New Metal–Ligand Vibrational Correlations for Rh^{I}, Pd^{II}, and Pt^{II} Complexes

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WE have examined the far-infrared spectra (60—500 cm.$^{-1}$) of some planar halide-bridged complexes of the types $[RhX(diolefin)]_2$, $[M_2X_2]_6^{2-}$, and $M_2X_4L_2$, (M = Pd, Pt; X = Cl, Br, I; L = PCl_3, $P(OEt)_3$, PR_3, AsR_3, SR_2, SeR_2, TeR_2, Py, or an olefin). We have also investigated some Pd^{II} complexes containing bridging sulphide groups and some Pt^{IV} compounds. We summarise here our main findings which can be used as correlations.

(i) *Halogen-sensitive vibrations*

As required by theory all the halide-bridged complexes exhibit two bands associated with the MX_2M unit, due mainly to bridge bond stretching. For the Rh^{I} complexes two strong bands of roughly equal width and intensity are found; for Pd^{II} and Pt^{II}, the higher-frequency band is generally medium to strong in intensity and much sharper than the lower band which is intense in the $M_2X_4L_2$ series but may be weak or very weak in $[M_2X_6]^{2-}$. Terminal ν_{M-X} absorption is found up to 20 cm.$^{-1}$ higher than in corresponding *trans*-mononuclear complexes (for chlorides); in the $[M_2X_6]^{2-}$ series the two terminal modes are mostly within 5 cm.$^{-1}$ of each other. The following ranges (in cm.$^{-1}$) hold for the $M_2X_4L_2$ compounds, but also include most of the $[M_2X_6]^{2-}$ frequencies:

		$\nu_{M-X}t$	$\nu_{M-X}b$	
A:	Pt^{II}			
	X = Cl	365—340	335—310	295—250
	Br	260—235	230—210	190—175
	I	200—170	190—150	150—135
B:	Pd^{II}			
	X = Cl	370—345	310—300	280—250
	Br	285—265	220—185†	200—165†

† For most compounds the ranges 195—185 and 182—166 cm.$^{-1}$ hold.

Too few iodides of palladium have been examined to establish a range. The ranges 290—275; 270—260 and 200—185; 185—175 cm.$^{-1}$ hold for chloride and bromide complexes respectively of Rh^{I}.

In *trans*-$[PtX_4L_2]$ compounds, (X = Cl, Br,) a single (e_u) $\nu_{M-X}b$ and is found close to the position characteristic of the corresponding *trans*-$[PtX_2L_2]$. For *cis*-$[PtCl_4L_2]$ compounds a complex pattern containing at least two ν_{Pt-Cl} bands is found in the region 350—330 cm.$^{-1}$ followed by a further strong band at 288—265 cm.$^{-1}$ This pattern clearly corresponds to that found by Beattie and Rule[1] for compounds of the type *cis*-$[SnCl_4L_2]$.

(ii) *Other metal–ligand vibrations*

Goggin and Goodfellow[2] have recently shown that ν_{Pt-P} lies in the range 442—410 cm.$^{-1}$ in *cis*- and *trans*-mononuclear complexes: Coates and Parkin[3] had previously made some more tentative assignments covering a slightly wider range. We support the conclusions of Goggin and Goodfellow because we are led to assign ν_{Pt-P} in a similar region in $[Pt(PEt_3)_4][PtBr_4]$ and $Pt_2Cl_4(PCl_3)_2$. For the former compound, all but three of the bands correlate with known absorption due to $[PtBr_4]^{2-}$ or PEt_3; these are at 389, 200, and 185 cm.$^{-1}$ and we assign them as ν_5, ν_{Pt-P}; ν_6, δ_{Pt-P} and ν_2,π_{Pt-P} respectively. For $Pt_2Cl_4(PCl_3)_2$ we observe six bands in the region 375—320 cm.$^{-1}$, none of which can be due to internal vibrations of the ligand. We cannot unambiguously assign them all but ν_{Pt-P} is probably either at 373 or 346 cm.$^{-1}$ The following correlations for ν_{M-P} are based upon the spectra of our bridge compounds and the data of a previous study.[4]

trans-$[PtX_4(PEt_3)_2]$, *trans*-$[PtX_2(PEt_3)_2]$, and *trans*-$[PtXY(PEt_3)_2]$, a medium-to-strong bond in the range 418—406 cm.$^{-1}$; there is sometimes also a weak component some 4—6 cm.$^{-1}$ to lower frequency.

cis-$[PtX_2(PEt_3)_2]$, and *cis*-$[PtX_4(PEt_3)_2]$ a medium-to-strong doublet with components close to 440 and 425 cm.$^{-1}$

$M_2X_4(PEt_3)_2$, (M = Pd, Pt), a single strong band 450—434 cm.$^{-1}$ It is of particular interest that $Pt^0(PPh_3)_4$ has an intense band at 424 cm.$^{-1}$ which may be due to ν_{Pt-P}.

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[3] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

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