1250. *Metal–β-Diketone Complexes. Part I. Metal–Carbon Bonding in Some Platinum Acetylacetonates*

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In a series of platinum(II)–acetylacetone derivatives, it has been established that platinum is bonded to the 3-carbon atom. Criteria for the determination of the presence of metal–carbon bonding in these and related complexes, from the infrared and n.m.r. spectra have been investigated. Characteristic chemical shifts and coupling constants of the methyl and 3-CH protons in the n.m.r. spectra have been observed. In the infrared spectra the presence of a carbon-bonded grouping in the keto-form is best detected in the regions associated with the carbon–hydrogen stretching vibration, the carbon–oxygen stretching vibration, and the low-frequency region.

ACETYLACETONE was the first compound employed as a chelating agent by Werner.[1] Since then acetylacetone in particular, and β-diketones in general, have proved to be one of the most versatile groups of ligands available in the study of co-ordination complexes. Virtually every metal has been found to give acetylacetone complexes, and in many cases these have provided examples of interesting stereochemical arrangements. *X*-Ray structural work has established that the bonding in these complexes occurs *via* the two oxygen atoms, *e.g.*, $Cu(acac)_2$,[2] and in $Fe(acac)_3$ [3] (acac = acetylacetonate anion). Recent work on the trimer bisacetylacetonatonickel(II),[4] and the tetramer bisacetylacetonatocobalt(II) [5] have provided an example of a new bonding pattern for acetylacetone; an oxygen atom serves as a bridging group between two metal ions and hence provides an example of three-co-ordinate oxygen. The function of β-diketones as an oxygen donor system is therefore well established. However, recently *X*-ray structural determinations of some Pt^{IV} and Pt^{II} complexes have provided examples in which this group in bonded to the metal *via* the 3-carbon atom. Truter *et al.*[6] showed that the dimeric complex $[Me_3Pt(acac)]_2$ involved bonding of both the carbon and the oxygen atoms of the acetylacetone. When the compound reacted with dipyridyl (dpy) the oxygen–platinum bond was broken with retention of the platinum–carbon bond giving the complex $[Me_3Pt(acac)dpy]$.[7] Subsequent *X*-ray investigations on the platinum(II) complex, $KPt(acac)_2Cl$,[8] established the presence of both an oxygen-bonded group and a carbon-bonded moeity, resulting in retention of the normal four-co-ordinate planar arrangement around the platinum (I). This complex was first isolated by Werner in 1901,[1] who suggested a structure in which the planar four-co-ordination of the platinum was maintained by bonding one of the acetylacetone groups by one of the oxygen atoms only. Essentially the same structure was postulated by Grinberg and Chapurskii, on the basis of conductivity measurements, in 1959.[9]

In addition to the complex $K[Pt(acac)_2Cl]$, Werner obtained the complexes $Pt(acac)_2$, $K[Pt(acac)Cl_2]$, and $Na_2[Pt(acac)_2Cl_2]5H_2O$ from the interaction of acetylacetone with the chloroplatinite ion in alkaline solution. We have also prepared two related complexes $KPt(acac)_3$ and $Na_2[Pt(acac)_2Br_2]2H_2O$ by modifying slightly the method of preparation.

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[1] A. Werner, *Ber.*, 1901, **34**, 2584.

[2] H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ., Ser. C.*, 1953, **4**, 43.

[3] R. B. Roof, *Acta Cryst.*, 1956, **9**, 781.

[4] G. T. Bullen, *Nature*, 1956, **177**, 537.

[5] F. A. Cotton and R. C. Elder, *J. Amer. Chem. Soc.*, 1964, **86**, 2294.

[6] A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1960, *A*, **254**, 205.

[7] A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1962, *A*, **266**, 527.

[8] B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, 1962, **195**, 1278.

[9] A. A. Grinberg and I. N. Chapurskii, *Russ. J. Inorg. Chem.*, 1959, **4**, 137.

The compounds $Pt(acac)_2$ and $K[Pt(acac)Cl_2]$ may be readily formulated, on the basis of a four-co-ordinate platinum(II) system, with oxygen-bonded acetylacetone groups; however, if the acetylacetone bonds *via* both oxygen atoms for the compounds $K[Pt(acac)_3]$ and $Na_2[Pt(acac)_2X_2],2H_2O$ (X = Cl, Br) six-co-ordination is implied for the platinum atom. Six-co-ordinate platinum(II) derivatives have been observed for some nitrosylplatinum(II) adducts,[10] but this is not a common co-ordination number for platinum(II) compounds. The normal co-ordination number of platinum(II) however may be maintained if carbon-bonded acetylacetone groups are present. We have investigated the properties of these complexes in order to establish the mode of co-ordination of the acetylacetone.

Bonding of the acetylacetone group through carbon may be expected to modify the carbon–hydrogen vibrations in the infraspectra and also the nuclear magnetic resonance spectra of the protons in the system. The carbon–oxygen vibrations may also be materially affected, as they will approach more closely to that of the tautomeric keto-form of the molecule. We have therefore investigated the infrared spectra and n.m.r. proton spectra of this series of complexes in order to establish a criterion for the determination of the presence of metal–carbon bonding.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra of a series of metal acetylacetonates has been reported by Cotton and Holm;[11] the 3-CH protons were found to absorb in a relatively narrow range (~350 c./sec.), being "nearly independent" of the metal ion. The data for the complexes studied in this present work are given in Table 1.

TABLE 1

Proton magnetic resonance data

Compound	C./sec. down-field [a]	Relative intensity	Multiplicity	Separation, *i.e.*, J_{Pt-H} (c./sec.)	Assignment
$Pt(acac)_2$ [b]	125	6	3	5	$-CH_3$
	332	1	3	11	–C–H
$KPt(acac)Cl_2$	112	6	3	5	$-CH_3$
	339	1 *	3	2	–C–H
$KPt(acac)_2Cl$	106	6	3	6	$-CH_3$
	135	6	3	10	$-CH_3$
	348	1 *	3	2	–C–H
	337	1 *	3	120	–C–H
$KPt(acac)_3$	105	12	3	16	$-CH_3$
	77	6	3	2	$-CH_3$
	260	2 *	3	123	–C–H
	305	1 *	1		–C–H
$Na_2Pt(acac)_2Cl_22H_2O$	135	6	3	10	$-CH_3$
	322	1 *	Not observable	—	–C–H
$Na_2Pt(acac)_2Br_22H_2O$	131		3	8	$-CH_3$
	320	Very weak	Not observable		–C–H

* Disappears on deuteration.

[a] Measured in D_2O relative to dioxan referenced to tetramethylsilane. [b] Measured in $CDCl_3$.

Proton absorption occurs in two regions associated with the terminal methyl groups (~100 c./sec. relative to tetramethylsilane) and the 3-proton (~300 c./sec.). Since platinum contains 34% of the isotope ^{195}Pt with a nuclear spin of $\frac{1}{2}$, each in the proton spectrum should be split into a triplet of intensity 1 : 4 : 1. In general the magnitude of the splitting by a nucleus is related to the number of intermediate atoms between the two interacting nuclei, so that a much larger coupling constant would be expected for the 3-CH proton in molecules containing a carbon-bonded entity. The spin–spin coupling between the platinum and the proton has been of considerable utility in identifying the presence of the carbon-bonded grouping.

Coupling constants of 70 c./sec. for protons (J_{Pt-H}) by platinum have been reported

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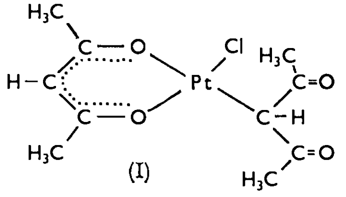
[10] J. Lewis, R. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

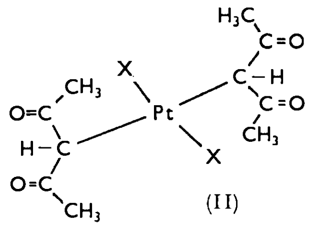
[11] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1958, **80**, 5658.

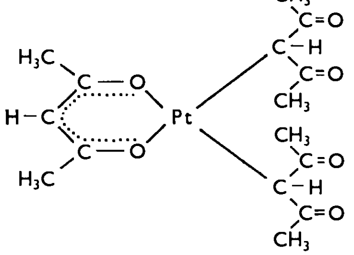
by Smith in some methyl–platinum(IV) complexes.[12] For the 3-CH protons, in the compounds $Pt(acac)_2$ and $K[Pt(acac)Cl_2]$, small coupling constants are observed (J_{Pt-H} ~5), whereas for the compound $KPt(acac)_2Cl$ two 3-CH proton signals are observed, one of which is split by 120 c./sec. and is attributed to the proton on metal–carbon bonded acetylacetone and one by 2 c./sec., associated with the oxygen-bonded ligand. The methyl protons in $Pt(acac)_2$ and the salt $K[Pt(acac)Cl_2]$ show a small splitting with J_{Pt-H}, ~5 cps. For the complex $K[Pt(acac)_2Cl]$ two set of methyl protons are observed, with slightly different coupling constants (see Table 1). In a structure (I), established by *X*-ray data for the solid, there are three methyl environments expected as the two methyl groups of the oxygen-bonded acetylacetone are not identical. It appears, therefore, that the difference in chemical shift between this latter pair is negligible. The methyl protons of the carbon-bonded acetylacetone group absorb at about 30 c./sec. down-field from those of the oxygen bonded entity and this appears to be the case for the anionic complexes studied to date.

For the complexes $Na_2[Pt(acac)_2X_2],2H_2O$ ($X = Cl, Br$) difficulties were encountered as these salts appeared to be unstable in solution. The decomposition products gave infra-red and n.m.r. spectra which were very similar to that of $K[Pt(acac)_2Cl]$. From the n.m.r. spectra of a freshly prepared solution, the coupling constant, the chemical shift for the methyl protons together with the appearance of only one methyl resonance indicated the presence of only one type of methyl environment, and is consistent with bonding of both acetylacetone groups by the carbon (II). In agreement with this formulation it has also been possible to isolate a di-2,4-dinitrophenylhydrazine adduct of these complexes (see also ref. 13). Because of the instability of the solutions, it was not possible to determine the coupling constant for the 3-CH proton.

The potassium trisacetylacetonatoplatinum(II) shows two sets of methyl absorptions and 3-CH proton signals. For the 3-CH protons, the ratio of the intensities of these two bands is 2 : 1, the higher-intensity component showing a coupling constant of J_{Pt-H} ~120 c./sec. These data imply two carbon-bonded and one oxygen-bonded acetylacetone group in the molecule (III). The position and intensities of the methyl protons are also in agreement with this formulation; the splitting of the methyl resonance by the platinum isotope being slightly greater for the carbon-bonded molecules.


(I)


(II)


(III)

Infrared Spectra.—The infrared spectra of the acetylacetone derivatives have been summarised by Nakamoto[14] for Co^{III}, Fe^{III}, Al^{III}, Pd^{II}, Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}. In the

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[12] J. A. S. Smith, *J.*, 1962, 4736.

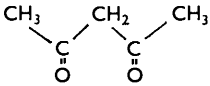
[13] C. H. Bruhaker and R. A. D. Wentworth, *Inorganic Chem.*, 1964, **3**, 1472.

[14] K. Nakamoto, " Infrared Spectra of Inorganic and Coordination Compounds," Wiley, London, 1963, p. 216.

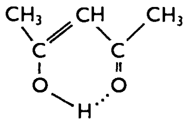
subsequent discussion the ranges of frequencies will refer to this group of metal ions. A normal co-ordinate analysis of one of the acetylacetone rings in the complex bisacetylacetonatocopper(II) has been carried out by Nakamoto and Martell[15] for the region 1700—350 cm.$^{-1}$; good agreement being obtained between observed and calculated band positions. As in chelating acetylacetone complexes the oxygen–carbon–metal atoms lie in a plane, it is convenient to use this plane to define the infrared vibrations in this molecule. For the subsequent discussion we may divide the spectrum into five regions associated with the carbon–hydrogen stretching vibration, the " carbon–oxygen " stretching vibration, carbon–hydrogen " in plane " deformation, carbon–hydrogen " out of plane " deformation frequencies and the low-frequency region. Table 2 summarises the infrared spectra of the normal and 3-carbon deuterated acetylacetone complexes studied in this work and from these results some tentative assignments and general trends can be noted. In making the assignments appeal has been made to the normal co-ordinate analysis of bisacetylacetonatocopper(II) reported by Nakamoto and Martell,[15] the ratio of the isotopic shifts on deuteration of the complexes and the intensity of the new bands in the deutero-complexes It must be emphasised therefore, that many of these assignments must be considered as tentative.

(*a*) *Carbon–hydrogen stretching region.* Two classes of C–H absorption would be expected in this region corresponding to the 3-CH proton and to the methyl protons. For an oxygen-bonded ligand the 3-CH vibration absorbs above 3000 cm.$^{-1}$,[16] whereas for the carbon–bonded system this falls below 3000 cm.$^{-1}$, in agreement with the less " aromatic " nature of the protons in these systems. The assignment of these frequencies has been verified by deuterium substitution when a ratio ν_H/ν_D of the order 1·35 has been observed (Table 2). An examination of the normal and deutero-compounds, in this region, is one of the best means of detecting the presence of a carbon-bonded group if this is present in the keto-form. The carbon-bonded complexes may be viewed as 3-substituted pentane-2,4-diones. It is possible therefore for the molecule to exist in both a keto and an enol form, for this latter case there would be no 3-CH vibration, but a corresponding O–H vibration should then be present in this region. Although it was possible readily to detect the isotopic shift for molecules containing carbon-bonded species, for the two acetylacetonates containing only oxygen-bonded groups the 3-CH vibrations were much weaker and although they disappeared on deuteration the corresponding C–D vibrations were not detected.

(*b*) *Carbon–oxygen vibration.* Acetylacetone has been shown to be a mixture of the tautomers (a) and (b) and the infrared spectrum has been assigned accordingly.[17] The carbonyl frequency in the keto-tautomer (a) has been established at 1720 cm.$^{-1}$, whereas



(a)



(b)

in the " enol " form (b), the carbonyl frequency interacts with the C=C vibration so that strictly there is no frequency characteristic of a simple carbonyl stretching mode. However in keeping with the lower bond order of the carbon–oxygen bond in the enol form, the highest frequency observed in the region 1500—1750 cm.$^{-1}$ is at 1610 cm.$^{-1}$. In the metal complexes the structure (b) is stabilised, and Nakamoto has shown that the two highest frequencies that appear in this region are a mixture of the C=C and C=O vibrations and these occur at 1600—1570 and 1554—1520 cm.$^{-1}$.

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[15] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, 1960, **32**, 588.

[16] J. Lewis and R. G. Wilkins, " Modern Co-ordination Chemistry," Interscience, New York, 1960, p. 382.

[17] S. Bratoz, D. Hadzi, and G. Rossmy, *Trans. Faraday Soc.*, 1956, **52**, 464.

TABLE 2

Infrared data

$Pt(acac)_2$		$KPt(acac)Cl_2$		$KPt(acac)_2Cl$		$KPt(acac)_3$		$Na_2Pt(acac)_2Cl_2,2H_2O$		$Na_2Pt(acac)_3Br_2,2H_2O$		Previous assignment	Ref.
H	D	H	D	H	D	H	D	H	D	H	D		
								3500m → 2595m		3560m → 2610m		O–H	
								3415m → 2570m		3480m → 2560m			
3084w → ?		3094w → ?		3081w → 2386w		3081w → 2370w						3090 cm.$^{-1}$ 3C–H	(16)
2999s	2998s	2999s	2999s	2998s	2998s	2998m	2998sh	2998w	2998w	2998m	2999m		
2960s	2962s	2966s	2966s	2969sh	2972sh	2975m	2975m	2978m → 2178w	2966w	2975s → 2172m	2975m		
				2943s → 2178m	2943w	2945m → 2182m	2945w						
2922s	2922s	2922s	2922s	2922s	2922m	2923w	2923w	2914w	2914w	2920w	2920w		
									2595m		2610m		
									2570m		2560m		
					2386w		2370w						
					2178m		2182m		2178w		2172m		
				1764w	1795w	1679s	1679s						
				1695s	1695s	1658s	1657s	1646sh		1650s	1649s		
						1642s	1644s	1645s → 1581m	1644s	1646s → 1580sh			
				1653m	1653m	1624sh → 1617sh		1608m → 1245w		1618s → 1245w	1615m		
				1570s → 1560s			1617sh		1581m		1580sh		
1565s	1563sh	1558sh	1562sh	1565ssh	1563ssh	1570s	1568s					1570—1600 cm.$^{-1}$	(14) (15)
					1560s							C=C + C=O	
1555s	1543s	1546s	1546s	1546s	1546s	1556sh	1556sh					1520—1554 cm.$^{-1}$	(14) (15)
												C=O + C=C	
1527s → 1490s	1527w	1531s → 1497s		1522s → 1484s		1515s → 1473s	1514w					1425—1523 cm.$^{-1}$	(14) (15)
		1504sh	1508sh									C=O + 3C–H	
	1490s		1497s		1484s		1473s						
							1448wsh						
1430sh	1430sh	1422m	1425m	1430sh → 1309m	1430sh	1413sh → 1326m	1398m	1424s → 1377s	1419m	1425s → 1367s	1419w	1430 cm.$^{-1}$	(14) (15)
1390s	1390s			1376s	1376s			1419sh	1377s		1367s	CH_3 deformation	
1360m	1360m	1372s	1372s	1362s	1362s	1362s	1362s	1366s → 1340m	1366sh	1354s → 1339m	1354w	1387—1356 cm.$^{-1}$	(14) (15)
				1340s → ?		1341sh → 1215w			1340m		1339m	CH_3 deformation	
	1297w		1300w		1309m		1326m						
1277m	1277m	1282m	1282m	1279m	1279m	1277m	1276m						
				1245w	1245w	1243m	1215w		1245w		1245w		
1200m → 914w		1203w → 917w		1203w → 907w		1197ssh → 912wsh	1197m	1200s	1200s	1193s	1193s	1190—1199 cm.$^{-1}$	(14) (15)
				1188m → ?	1182w	1186m → 934m						3C–H in plane	
				1172s → 895w	1171w								
				1160m	1159w	1170m → 902m	1170w		1170sh		1061w		
		1042w		1054m → 778w									
1021m	1020m	1032w	1034w	1024w	1024w	1068m	1061m	1031m	1031m	1023sh	1022sh	1015—1028 cm.$^{-1}$	(14) (15)
						1042s → 769w	1031m					CH_3 rock	
1018sh	1018sh	1014w	1014w	1007m → 766w		1013m → 746s	1011w	1010s → 744m		1007s → ?			
					973w	991m	992m		987s		999s		
				955w		953m							
940m	943m	952w	958w	943w	945w	932w	934m	948w	948w	950m	950w	927—937 cm.$^{-1}$	(14) (15)
936sh → ?		939w	933w	929w								C–CH_3 symmetric	
												and asymmetric	
									908m			overlap	
	914w		917w	918w	918w		912wsh	902m → ?		901m → ?			
				883w	907w	892w	902m						
782w				862m	895w	867m	850w	863s	863w	856s	860w		
					835w	801w	786m						
774s		813m		780m	778w	769s	769w					764—800 cm.$^{-1}$	(14) (15)
					766w		746s		744m	740w	740wsh	3C–H out of plane	
					742w		745sh	716w	722s				
708w	708w	702w	700w	703w	703w								

For the carbon-bonded acetylacetone molecules as discussed above the spectra may be considered to be similar to that of a 3-substituted pentane-2,4-dione; here higher frequencies may be expected corresponding to a contribution from the keto-form. However, it must be emphasised that the absence of such frequencies does not necessarily exclude the possibility of carbon-bonded groupings as the diketone may be stabilised entirely in the enolic form. For those compounds in which the acetylacetone group is bonded *via* oxygen, the highest frequencies observed in this region are below 1600 cm.$^{-1}$, whereas for the molecules containing carbon-bonded ligands, frequencies are found above 1600 cm.$^{-1}$, implying for the latter class of compound the presence of some keto-tautomer of the diketone.

On deuteration, only minor changes in frequency occur in this region. For oxygen-bonded molecules a frequency around 1520 cm.$^{-1}$ is deuterium-sensitive, the change (ν_H/ν_D) being of the order of 1·03 in agreement with the assignment by Nakamoto as a coupled carbon–oxygen/carbon–hydrogen vibration. A similar observation has been made for the deuterated and normal acetylacetone complex of copper(II).[18]

For complexes which the n.m.r. data indicate contain carbon-bonded acetylacetone groups, an additional two bands occur in the regions 1410—1430 and 1340—1366 cm.$^{-1}$ both of which are deuterium-sensitive, the ratio for the first of these being $\nu_H/\nu_D = 1{\cdot}07$; the assignment of the position of the second band in the deuterium compound has not been possible for KPt(acac)$_2$Cl. The low value of this ratio for these bands implies that these are not pure C–H vibrations.

TABLE 3

Summary of isotopic shifts in deuterium compounds

Pt(acac)$_2$	KPt(acac)Cl$_2$	KPt(acac)$_2$Cl	KPt(acac)$_3$	Na$_2$Pt(acac)$_2$Cl$_2$	Na$_2$Pt(acac)$_2$Br
$3084 \longrightarrow ?$	$3094 \longrightarrow ?$	$3081 \xrightarrow{1\cdot 29} 2386$	$3081 \xrightarrow{1\cdot 30} 2370$		
		$2943 \xrightarrow{1\cdot 35} 2178$	$2945 \xrightarrow{1\cdot 35} 2182$	$2978 \xrightarrow{1\cdot 37} 2178$	$2975 \xrightarrow{1\cdot 37} 2172$
				$1608 \xrightarrow{1\cdot 29} 1245$	$1618 \xrightarrow{1\cdot 29} 1245$
		$1570 \xrightarrow{1\cdot 01} 1560$	$1624 \xrightarrow{1\cdot 01} 1617$	$1646 \xrightarrow{1\cdot 04} 1581$	$1646 \xrightarrow{1\cdot 04} 1580$
$1527 \xrightarrow{1\cdot 02} 1490$	$1531 \xrightarrow{1\cdot 02} 1497$	$1522 \xrightarrow{1\cdot 03} 1484$	$1515 \xrightarrow{1\cdot 03} 1473$		
		$1430 \xrightarrow{1\cdot 1} 1309$	$1413 \xrightarrow{1\cdot 1} 1326$	$1424 \xrightarrow{1\cdot 03} 1377$	$1425 \xrightarrow{1\cdot 04} 1367$
		$1340 \longrightarrow ?$	$1341 \xrightarrow{1\cdot 1} 1215\text{w}$	$1366 \xrightarrow{1\cdot 02} 1340$	$1354 \xrightarrow{1\cdot 01} 1339$
$1200 \xrightarrow{1\cdot 31} 914$	$1203 \xrightarrow{1\cdot 31} 917$	$1203 \xrightarrow{1\cdot 33} 907$	$1197 \xrightarrow{1\cdot 31} 912$		
		$1188 \longrightarrow ?$	$1186 \xrightarrow{1\cdot 27} 934$		
		$1172 \xrightarrow{1\cdot 40} 835$	$1170 \xrightarrow{1\cdot 29} 902$		
		$1054 \xrightarrow{1\cdot 38} 766$	$1042 \xrightarrow{1\cdot 39} 746$		
		$1007 \xrightarrow{1\cdot 35} 742$	$1013 \xrightarrow{1\cdot 36} 745$	$1010 \xrightarrow{1\cdot 40} 722$	$1007 \longrightarrow ?$
$936 \longrightarrow ?$	$939 \xrightarrow{1\cdot 40} 673$	$929 \xrightarrow{1\cdot 41} 660$	$932 \xrightarrow{1\cdot 41} 658$		
		$862 \xrightarrow{1\cdot 41} 612$	$867 \xrightarrow{1\cdot 36} 636$	$863 \xrightarrow{1\cdot 37} 630$	$856 \longrightarrow ?$
$774 \xrightarrow{1\cdot 38} 574$	$813 \xrightarrow{1\cdot 36} 598$	$780 \xrightarrow{1\cdot 35} 578$	$769 \xrightarrow{1\cdot 35} 571$		

For the compounds Na$_2$[Pt(acac)$_2$X$_2$],2H$_2$O (X = Cl or Br) the absence of bands at 1520 cm.$^{-1}$ and 1570 cm.$^{-1}$ is consistent with the formulation of these as carbon-bonded groups

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[18] C. Djordjevic, J. Lewis, and R. S. Nyholm, *J.*, 1962, 4778.

with the diketone mainly in the keto-form. In the deuterated form, the weak bands at 1618(Br), 1608(Cl) in the normal form appear at 1245 cm.$^{-1}$, as expected for the assignment of these as H_2O frequencies. In the molecules containing carbon-bonded groupings a frequency at 1600 cm.$^{-1}$ appears to be deuterium sensitive with $\nu_H/\nu_D = 1{\cdot}02$.

C–H *in-plane vibration.*—Nakamoto has assigned a weak vibration in the region 1190—1199 cm.$^{-1}$ to an " in plane " C–H mode. As expected for those compounds bonded *via* the oxygen, this frequency is deuterium-sensitive and displaced by the order expected for a pure C–H vibration, *i.e.*, $\nu_H/\nu_D = 1{\cdot}31$. For the salts $Na_2Pt(acac)_2X_2$, X = Br, Cl a corresponding frequency would not be expected however, and a strong sharp band is obtained in this region, at 1200 cm.$^{-1}$, which is unaffected by deuteration. For carbon-bonded systems in addition to a band due to the methyl group a strong absorption band occurs in the region of 1000 cm.$^{-1}$ which is deuterium-sensitive with $\nu_H/\nu_D = 1{\cdot}37$. This deuterium-sensitive frequency also occurs in the complexes containing mixed oxygen–carbon-bonded acetylacetone groups but is absent from those containing only oxygen-bonded entities.

For molecules containing both oxygen and carbon-bonded acetylacetones, strong absorption bands occur in this region but it is possible to identify the weak C–H " in plane " vibration of the oxygen–bonded molecule as a shoulder on the side of the stronger band at 1200 cm.$^{-1}$ of the carbon-bonded entity. The presence of a deuterium-sensitive band at ~1000 cm.$^{-1}$ in these complexes is indicative of the presence of the keto-form of the carbon-bonded system. For molecules containing both classes of ligand, an additional band also occurs at 1170 cm.$^{-1}$ which is deuterium-sensitive with $\nu_H/\nu_D = 1{\cdot}35$, as the intensity of the band in this position is considerably reduced in the deuterium complex.

C–H " *out-of-plane* " *vibration.* Nakamoto assigns the 3-CH " out-of-plane " vibration in oxygen-bonded systems to a band at 764—800 cm.$^{-1}$. For the molecules containing oxygen-bonded groups a frequency in this region is deuterium-sensitive with $\nu_H/\nu_D = 1{\cdot}36$, as expected for a pure carbon–hydrogen vibration (Table 2); an additional weak band at 940 cm.$^{-1}$ appears to be deuterium-sensitive. This, however, is partly obscured by another band in the same region assigned as the overlap of the asymmetric + symmetric $C{-}CH_3$ stretching modes. For molecules containing metal–carbon bonding, the band in the region 764—800 cm.$^{-1}$ is absent but a strong absorption appears in the region 850—867 cm.$^{-1}$ ($\nu_H/\nu_D \sim 1{\cdot}37$). In addition, in these complexes, a weak band at 900 cm.$^{-1}$ appears to be deuterium-sensitive but at the moment we cannot assign the corresponding deuterium frequency.

Low-frequency region.—The assignments of absorption in this region are complicated because of the various interactions possible and it is obvious that the normal co-ordinate analysis suggested by Nakamoto and Martell will have least success in this region, as coupling of metal–oxygen vibrations between the various ring systems may be expected. The situation has recently been summarised by Gillard *et al.*[19] Oxygen–platinum vibrations are expected in the region 350—500 cm.$^{-1}$, and for molecules considered to contain oxygen-bonded groups frequencies appear in this region (Table 4). For complexes involving carbon–platinum bonds, bands are observed in the region 500—600 cm.$^{-1}$ in agreement with the assignments made by Chatt and his co-workers [20] for the Pt–C vibrations, in some Pt^{II}-alkylphosphine adducts. This region appears to be potentially the most diagnostic for carbon-bonded entities in molecules of this type, as the variation in carbon–hydrogen and carbon–oxygen vibrations discussed above may be considerably modified by the keto–enol isomerisation in a carbon-bonded metal acetylacetonate.

To summarise, for the platinum complexes studied the presence of a carbon-bonded grouping is most readily indicated in the n.m.r. spectra by a large splitting of the 3-CH proton. In the infrared, the most significant criterion appears to be the position of 3-CH stretching vibration, the presence of a band in the metal–carbon stretching region, and a high frequency " carbonyl " band above 1600 cm.$^{-1}$.

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[19] R. D. Gillard, H. G. Silver, and J. L. Wood, *Spectrochim. Acta*, 1964, **20**, 63.

[20] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J.*, 1964, 734.

TABLE 4

Low-frequency region, *i.e.*, below 700 cm.$^{-1}$

$Pt(acac)_2$		$KPt(acac)Cl_2$		$KPt(acac)_2Cl$		$KPt(acac)_3$		$Na_2Pt(acac)_2Cl_2,2H_2O$		$Na_2Pt(acac)_2Br_2,2H_2O$		
H	D	H	D	H	D	H	D	H	D	H	D	
684m	684m	689w		685w		680s	680w		690m		696s	
		939 →	673w	929 →	669w	932 →	658w	645bd	645w			
				656w						657m	650w	
658w	663w	662m	662m			645w				645m	640m	
				632m	632m	867 →	636w	863 →	630w			
				862 →	612sh							
				628sh		620sh	625sh					
782 →	582sh					613m	613m					
774 →	574m	813 →	598w	780 →	578w	769 →	571m					
				565m	565sh			565w	564w	565w	565w	
				534w		540m	530sh					*
				522m	515bd	523m	521m	535m	533m	539m	533m	
473m	475m	476m	476m						512w			
444w	443w	450m	451m	451m	450m	440mbd	437mbd					
				431w	429sh	435sh	435sh					†
						427sh	427sh					
				374w	371w	383wbd	379wbd	382mbd	382mbd	387wbd	382w	‡
		339m	340m	341mbd	341m							
		327m	329m					321mbd	320mbd			

* Previous assignment, 500—600 Pt–C; ref. 3. † Previous assignment, 350—500 Pt–O; ref. 4. ‡ Previous assignment, 340—269 Pt–Cl; ref. 5.

EXPERIMENTAL

With the exceptions of the new compounds, the complexes were prepared as described previously.[1,9]

Potassium Trisacetylacetonatoplatinum(II).—Potassium bromoplatinite (1 mol.) in water was treated with an aqueous solution of potassium hydroxide (5 mol.) together with acetylacetone (7 mol.). After shaking for 1 hr. at 55—60° and cooling, green crystals separated which were washed with benzene, ethanol, and ether to give *potassium trisacetylacetonatoplatinum*(II) (50% yield) (Found: C, 33·8; H, 4·05; O, 18·0; Pt, 36·6. $C_{15}H_{21}KO_6Pt$ requires C, 33·9; H, 4·0; O, 18·1; Pt, 36·7%).

Sodium Dibromobisacetylacetonatoplatinum(II) *Dihydrate*.—Potassium bromoplatinite (1 mol.) in water was treated with an aqueous solution of sodium hydroxide (3·5 mol.) together with acetylacetone (7 mol.). After shaking for 1 hr. at 55—60°, orange crystals separated which were washed with benzene, ethanol, and ether to give the *dihydrate* (65% yield) (Found: O, 15·1; Pt, 30·9. $C_{10}H_{18}Br_2Na_2O_6Pt$ requires O, 15·2; Pt, 30·7%) and after removal of water of crystallisation, the *anhydrous complex* (Found: C, 20·0; H, 2·1. $C_{10}H_{14}Br_2Na_2O_4Pt$ requires C, 20·0; H, 2·3%).

Infrared Spectra.—Measurements were made on a Perkin-Elmer model 221 Spectrometer.

Proton Magnetic Resonance.—Measurements were made on a Varian A60 Spectrometer at 60 Mc./sec.

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