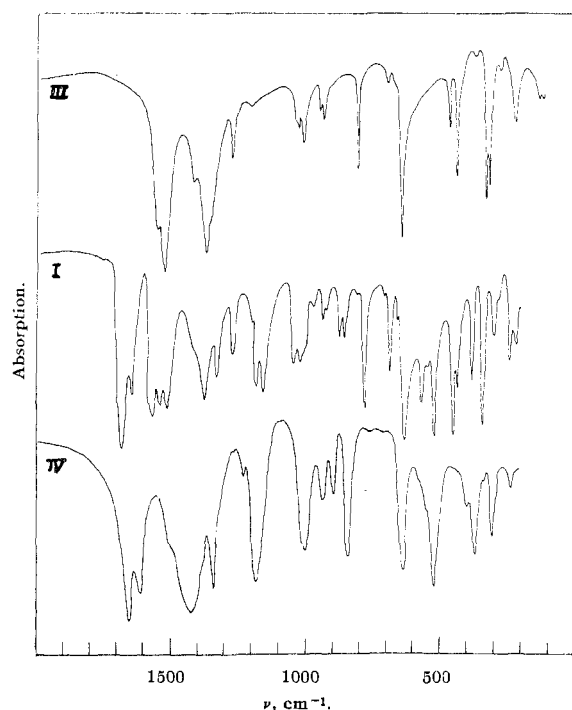

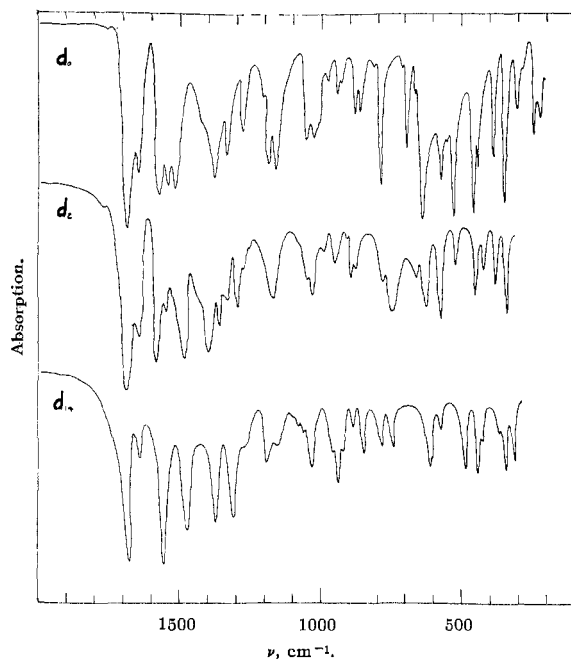Figure 1.—Infrared spectra of K[Pt(acac)Cl$_2$] (III), K[Pt(acac)$_2$-Cl] (I), and Na$_2$[Pt(acac)$_2$Cl$_2$]·2H$_2$O (IV).

Figure 2.—Infrared spectra of K[Pt(acac)$_2$Cl]-d_0, K[Pt(acac-d_1)$_2$Cl]-d_2, and K[Pt(acac-d_7)$_2$Cl]-d_{14}.

tra of the three isotopic species of I below 1800 cm^{-1}. It is seen that the complex spectra of d_0 and d_2 compounds in the region between 1700 and 1200 cm^{-1} are greatly simplified in the d_{14} compound, since all of the CH$_3$ group vibrations in this region are shifted to lower frequencies. Table II lists the observed frequencies for the three isotopic species of I. The band assignments listed in the last column of Table I were obtained based on those of III and IV together with the present deuteration experiments.

Table I

Comparison of Observed Frequencies for Potassium Chloroacetylacetonato(γ-acetylacetonato)platinate (I), Potassium Dichloro(acetylacetonato)platinate (III), Sodium Dichlorobis(γ-acetylacetonato)platinate (IV), and Potassium Bis(γ-acetylacetonato)(acetylacetonate)platinum (II), in Cm^{-1a}

	I	III	IV	II	Assignment
ν_1	1686 s		1652 s	1681 s	$\nu(C{=}O)$
ν_2	1645 m		1626 s	1652 m	$\nu(C{=}O)$
				1644 m	$\nu(C{=}O\cdots Pt)$?
ν_3	1567 s	1563 s		1568 s	$\nu(C{\doteq}O)$
ν_4	1542 w			1543 w	Combination?
ν_5	1519 s	1538 s		1519 s	$\nu(C{\doteq}C) + \delta(C{-}H)$
ν_6	1417 sh	1429 m	1465 sh	1417 sh	$\delta_d(CH_3)$
ν_7	1384 s	1380 s		1388 s	$\nu(C{\doteq}O)$
ν_8	1358 sh	1363 sh	1433 s	1353 m	$\delta_s(CH_3)$
ν_9	1333 m		1350 s	1334 m	$\nu(C{-}C) + \delta(C{-}CH_3)$
ν_{10}	1275 m	1288 m		1275 m	$\nu(C{\doteq}C)$
ν_{11}	1200 w	1212 w		1236 m	$\delta(C{-}H)$
ν_{12}	1182 s		1193 s	1194 sh	$\nu(C{-}C)$
ν_{13}	1166 s		1193 s	1182 s	$\delta(Pt{-}C{-}H) + \nu(C{-}CH_3)$
				1165 sh	
ν_{14}	1038 m	1033 m		1038 m	$\rho_r(CH_3)$
ν_{15}	1020 m	1018 m	1024 m	1020 m	$\rho_r(CH_3)$
ν_{16}	1005 m		1007 m	1008 m	$\rho_r(CH_3)$
ν_{17}	968 m	952 m		965 m	$\nu(C{-}CH_3)$
ν_{18}	930 m	941 m		965 m	$\nu(C{-}CH_3)$
ν_{19}	927 m		948 m	928 m	$\nu(C{-}CH_3)$
ν_{20}	875 s		901 m	877 m	$\nu(C{-}CH_3)$
ν_{21}	858 m		852 s	862 m	$\delta(C{-}C{-}C) + \nu(C{-}C) + \nu(C{-}CH_3)$
ν_{22}	773 m	817 s		772 s	$\pi(C{-}H)$
ν_{23}	678 w	703 w		677 w	$\nu(Pt{-}O) + \nu(C{-}CH_3) +$ ring def
ν_{24}	658 m		652 s	657 sh	$\delta(C{=}O) + \nu(Pt{-}C) + \nu(C{-}CH_3)$
ν_{25}	636 s	650 s		633 s	$\nu(Pt{-}O)$
				619 sh	
ν_{26}	568 s		567 w	565 m	$\nu(Pt{-}C)$
				542 m	$\nu(Pt{-}C)$
ν_{27}	523 s		537 s	523 s	$\delta(C{-}CH_3)$
ν_{28}	454	478 s		453 s	$\nu(Pt{-}O)$
ν_{29}	435 m	448 m	443 w	433 m	Ring def
				414 w	$\delta(C{=}O)$
ν_{30}	382 s		384 w	382 s	$\delta(C{=}O)$
ν_{31}	345 m	345 s	327 m		$\nu(Pt{-}Cl)$
		327 s			$\nu(Pt{-}Cl)$
ν_{32}	306 w		318 sh	344 w	$\delta(C{-}CH_3) + \delta(C{=}O)$
				298 m	
ν_{33}	278 w	283 w		285 w	$\delta(C{-}CH_3)$
ν_{34}	238 m	228 m	250 m	248 s	Ring def
				237 w	
ν_{35}	217 m		211 m	214 m	$\rho_t(Pt{-}CH)$

^{a} ν, stretching; δ, bending; δ_d, degenerate bending; δ_s, symmetric bending; ρ_r, rocking; ρ_t, twisting; π, out-of-plane bending. Intensity designations: s, strong; w, weak; m, medium; sh, shoulder. Compound I exhibits the following bands below 200 cm^{-1}: 157 m, 148 m, 127 m, 112 w, 93 m, 90 m, 80 m, 77 sh, 57 m, 38 m, 36 m. Bands are listed in decreasing order of frequency.

The high-frequency carbonyl modes of I at 1686 (ν_1) and 1645 (ν_2) cm^{-1} are at somewhat higher frequency than the 1652- and 1626-cm^{-1} bands of B and are most characteristic of the presence of uncomplexed carbonyl oxygens and the attendant higher bond order. These carbonyl modes are not significantly sensitive to deuterium substitution. The carbonyl modes of moiety A are assigned at 1567 and 1384 cm^{-1}, consistent with their lower bond order upon chelation. At 1519 cm^{-1} (ν_5) the C$\doteq$C stretching coupled with δ(C–H) of A may be assigned as a consequence of its deuterium sensitivity. The shift from 1519 to 1482 cm^{-1} upon deuterium substitution at the γ-carbon may be compared with the shift of 38 cm^{-1} observed for the same deuterium substitution in compound III.[4] This separation of the carbonyl and carbon–carbon stretching

modes upon deuterium substitution is highly characteristic of bidentate oxygen-bonded acetylacetone regardless of the over-all symmetry of the complex. It is observed clearly even in the hydrogen-bonded enol form of acetylacetone itself.[9] The nature of a weak band at 1542 cm^{-1} is not clear. It may be an overtone or combination band or a perturbed C$\doteq$O stretching, as discussed later. It is not observed in either III or IV.

The degenerate and symmetric deformations of the methyl groups which were previously assigned[4,5] from group frequency tables for III and IV are again expected to conform well with this classification. Consequently, the overlap expected for these modes results in the observation of only two bands. The degenerate

(9) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1963).

TABLE II

OBSERVED FREQUENCIES OF POTASSIUM
CHLORO(ACETYLACETONATO)(γ-ACETYLACETONATO)-
PLATINATE(II) AND TWO OF ITS DEUTERIO ANALOGS (CM^{-1})^a

	Non-deuterated compound	d_2 compound	d_{14} compound		Non-deuterated compound	d_2 compound	d_{14} compound
ν_1	1686	1685	1685	ν_{18}	930	888	884
ν_2	1645	1642	1642	ν_{19}	927	907	
ν_3	1567	1563	1548	ν_{20}	875	772	768
ν_4	1542	1520	...	ν_{21}	858	752	732
ν_5	1519	1482	1480	ν_{22}	773	581	575
ν_6	1417	1415	1055	ν_{23}	678	667	602
ν_7	1384	1383	1387	ν_{24}	658	635	595
ν_8	1358	1362	1025	ν_{25}	636		
ν_9	1333	1342	1307	ν_{26}	568	522	569
ν_{10}	1275	1273	1239	ν_{27}	523	511	474
ν_{11}	1200	872	Not obsd	ν_{28}	454	450	435
				ν_{29}	435	429	425
ν_{12}	1182	1167	1173	ν_{30}	382	375	
ν_{13}	1166	987	...	ν_{31}	345	344	344
ν_{14}	1038	1038	950	ν_{32}	306	302	302
ν_{15}	1020	1026	942	ν_{33}	278	277	277
ν_{16}	1005	1000	932	ν_{34}	238	238	230
ν_{17}	968	942	912	ν_{35}	217	...	...

^{a} Bands are listed in decreasing order of frequency.

CH$_3$ deformation (ν_6) is assigned at 1417 cm^{-1}, shifting to 1055 cm^{-1} upon methyl deuteration, and the symmetric CH$_3$ deformation (ν_8) at 1358 cm^{-1} similarly shifts to 1025 cm^{-1} in the completely deuterated compound. The lower frequency carbon–carbon stretching modes of moiety B are found at 1333 (ν_9) and 1182 cm^{-1} (ν_{12}). The 1333-cm^{-1} band being sensitive to methyl group deuteration indicates that it is coupled with the C–CH$_3$ bending in a ratio similar to that found for IV. It is interesting to note that the band at 1193 cm^{-1} of compound IV which was previously shown[5] to be an overlap of two bands is now split into two bands at 1182 and 1166 cm^{-1} in compound I. Two bands in the 1200–1100-cm^{-1} region exhibit very large shifts upon deuteration at the γ-carbon, and on this basis the weak band at 1200 cm^{-1} (ν_{11}) is assigned to the in-plane C–H bending of moiety A, while that at 1166 cm^{-1} (ν_{13}) is attributed to Pt–C–H bending coupled with C–CH$_3$ stretching of moiety B. Upon deuterium substitution of the γ-hydrogens, they shift to 872 and 987 cm^{-1}, respectively.

Three bands at 1038 (ν_{14}), 1020 (ν_{15}), and 1005 cm^{-1} (ν_{16}) are attributed to the methyl group rocking modes. Evidently these modes are found partially overlapped for each of the two types of acetylacetone. While they are only slightly sensitive to deuteration at the γ-carbon, they are shifted to 950, 942, and 932 cm^{-1}, respectively, when the methyl groups are deuterated. The C–CH$_3$ stretching modes of the two moieties occur in the same region, but since the hybridization of the skeletal carbon is quite different for each, it is possible to distinguish clearly the four bands due to these vibrations. The higher frequency bands at 968 (ν_{17}) and 930 cm^{-1} (ν_{18}) are ascribed to the delocalized ring structure of moiety A, while those at 927 (ν_{19}) and 875 cm^{-1} (ν_{20}) are due to B. All of these bands are sensitive to deuterium substitution on both methyl positions and at the γ-carbon. The band at 858 cm^{-1} (ν_{21}) is due to the bending of the skeletal framework of B but

is coupled with carbon–carbon stretching, both skeletal and involving the methyl group. The out-of-plane bending of γ-hydrogen is observed at 773 cm^{-1} (ν_{22}), a considerable shift from the 817 cm^{-1} of A. Since these spectra are taken in the solid state, this shift may be due to crystal lattice interaction. The disappearance of this band remains a sensitive indicator of the completeness of deuteration of this γ-hydrogen of ring A.

In the coordinate bond stretching region may be found several bands in addition to other bending modes. Among these are the strong band at 658 cm^{-1} (ν_{24}), which, due to vibrational coupling, is assigned to δ(C=O) + ν(Pt—C) + ν(C—CH$_3$) of moiety B and to δ(C—CH$_3$) at 523 cm^{-1}. The δ(C=O) bending mode is observed at 382 cm^{-1} (ν_{30}), consistent with the analogous band of moiety B. Moiety A is responsible for the ring deformation at 435 cm^{-1} (ν_{29}). It is to be expected that upon the reduction in symmetry in this compound due to the influence of carbon-bonded acetylacetone, changes might be expected to occur in the coordinate bond stretching region. In comparison to chloride, the *trans*-directing influence of the carbon-bonded ligand (B) is expected to be much greater and could effect changes *via* this mechanism in the bond order of the coordinate bond *trans* to it. The nature of vibrational frequency changes due to this mechanism should result in the lowering of the bond order of one coordinated bond, consequently increasing the separation between the two platinum–oxygen stretching frequencies. This, in fact, is observed for the ν(Pt–O) stretching frequencies at 636 (ν_{25}) and at 454 cm^{-1} (ν_{28}), each of which is found at lower frequencies than the corresponding 650- and 478-cm^{-1} bands of the more symmetrical compound III.[4] In addition, the weak band at 678 cm^{-1} (ν_{23}), by analogy with the 703-cm^{-1} band of A which contains a significant contribution of Pt–O stretching, has also been similarly lowered in frequency. The Pt–C stretching frequency of 568 cm^{-1} (ν_{26}) is in contrast to the Pt–O stretching frequency not found to be significantly lowered by comparison with the 567-cm^{-1} band of moiety B. The same *trans*-directing mechanism should, of course, be operative in this case. The significant difference between these two cases lies, however, in the presence of some delocalization in the Pt–O bonds and about the chelate ring. Thus the Pt–O bonds when contrasted with the strictly σ-bonded Pt–C bond, as deduced from the similar frequencies of methyl- and carbon-bonded acetylacetone, have more mobile electrons. On this basis, the frequency shifts of these coordinate stretching bands may be interpreted without regard for changes in vibrational coupling, which cannot, of course, be assessed without a more complete theoretical treatment of the entire molecule. The Pt–Cl stretching frequency of 345 cm^{-1} (ν_{31}) is similar to those found in both III and IV.

A weak band at 306 cm^{-1} (ν_{32}) is assigned to δ(C–CH$_3$) of moiety B, which is observed at 318 cm^{-1} in IV. The corresponding bending frequency of moiety A is observed at 278 cm^{-1} (ν_{33}), closely approximating

the 283-cm^{-1} band of compound III. Each of these weak bands must be considered to be the overlap of two closely spaced bands which have not been separated because of the absence of a mechanism through which vibrational interaction can be transmitted. A ring deformation is observed at 238 cm^{-1} (ν_{34}), and ρ_t(Pt–CH) of moiety B is found at 217 cm^{-1} (ν_{35}). Table I also lists the observed frequencies of compound I below 200 cm^{-1}. It is not possible to assign these bands due to the limitations of this method of interpretation discussed above.

Potassium Bis(γ-acetylacetonato)(acetylacetonato)-platinum (II), K[Pt(acac)$_3$] (II).—As is shown in Table I, the infrared spectrum of K[Pt(acac)$_3$] is essentially the same as that of K[Pt(acac)$_2$Cl] in the high-frequency region. Figure 3 compares the spectra of these two compounds in the low-frequency region. It is seen that the Pt–C stretching band which is found at 567 cm^{-1} in IV and at 568 cm^{-1} in I is now split into two bands at 565 and 542 cm^{-1} (antisymmetric and symmetric Pt–C stretching). The separation observed here of 23 cm^{-1} is larger than that observed for the antisymmetric and symmetric Pt–Cl stretching bands (12 cm^{-1}), but is much smaller than that observed for the Pt–O stretching bands of III (72 cm^{-1}). The presumed partial double-bond character of the Pt–O bonds is mainly responsible for this large separation, owing to the stronger interactions occurring in delocalized systems. This result also infers that the Pt–C bonds in I, II, and IV have mainly σ-bond character.
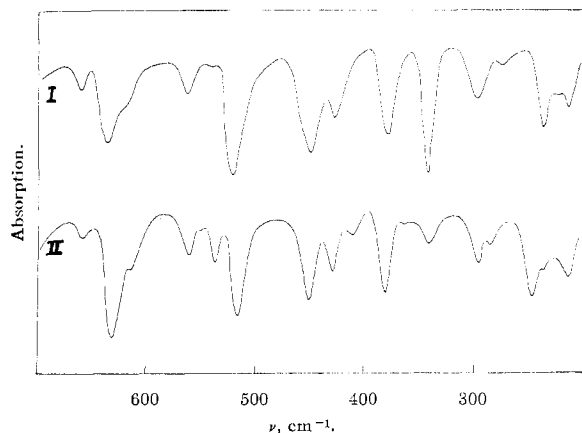

Figure 3.—Infrared spectra of K[Pt(acac)$_2$Cl] (I) and K[Pt-(acac)$_3$] (II).

Both the Pt–O stretching bands of III at 650 and 478 cm^{-1} are shifted to 636 and 454 cm^{-1} in I and to 633 and 453 cm^{-1} in II, respectively. The direction of these shifts is anticipated since interactions between O-bonded and C-bonded acetylacetonato ligands decreased the Pt–O bond order. In the low-frequency region, some additional bands of weak intensity appear at 414 and 344 cm^{-1} in II. The nature of the former band together with that of the 1644-cm^{-1} band will be discussed in the next section.

Stereochemistry.—So far, X-ray analyses have been carried out on three Pt complexes containing C-bonded

acetylacetone: I,[7] trimethyl(acetylacetonato)platinum dimer,[10] and trimethyl(acetylacetonato)(2,2'-bipyridine)platinum(IV);[11] in the former two compounds, the two CO bonds in the C-bonded acetylacetonato group are almost parallel to each other (cisoid form) whereas they are not parallel in the last compound (transoid form)
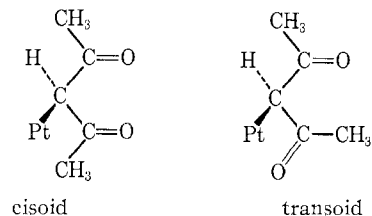
The distinction of these two structures from infrared spectra is rather difficult to make in the present stage, since the results of normal coordinate analysis will be almost the same for both. However, the following chemical observations may be useful in elucidating the relative position of two CO groups. Lewis and Oldham[12] have noted that the reaction of compound I with a variety of divalent metals leads to the formation of complexes of the type M(compound I)$_2$, indicating significant remaining donor properties of the two oxygens of the C-bonded acetylacetonato ligand. The occurrence of such reactions seems to favor the cisoid form of the C-bonded acetylacetonato ligand in compound I. Similar reactions give only M(compound II)$_2$ although compound II has twice as many prospective coordination sites as compound I. This may indicate that one of the C-bonded acetylacetonato ligands in compound II may take the transoid structure.

It is rather difficult to determine the relative position of the two C-bonded acetylacetonato ligands of compound II without X-ray analysis. The use of molecular models indicates that the following structure would minimize the repulsion between two bulky ligands. This structure contains one transoid and one
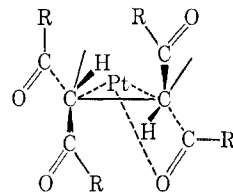
cisoid ligand. If this structure is correct, the repulsion between two γ-hydrogens is important in predicting the formation of *cis*-bis(γ-acetylacetonato) complexes. It has been noted[12] that carbon-bonded forms could not be prepared using analogs of acetylacetone substituted at the γ-carbon. Additional attempts in this investigation were made using the following ligands: γ-chloroacetylacetone, γ-bromoacetylacetone, γ-cyanoacetylacetone, γ-methylacetylacetone, γ-ethylacetylacetone, γ-*n*-propylacetylacetone, and γ-isopropylacetylacetone.

(10) A. Robson and M. R. Truter, *J. Chem. Soc.*, 630 (1965).

(11) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), **A266**, 527 (1962).

(12) J. Lewis and C. Oldham, *J. Chem. Soc.*, Sect. *A*, 1456 (1966).

The variety of electronic effects expected from this series were uniformly unsuccessful in producing a single carbon-bonded structure. It may be concluded, therefore, that the steric effect of a substituent at this position is more important than the electronic effect in determining the position of keto–enol equilibrium or hybridization. The presence of transoid structures places an oxygen atom within approximate bonding distance of the platinum. Furthermore, it is oriented close to the axis of the d_{xz} or d_{yz} orbitals of the platinum. Since these orbitals are filled, a strong bonding would of course not be expected to occur. However, the symmetry of the crystal field about the platinum, the primary factor in determining electronic transition

energies, will have changed drastically. The result of this change is expected to shift electronic transition energies and in fact conforms to the observation that II is green although most platinum complexes are yellow.

The presence of interaction between filled orbitals of the Pt atom and the oxygen atom of a ligand has been demonstrated by Allen and Theophanides for Pt(II) complexes containing α-hydroxyacetylenes.[13] The infrared spectrum of compound II is different from that of compound I in that the former exhibits two extra bands at 1644 and 414 cm^{-1}. These bands may correspond to the stretching and bending of the C=O group perturbed by the interaction with the Pt atom.

(13) A. D. Allen and T. Theophanides, *Can. J. Chem.*, **44**, 2703 (1966).

Diethylenetriamine Complexes of Platinum(II) Halides

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The major product of a previously described synthesis of [Pt(dien)X]X has been shown to be $Pt_3C_8H_{30}ON_6Cl_8$ for the case where X = Cl. On the basis of both chemical and physical evidence, a structure for the latter is proposed and an alternate procedure for the synthesis of [Pt(dien)Cl]Cl in high yield is described.

In 1934, Mann[1] described a procedure for the synthesis of [Pt(dien)X]X, where dien = diethylenetriamine and X = Br or I but not Cl. For the case where X = Cl, Mann isolated a product to which he assigned the empirical formula $PtC_8H_{30}ON_6Cl_8$ although his analytical data require $Pt_3C_8H_{30}ON_6Cl_8$. Basolo, et al., reported[2] the synthesis of [Pt(dien)Cl]Cl but without details other than the statement that the procedure employed was essentially that described by Mann. However, it was subsequently learned[3] that the method actually used by Basolo and co-workers was closely similar to that devised in this laboratory and described in the present communication. Din and Bailar[4] prepared [Pt(dien)Br]Br in 45% yield by Mann's procedure but it appears that they separated and discarded the more complex halide during the early stages of their synthesis process.

The work described below serves to clarify the nature of $Pt_3C_8H_{30}ON_6Cl_8$ and includes a procedure for the synthesis of pure [Pt(dien)Cl]Cl in high yield.

Experimental Section

Methods.—Infrared spectral data (Table I) were obtained using Beckman IR-7 and IR-11 instruments. Spectra in the 600–4000-cm^{-1} region were taken in KBr pellets and in KI pellets

in the 200–700-cm^{-1} region. Typical spectra are shown in Figure 1.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kv and 15 ma. Exposure times were 6–12 hr; relative intensities were estimated visually. The *d* spacings corresponding to the most intense lines (with relative intensities in parentheses) are listed immediately following analytical data.

Standard methods of analysis were used in all cases.

Materials.—With the exceptions that follow, all materials used were reagent grade chemicals that were used without further purification.

Solutions of K_2PtCl_4 or $(NH_4)_2PtCl_4$ were prepared as described earlier.[5]

Technical grade dien was purified by distillation in a Nester–Faust annular-spinning-band molecular still. After discarding a yellow low-boiling fraction, a colorless distillate was collected, bp 70–71° (3 mm). For analysis, a sample was converted to the trihydrochloride by treatment with concentrated hydrochloric acid followed by precipitation with ethanol saturated with HCl. The solid was filtered, washed with ethanol, and dried under reduced pressure. *Anal.* Calcd for dien·3HCl: C, 22.60; H, 7.59. Found: C, 22.59; H, 7.65.

Synthesis of $PtI_2·H_2O$.—A solution of 12.45 g, 0.030 mole, of K_2PtCl_4 in 200 ml of water at 90° was treated with excess KI (15.0 g, 0.09 mole) to precipitate virtually insoluble $PtI_2·H_2O$ which was separated by filtration, washed with water, and dried in air. (This product resembles finely divided carbon black and is difficult to dry since it invariably migrates from its container when placed in a vacuum desiccator.) The yield was 13.8 g or 98.5% based on K_2PtCl_4. *Anal.* Calcd for $PtI_2·H_2O$: Pt, 41.78. Found: Pt, 41.53.

(1) F. G. Mann, *J. Chem. Soc.*, 466 (1934).
(2) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).
(3) F. Basolo, private communication.
(4) B. Din and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **22**, 241 (1961).

(5) N. G. Kluchnikov and R. N. Savel'eva, *Z. Neorgan. Khim.*, **1**, 2764 (1956).