Vibrational Frequencies of New Types of Metal–Metal Bonds

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Summary I.r. stretching frequencies are reported for new metal–metal bonds in the complexes *trans*-$M^1M^2_2L_2$, M^1 = Pt, Pd, M^2 = $Mn(CO)_5$, $Co(CO)_4$, π-$C_5H_5Mo(CO)_3$; L = pyridine, 3-methylpyridine, and 4-methylpyridine.

The compounds reported in the Table have been prepared by the action of the carbonyl anions $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, and $[\pi$-$C_5H_5Mo(CO)_3]^-$, on the substrate, *trans*-ML_2Cl_2 (M = Pt, Pd L = py, 3-Mepy, 4-Mepy).[1] Reaction proceeds *via* a S_N2 mechanism with retention of configuration.[2] The crystal structures of *trans*-$Ptpy_2[Mn(CO)_5]_2$ and *trans*-$Ptpy_2[Co(CO)_4]_2$ [3] confirm the *trans*-square-planar configuration.

With the exception of *trans*-$Ptpy_2Cl[Mo(CO)_3\pi$-$C_5H_5]$, all these compounds contain a linear triatomic chain M^2–M^1–M^2 derived from a square-planar skeleton $M^1M^2_2N_2$ where N represents the donor atom of the ligand. In this case, two types of stretching frequencies would be expected: one i.r.-active asymmetrical vibration $\nu_{as}(M^1$–$M^2)$ and one Raman-active symmetrical vibration.

In the solid state or in solution the products are decomposed by laser radiation and the Raman frequencies measured are uncertain. On the other hand, an unambiguous assignment of $\nu_{as}(M^1$–$M^2)$, can be made by virtue of the position and intensity of the observed band, since all the binding vibrations of the type δ M^2–C–O are found above 300 cm^{-1} and those of the type δ C–M^2–C lie below 120 cm^{-1}.

The measured values of $\nu_{as}(M^1$–$M^2)$ given in the Table appear to be independent of L for the respective pairs of metals represented by M^1 and M^2. The force constant $k(M^1$–$M^2)$ is estimated on the basis of a linear triatomic model[4] in which M^1 corresponds to the mass of Pt or Pd and M^2 = Mn, Co, or Mo. The same trend is observed when allowance is made for the total mass of the M^2 group. However as indicated by Quicksal and Spiro[5] the force constants then appear to be too high. In comparison, the force constants for the analogous mercury compounds M^2–Hg–M^2 are calculated using the same approximation. It is noteworthy that in all of our compounds the force constant is smaller than for the corresponding mercury

Metal–metal frequencies (solid samples) and force constants

Compound	Bond	ν_{as}(M^1–M^2)obs. (cm^{-1})	$k_{M^1M^2}$ (millidynes $Å^{-1}$)
trans-$Ptpy_2[Mn(CO)_5]_2$	Mn–Pt–Mn	155s	0·50
$Pt(3\text{-}Mepy)_2[Mn(CO)_5]_2$		153s	0·48
$Pt(4\text{-}Mepy)_2[Mn(CO)_5]_2$		154s	0·49
$Hg[Mn(CO)_5]_2$[a]	Mn–Hg–Mn	188	0·74
trans-$Pdpy_2[Mn(CO)_5]_2$	Mn–Pd–Mn	149s	0·35
$Pd(3\text{-}Mepy)_2[Mn(CO)_5]_2$		148s	0·35
$Pd(4\text{-}Mepy)_2[Mn(CO)_5]_2$		149s	0·35
trans-$Ptpy_2[Co(CO)_4]_2$	Co–Pt–Co	177s	0·68
$Hg[Co(CO)_4]_2$[b]	Co–Hg–Co	197	0·85
trans-$Pdpy_2[Co(CO)_4]_2$	Co–Pd–Co	168s	0·46
trans-$Ptpy_2[Mo(CO)_3\pi\text{-}C_5H_5]_2$		144w	0·59
$Pt(3\text{-}Mepy)_2[Mo(CO)_3\pi\text{-}C_5H_5]_2$	Mo–Pt–Mo	140m	0·56
$Hg[Mo(CO)_3\pi\text{-}C_5H_5]_2$[c]	Mo–Hg–Mo	178	0·01
trans-$Pdpy_2[Mo(CO)_3\pi\text{-}C_5H_5]_2$	Mo–Pd–Mo	134m	0·36
trans-$Ptpy_2Cl[Mo(CO)_3\pi\text{-}C_5H_5]$	Pt–Mo	142m	

[a] From ref. 7; [b] from ref. 8; [c] from ref. 9.

derivatives. This result indicates a more pronounced anionic character of the metal carbonyl group, and this is reflected in the trend observed for the CO stretching frequencies.[1b]

The force constants of the M^1–M^2 bonds in the compounds *trans*-$Ptpy_2[Mn(CO)_5]_2$, *trans*-$Ptpy_2[Co(CO)_4]_2$, and $Hg[Co(CO)_4]_2$ are inversely proportional to the interatomic distances Pt–Mn 2·74 Å,[3] Pt–Co (2·61 Å),[3] and Hg–Co (2·50 Å).[6] Further, Pd–M^2 bonds are weaker than the corresponding Pt–M^2 bonds.

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