461. *Metal Carbonyl Compounds. Part IV.* An Infrared Spectroscopic Investigation of Some Platinum*(II) *and Palladium*(II) *Carbonyl Compounds.*

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The relation between the bond properties of bonds M–A and A–B in various metal–ligand systems M–A–B has been examined, and the relevance of force constant data to the problem of metal–ligand bond properties is discussed. C–O, N–H, and Pt–N stretching frequencies for a number of carbonyl complexes of platinum and palladium are reported and discussed in connection with the configurations and *trans*-effects of the various ligands and the stabilities and structures of the complexes containing them.

FORCE constants derived from the stretching vibrational frequencies of bonds A–B in metal–ligand systems M–A–B (where M = metal) have been used by several investigators as a measure of the properties of the metal–ligand bond M–A.[1, 2] The relation between the bonds A–B and M–A in complex compounds is usually only vaguely understood and various assumptions about it have been made in interpretation of spectroscopic data of this type.

It is well known that the " true " stretching force constant of a bond is an excellent indication of the strength of attachment of the vibrating atoms. In practice, however, it is difficult to assess the effect on the stretching frequency of interaction with other vibrational modes of the molecule, or to assign correctly the different types of frequencies which may occur. Except in a few isolated cases (*e.g.*, the binary carbonyls [3]) use of stretching frequencies to calculate absolute force constants and bond strengths is unwarranted for these reasons alone, and it should be restricted to comparison with analogous systems. It is possible to correct stretching frequencies for " mechanical " (stretch-stretch) interaction with adjacent bonds, and in systems where large variations in stretching frequencies occur these corrections can be very important [4] and should be considered in any comparison.

Though there is an obvious need for further study of M–A–B systems where both M–A and A–B stretching frequencies are simultaneously observable, knowledge now suffices for a preliminary appraisal of the method. Metal–ligand systems of this kind fall into two main types: (i) either or both of the M–A and A–B bonds are pure σ-bonds (*e.g.*, in metal hydrates, ammines); and (ii) conjugation occurs between the M–A and the A–B bond (*e.g.*, in metal carbonyls, cyanide complexes). In general the A–B frequency shifts of complexes of the first type reflect only weakly the corresponding changes in the M–A bonds in a series of compounds, and the latter changes are in many cases considerable.

In a recent study [2] of a number of metal ammines—the type of complex most frequently examined spectroscopically—the metal–nitrogen frequencies have been compared with the nitrogen–hydrogen frequencies. Some of these results, and some from the present investigation, are given in Table 1. The maximum variation of the mean N–H stretching frequency in a large series of complexes of the type *trans*-[L,am $PtCl_2$] is only 15 cm.$^{-1}$, corresponding to a change in the force constant of only ~1% where the corresponding Pt–N force constant varies by approximately 10%.[2b] Some of the larger variations of the N–H frequency shown in Table 1 arise because of different types of N–H vibration, and the frequencies are then not comparable, though they are comparable, for example, in nos. 4, 5, and 6, where the environments of the vibrating atoms are the same. The

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* Part III, *J.*, 1957, 2018.

[1] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; Irving and Magnusson, *J.*, 1957, 2018.

[2] (*a*) Powell and Sheppard, *J.*, 1956, 3105; (*b*) Powell, *J.*, 1956, 4495.

[3] King and Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 4192.

[4] (*a*) Nyholm and Short, *J.*, 1953, 2673; (*b*) Magnusson, Thesis, Sydney, 1957.

large variations between the frequencies for compounds 7, 8, and 9 undoubtedly arise from hydrogen-bonding interaction with the anion. Because of hydrogen bonding, O–H frequencies in hydroxy-compounds and hydrates are often difficult to interpret but a few compounds have been examined.[5] In azide and *iso*thiocyanate complexes N–N and C–N frequency variations are small between complexes of the same metal, but they may differ appreciably in other cases.

TABLE 1. *Stretching frequencies of metal complexes of σ-bonding ligands.*

No.	Compound	Frequencies				Ref.
1	*trans*-$[(C_2H_4)(NH_3)PtCl_2]^0$	481	Pt–N;	3300	N–H	2*b*
2	*trans*-$[(Et_2S)(NH_3)PtCl_2]^0$	493	Pt–N;	3170, 3200	N–H	2*b*
3	*trans*-$[(NH_3)_2PtCl_2]^0$	507	Pt–N;	3170, 3270	N–H	2*b*
4	*trans*-$[(CO)(C_7H_7{\cdot}NH_2)PtCl_2]^0$	488	Pt–N;	3257, 3319	N–H	*a*
5	*trans*-$[(CO)(C_7H_7{\cdot}NH_2)PtBr_2]^0$	492	Pt–N;	3251, 3312	N–H	*a*
6	*trans*-$[(CO)(C_7H_7{\cdot}NH_2)PtI_2]^0$	493	Pt–N;	3248, 3309	N–H	*a*
7	$[Co(NH_3)_6]Cl_3$			*ca.* 3070	N–H	*b*
8	$[Co(NH_3)_6Br_3$			*ca.* 3120	N–H	*b*
9	$[Co(NH_3)_6]I_3$			*ca.* 3150	N–H	*b*

[a] This investigation. [b] Fujita, Nakamoto, and Koboyashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

Small variations are to be expected in type (i) systems since the very nature of the bonding precludes any serious change in A–B bonding. " Mesomeric " effects should be largely inoperative and " inductive " effects[6] appear to be only weakly transmitted through the X–M–A–B systems, paralleled by the minor shifts produced in N–H frequencies of aromatic primary amines by inductive substituents in the ring.

A–B frequencies in type (ii) systems should be much more sensitive to changes in M–A bond type and bond order owing to the contributions of both forms (I) and (II) to the structure. The availability of π-electrons in systems involving structures (I) and (II) is such that the π-bond orders are very roughly complementary and, in a series of analogous

$$\text{(I)}\quad M{-}A{\equiv}B \qquad\qquad M{=}A{=}B\quad \text{(II)}$$

compounds, an increase in either the M–A or the A–B frequency is accompanied by an appreciable decrease in the other. Of course, A–B σ-bonds are unlikely to be affected by inductive effects any more than they are in type (i) systems, but there is still a greater contribution by inductive modification of the more easily polarisable π-electrons.

Reported work on A–B frequencies of this type generally supports the suggested relation between M–A and A–B bonds,[3,4,7] though much of the work has been on isolated compounds rather than on series containing comparable M–A–B systems.

Platinum Carbonyl Compounds.—In an effort to provide more information on both M–A and A–B bonds in series of compounds of a particular metal we have examined the infrared spectra of numerous platinum carbonyl compounds in the range where Pt–C stretching frequencies could be expected (600—250 cm.$^{-1}$) but have been unable to locate any band. Because of their colour few of the compounds can be studied by Raman spectroscopy and even where this was possible again no band capable of unequivocal assignment could be observed.

The C–O stretching frequencies of a number of chloro-, bromo-, and iodo-complexes of platinum(II) containing carbon monoxide and various other ligands are listed in Table 2. Except in the case of the dicarbonyl complex (*a*) each co-ordination entity exhibited only one band in the region 1800—2300 cm.$^{-1}$. The positions of the bands, which were very strong and sharp, were unaffected by the physical state of the samples.

Table 2 shows that the variations between the chloro-, bromo-, and iodo-complexes are predominantly due to " inductive " effects. The same order is observed in each of the horizontal series, the shifts being in the opposite order to those expected from mesomeric weakening of the Pt–C bond where the effects of the halogens are in the order

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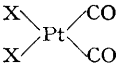
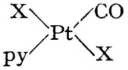
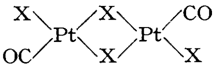
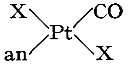
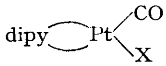
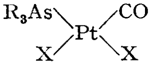
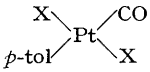
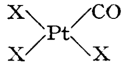
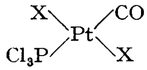
[5] Fujita, Nakamoto, and Koboyashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.
[6] Chatt, Duncanson, and Venanzi, *J.*, 1956, 4456.
[7] Hawkins, Mattraw, Sabol, and Carpenter, *J. Chem. Phys.*, 1955, **23**, 2422.

I > Br > Cl, and therefore νC–O (iodo-complex) > νC–O (bromo-complex) > νC–O (chloro-complex). "Orbital contraction," discussed by Craig and Magnusson,[8] should give a reliable indication of the "inductive effects" of these ligands. For this case, the effective nuclear charge on the platinum atom might be expected to be increased by charge increments in the approximate ratio 5 : 4 : 3 for the interactions of chlorine, bromine, and iodine respectively. For compounds of this type, an increase in the effective nuclear charge should lead to bond weakening and the effects of the halogens should thus be in the order Cl > Br > I, and νC–O (chloro-complex) > νC–O (bromo-complex) > νC–O (iodo-complex). This order is observed in each of the horizontal series of C–O frequencies in Table 2 (*i.e.*, for X = Cl, Br, I in each complex [(CO)LPtX$_2$]).

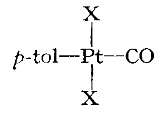
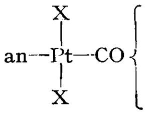
TABLE 2. C–O *Stretching frequencies* (*cm.*$^{-1}$) *of platinum carbonyl complexes.*

		X = Cl	Br	I			X = Cl	Br	I
(*a*)		2200 2162	—	—	(*f*)		2135	2130	2119
(*b*)		2146	2135	2122	(*g*)		2132	2128	2117
(*c*)		2145	2132	2120	(*h*)		2111	2106	2092
(*d*)		2136	2129	2120	(*i*)		2106	2096	2076
(*e*)		2135	2130	2103					

dipy = 2 : 2′-dipyridyl, py = pyridine, an = aniline, *p*-tol = *p*-toluidine.

Additional evidence for the assignment of the horizontal νC–O shifts to the relative "inductive effects" of the halogens is obtained from the νN–H and νPt–N shifts of complexes of the same type where L is an ammine. The C–O, N–H, and Pt–N frequencies of some of these are given in Table 3. Assignments of the Pt–N frequencies follow those made for analogous compounds by Powell.[2b] Although different amines are involved mesomeric electron-withdrawal by the CO group *trans* to the amine may be partly responsible for the shift in Pt–N frequencies (~490 cm.$^{-1}$) relative to those observed [2b] for ammine complexes which do not contain groups of high *trans*-effect (~510 cm.$^{-1}$).

TABLE 3. N–H, C–O, *and* Pt–N *frequencies* (*cm.*$^{-1}$) *of some platinum carbonyl ammines.*

		X = Cl	Br	I			X = Cl	Br	I
	N-H (symm.)	3257	3251	3248		N-H (symm.)	3257	3254	3248
	N-H (asymm.)	3319	3312	3309		N-H (asymm.)	3319	3315	3309
	C-O	2136	2129	2120		C-O	2132	2128	2117
	Pt-N	488	492	493		Pt-N	—	481	482

Superimposed on this are the shifts obviously due to the "inductive effects" of the halogen in the *cis*-positions. The shifts in the N–H frequencies occur in the opposite direction [Pt–N: 488 ⟶ 493; N–H (mean) 3288 ⟶ 3279] as expected, but they correspond to much smaller changes in the force constant. Comparison of the spectra of these *p*-toluidine complexes with those of the type *trans*-[*p*-tolLPtCl$_2$] (where L = PR$_3$, SbR$_3$, C$_2$H$_4$, SR$_2$, SeR$_2$, etc.) [1] again shows that the effect of "mesomeric" electron-withdrawal is not transmitted far enough to produce shifts in νN–H comparable to those in νPt–N.

The vertical shifts in C–O frequency in Table 2 are attributed to the various "inductive"

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[8] Craig and Magnusson, *J.*, 1956, 4895.

and " mesomeric " effects of the ligands but it is difficult to separate these contributions. The large shift (about 40 cm.$^{-1}$) between compounds (*b*) and (*i*) indicates that the bonding of bridging halogen atoms is quite different from that of terminal halogen. If inductive effects alone were operating, frequencies even lower than those of the compounds (*i*) would be expected for the bridged compounds because of the slightly greater bond lengths of the bridging halogens. It has been suggested that in some molecules *d*-orbitals may be involved in both σ- and π-bonds to halogen atoms.[9] Such a suggestion in this context would be purely speculative but such bonding should be favourable on overlap grounds in view of the fairly large effective nuclear charges which have been postulated.

The extreme rapidity of attack on these bridged complexes by nucleophilic groups, compared with attack on mononuclear complexes (see Part III) also suggests that contributions to the bond strength from platinum π-type orbitals are important here.

N-H frequencies of halogen-bridged ammine complexes are not available and comparison of the effect of terminal and bridging halogen atoms in this case is not possible.

The very high C-O frequencies of the dicarbonyl complex *cis*-$[Pt(CO)_2Cl_2]$ indicate considerable weakening of the Pt-C bond relative to that in the other complexes. Bond weakening due to the chlorine atoms might be expected to be less important here than in the case of the ions (*i*) since there are only two halogens present. It should be noted however, that π-bonding is possible between both the p_z and p_y orbitals of the carbon and the platinum π-type orbitals.[10] Bonding of this type, involving π-components in both the *z* and the *y* direction (the *x* direction being taken through the Pt-C σ-bond), should enhance the bond strength of a single Pt-C-O system by setting up an almost axially symmetrical conjugated Pt-C-O system similar to that in the carbon dioxide molecule. This would not be so if the overlap of the carbon p_z orbital with the $5d_{xz}6p_z$ hybrid of the platinum atom is so important relatively to the overlap of the carbon p_y with the unhybridized $5d_{xy}$ that the bonding is predominantly in the favour of the former, as is sometimes supposed. Overlap calculations seem to indicate that the admixture of the $6p_z$ and $5d_{xz}$ platinum orbitals does not increase bond strength enough to eliminate the possibility of bonding in the *y* direction.[4b] Thus, a *cis*-mesomeric effect, resulting from competition of the two CO groups for platinum d_π-orbitals in the plane of the four σ-bonds, is not only possible but in all probability quite important, the variation in Pt-C bond strength between the compounds (*i*) and the dicarbonyl compound (*a*) being considerable. It is obvious that, though carbon monoxide is only very weakly bonded, the various contributions to the bond strength are each important, though individually small.

Decomposition of Platinum Carbonyl Complexes.—The complicated mechanisms of decomposition by heat and moisture of these compounds have been mentioned by several authors. The stability to heat of the dimers $[Pt(CO)X_2]_2$ increases in the order Cl < Br < I, while the stabilities to moisture follow the reverse order.[11, 12] In general the dimeric compounds are more sensitive to moisture than the monomeric derivatives, the notable exception being the dicarbonyl compound[1, 12] $[Pt(CO)_2Cl_2]$. The behaviour of these compounds to both moisture and heat is difficult to reconcile to relative Pt-C bond strengths as indicated by the spectroscopic data.

Reaction of the dimeric complexes with water results in the liberation of carbon monoxide and carbon dioxide, the relative amounts varying a great deal with the conditions (temperature, relative proportions of water and complex, state of division of the compound, etc.). The proportion of the carbonyl compound actually decomposed (and thus the amount of carbon monoxide and dioxide liberated) is not constant and varying amounts of $[Pt(CO)X_3]^-$ are usually recovered. The latter probably result from the reaction of

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[9] Mulliken, *J. Amer. Chem. Soc.*, 1955, **77**, 884.

[10] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[11] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127; Manchot, *Ber.*, 1925, **58**, 2518.

[12] Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry," George Routledge and Sons, Ltd., London, 1938, p. 406.

as-yet-unchanged $[Pt(CO)X_2]_2$ with the dilute hydrohalic acids produced from the liberation of the hydrogen halides according to the equations:[12]

$$H_2O + [Pt(CO)X_2]_2 \longrightarrow Pt + 2HX + CO_2$$
$$2X^- + [Pt(CO)X_2]_2 \longrightarrow 2[Pt(CO)X_3]^-$$

A semiquantitative determination of the CO_2 : CO ratio for the reaction of water with the various carbonyl compounds was made by carrying out the decompositions in a gas cell fitted with rock-salt windows and examining the infrared spectra after reaction. In general, the more violent the reaction, the greater the proportion of carbon dioxide. Analogous results were obtained when the substances were decomposed by means of ethyl alcohol, acetone, and even diethyl ether, although the reactions were usually less violent, especially in the case of the ether.[4b] With the exception of $[Pt(CO)_2Cl_2]$ none of the carbonyl complexes liberates carbon monoxide on treatment with the hydrohalic acids, but the pH of the decomposing agent does not appear to be the most important factor. Although solutions containing the hydroxide ion cause rapid decomposition, it is noteworthy that neutral solutions of halide ions appear to prevent liberation of carbon monoxide just as well as do solutions of the corresponding acids. It may be that the stability of these complexes in the presence of halide ions is explained by the postulate of the formation of 6-covalent halogen complexes sufficiently robust to prevent attack of the platinum atom. Complexes of this type appear to be reasonably common with platinum(II) though few have been isolated in the solid state.[11]

Palladium Carbonyl Complexes.—An attempt was made to resolve some of the difficulties apparent in the literature of the carbonyl complexes of palladium, but in spite of great care it was not possible to obtain any of the compounds examined in a sufficiently pure state to permit complete characterization. Infrared spectroscopy, however, was reasonably informative.

The compound $Pd(CO)Cl_2$, first reported by Manchot[11] has been assumed to be analogous to $[Pt(CO)Cl_2]_2$, a halogen-bridged dimer. It is extremely sensitive to heat but is only comparatively slowly attacked by moisture. Anderson produced the compound[12] $[Pd(CO)\ en\ Cl][Pd(CO)Cl_3]$, by reaction of ethylenediamine with $Pd(CO)Cl_2$. This type of compound is well known as the product of the reaction of bidentate ligands with halogen-bridged platinum compounds. However, Gelman and Meilakh[13] considered Anderson's compound to be the ethylenediammonium salt of the anion $[Pd_2(CO)_2Cl_4]^{2-}$ although their preparation of the compound was carried out by an entirely different method from different starting materials. We repeated their preparation, namely, by the action of carbon monoxide on a saturated solution of ammonium chloropalladite in hydrochloric acid. A copious yellow precipitate was formed over a period of a week. The time for precipitation could be reduced to a few hours if the carbon monoxide was under moderate pressure.

This yellow precipitate was very unstable when dry, and surface decomposition to palladium was rapid. The partially decomposed product was diamagnetic and it absorbed strongly in the infrared region at 1920 ± 15 cm.$^{-1}$, showing a very wide band. The supposed ethylenediammonium salt prepared from the yellow product by the addition of ethylenediamine hydrochloride absorbed at 2056 cm.$^{-1}$, showing conclusively that the ligand produces a marked change in the structure of the complex and does not merely act as a cation. As a check, ethylenediamine hydrochloride was added to a solution of $[Pd(CO)Cl_2]_2$ in hydrochloric acid, and the spectrum of the resulting precipitate measured. This precipitate and that resulting from the action of anhydrous ethylenediamine on an acetone solution of $Pd(CO)Cl_2$ gave spectra identical with that of Gelman and Meilakh's compound, the infrared absorption being centred at 2056 ± 2 cm.$^{-1}$ in each case. This, and the fact that the absorption of the dimeric $[Pd(CO)Cl_2]_2$ occurs at 1976 cm.$^{-1}$, lead to the conclusion that the yellow compound obtained by Gelman and Meilakh

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[13] Gelman and Meilakh, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 748.

was actually $NH_4^+[Pd(CO)Cl_3]^-$, which reacted with ethylenediamine to give $[Pd(CO)\ en\ Cl]^+[Pd(CO)Cl_3]^-$, as also did the dimer. Each of these reactions is to be expected by analogy with the behaviour of the corresponding platinum complexes.

EXPERIMENTAL

The preparations of the compounds $[Pt(CO)LX_2]$ all involved the action of molar quantities of ligand on the dimeric complexes $[Pt(CO)X_2]_2$. Details are recorded in Parts I [14] and III [1] of this series.

Spectroscopic data were obtained by means of a double-beam single-pass spectrometer for the rock-salt region (νC–O). The instrument was designed and built in the Physical Chemistry Department of the N.S.W. University of Technology. Calibration was accomplished by a polystyrene film. Compounds were measured in the solid state as paraffin mulls and in many cases the measurements were repeated on 1% CCl_4 solutions. On no occasion was there any significant difference between the solid and the solution spectrum.

The spectra in the lithium fluoride (νN–H) and cæsium bromide (νPt–N) regions were obtained on a double-pass single-beam Perkin-Elmer model 112 spectrometer. Calibration in the lithium fluoride region was made from the standard water vapour bands, and in the cæsium bromide region from iodobenzene. The 20° cæsium bromide prisms enabled a lower limit of 250 $cm.^{-1}$ to be reached, and bands separated by as little as 8 $cm.^{-1}$ could be resolved. Measurements in the lithium fluoride region were made on 0·005—0·02M-carbon tetrachloride solutions of the complexes. Thick paraffin mulls supported between cæsium bromide plates were used in the cæsium bromide region.

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[14] Irving and Magnusson, *J.*, 1956, 1860.