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Force Constant Calculations for In-Plane Vibrations of Planar Platinum(II) and Palladium(II) Halide Anions $[M_2X_6]^{2-}$

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In-plane force constants for the planar halide-bridged anions $[M_2X_6]^{2-}$ (M = Pd or Pt, X = Cl, Br or I) have been calculated on the basis of a modified valence force field model, with some constrained interaction constants taken from earlier work on corresponding $[MX_4]^{2-}$ systems. The terminal stretching force constants are larger than the bridge stretching force constants but the difference diminishes for the heavier halides. The values are compared with those of the monomeric $[MX_4]^{2-}$ systems and it is shown that the relationships correlate with the chemical reactivity of the halide bridges.

Introduction

Halogen bridging is a very common structural feature in inorganic compounds. Although there have been several discussions on the spectroscopic behaviour of terminal and bridging metal–halogen bonds in square planar environments, in very few cases have these included force constant studies. The most widely studied systems have been Au_2Cl_6 [1–4] and I_2Cl_6 [2, 5] for which vibrational assignments have been proposed, based on spectra of the solids, and normal coordinate analyses undertaken.

A simplified force constant calculation for the infrared-active modes of the palladium and platinum anions $[M_2X_6]^{2-}$ (X = Cl, Br or I) [6] has been reported, but now that much more complete vibrational data are available [7], including measurements in solution, a more thorough study is possible.

Normal-coordinate Calculations

X-ray analysis has shown that $[NEt_4]_2[Pt_2Br_6]$ contains planar, halogen-bridged anions with inter-bond angles close to 90° [8, 9] and we shall assume similar geometry for the other anions. The interatomic distances used in the calculations, selected on consideration of published values of other complexes, are listed in Table I.

The vibrations of a D_{2h} ion $[M_2X_6]^{2-}$ have the symmetry properties $4A_g + A_u + 3B_{1g} + 2B_{1u} + 2B_{2g} + 3B_{2u} + B_{3g} + 3B_{3u}$. The A_g and B_{1g} vibrations are the Raman active in-plane modes; the B_{2u} and B_{3u} species relate to the infrared-active in-plane modes. The internal coordinates have been chosen as shown in Figure 1, and the G matrix calculation and force constant refinement procedures used have been outlined previously [10–12].

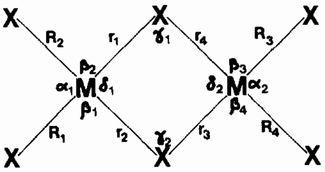

Figure 1. Internal coordinates for planar modes.

TABLE I. Interatomic Distances (pm).

	$[Pd_2X_6]^{2-}$			$[Pt_2X_6]^{2-}$		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
R (MX) terminal	230	240	258	223	241	257
r (MX) bridging	239	244	264	238	243	263

TABLE II. Redundancy Conditions for Planar $[M_2X_6]^{2-}$ Structures.

(1) $\alpha_1 + \beta_1 + \beta_2 + \delta_1 = 0$

(2) $\alpha_2 + \beta_3 + \beta_4 + \delta_2 = 0$

(3) $\gamma_1 + \gamma_2 + \delta_1 + \delta_2 = 0$

(4) $\sigma_b (r_1 - r_2 - r_3 + r_4) + \gamma_1 - \gamma_2 = 0$

(5) $\sigma_b (r_1 + r_2 - r_3 - r_4) + \delta_1 - \delta_2 = 0$

where $\sigma_b = \dfrac{1}{r(MX)}$ for the bridging bonds

There are five redundancy conditions for the in-plane vibrations and these are listed in terms of the internal coordinates in Table II, where the last three expressions arise from the cyclic redundancies in a four-membered ring. The symmetry coordinates for the in-plane modes are given in Table III, which also includes the redundancy conditions in symmetry coordinate terms.

The following internal-coordinate force constants have been considered: (a) stretching, f_R and f_r; (b) *cis* stretch–stretch interactions, f_{RR}, f_{rr}, f_{Rr}, and $f_{rr'}$ (adjacent bonds to different metal atoms);

TABLE III. Symmetry Coordinates for Planar $[M_2X_6]^{2-}$ Structures

A_g

$S_1 = ½(R_1 + R_2 + R_3 + R_4)$

$S_2 = ½(r_1 + r_2 + r_3 + r_4)$

$S_3 = ½(\alpha_1 + \alpha_2) - ½(\beta_1 + \beta_2 + \beta_3 + \beta_4)$

$S_4 = ½(\delta_1 + \delta_2) - ½(\beta_1 + \beta_2 + \beta_3 + \beta_4)$

B_{1g}

$S_6 = ½(R_1 - R_2 + R_3 - R_4)$

$S_7 = ½(r_1 - r_2 + r_3 - r_4)$

$S_8 = ½(\beta_1 - \beta_2 + \beta_3 - \beta_4)$

B_{2u}

$S_{12} = ½(R_1 - R_2 - R_3 + R_4)$

$S_{13} = ½(r_1 - r_2 - r_3 + r_4) - \sigma_b (\gamma_1 - \gamma_2)$

$S_{14} = ½(\beta_1 - \beta_2 - \beta_3 + \beta_4)$

B_{3u}

$S_{16} = ½(R_1 + R_2 - R_3 - R_4)$

$S_{17} = ½(r_1 + r_2 - r_3 - r_4) + ½\sigma_b(\beta_1 + \beta_2 - \beta_3 - \beta_4) - \sigma_b(\delta_1 - \delta_2)$

$S_{18} = ½(\alpha_1 - \alpha_2) - ½(\beta_1 + \beta_2 - \beta_3 - \beta_4)$

Redundant Symmetry Coordinates:

A_g

$½(\alpha_1 + \alpha_2) + ½(\beta_1 + \beta_2 + \beta_3 + \beta_4) + ½(\delta_1 + \delta_2) = 0$

$½(\gamma_1 + \gamma_2) + ½(\delta_1 + \delta_2) = 0$

B_{2u}

$\dfrac{\sqrt{2}}{2}\sigma_b (r_1 - r_2 - r_3 + r_4) + ½(\gamma_1 - \gamma_2) = 0$

B_{3u}

$½(\alpha_1 - \alpha_2) + \dfrac{\sqrt{2}}{2}(\beta_1 + \beta_2 - \beta_3 - \beta_4) + ½(\delta_1 - \delta_2) = 0$

$\dfrac{\sqrt{2}}{2}\sigma_b (r_1 + r_2 - r_3 - r_4) + ½(\delta_1 - \delta_2) = 0$

TABLE IV. Relationship between Symmetry Coordinate and Internal Coordinate Force Constants for Planar $[M_2X_6]^{2-}$ Structures.[a]

A_g

$F_{1\,1} = F_R + f_{RR}$

$F_{2\,3} = -\dfrac{1}{\sqrt{2}} r\, f_{r\beta}$

$F_{1\,2} = f_{Rr'} + f_{Rr}$

$F_{2\,4} = \sqrt{2}\, r\, (f_{r\delta} - \dfrac{1}{2} f_{r\beta})$

$F_{1\,3} = \sqrt{2}\, R(f_{R\alpha} - \dfrac{1}{2} f_{R\beta})$

$F_{3\,3} = R^2 f_\alpha + \dfrac{1}{2} Rrf_\beta - 2R^2 f_{\alpha\beta}$

$F_{1\,4} = -\dfrac{1}{\sqrt{2}} R\, f_{R\beta}$

$F_{3\,4} = \dfrac{1}{2} Rrf_\beta - R^2 f_{\alpha\beta} - r^2 f_{\beta\delta}$

$F_{2\,2} = f_r + f_{rr} + f_{rr'}$

$F_{4\,4} = \dfrac{1}{2} Rrf_\beta + r^2 f_\delta + r^2 f_\gamma - 2r^2 f_{\beta\delta}$

B_{1g}

$F_{6\,6} = f_R - f_{RR}$

$F_{7\,7} = f_r - f_{rr} - f_{rr'}$

$F_{6\,7} = f_{Rr'} - f_{Rr}$

$F_{7\,8} = -rf_{r\beta}$

$F_{6\,8} = R\, f_{R\beta}$

$F_{8\,8} = Rrf_\beta$

B_{2u}

$F_{12\,12} = f_R - f_{RR}$

$F_{13\,13} = f_r - f_{rr} + f_{rr'} + 2\, f_\gamma$

$F_{12\,13} = f_{Rr'} - f_{Rr}$

$F_{13\,14} = -r\, f_{r\beta}$

$F_{12\,14} = Rf_{R\beta}$

$F_{14\,14} = Rrf_\beta$

B_{3u}

$F_{16\,16} = f_R + f_{RR}$

$F_{16\,17} = f_{Rr'} + f_{Rr} + \dfrac{R}{r} f_{R\beta}$

$F_{16\,18} = \sqrt{2}R(f_{R\alpha} - \dfrac{1}{2} f_{R\beta})$

$F_{17\,17} = f_r + f_{rr} - f_{rr'} + 2(f_\delta + \dfrac{1}{2}\dfrac{R}{r} f_\beta - 2\, f_{\beta\delta}) - 4(f_{r\delta} - \dfrac{1}{2} f_{r\beta})$

$F_{17\,18} = -\dfrac{1}{\sqrt{2}} Rf_{R\beta} - \sqrt{2}\,(\dfrac{1}{2} Rf_\beta - \dfrac{R^2}{r} f_{\alpha\beta} - rf_{\beta\delta})$

$F_{18\,18} = R^2 f_\alpha + \dfrac{1}{2} Rrf_\beta - 2R^2 f_{\alpha\beta}$

[a] R = r(MX) terminal and r = r (MX) bridging bond lengths.

TABLE V. Force Constants of $[M_2X_6]^{2-}$ (M = Pd or Pt, X = Cl, Br or I) in Terms of Symmetry Coordinates.†

		$[Pd_2X_6]^{2-}$			$[Pt_2X_6]^{2-}$			Units
		X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	
A_g	$F_{1\,1}$*	1.999	1.531	1.293	2.132	1.978	1.640	a
	$F_{1\,2}$*	0.376	0.064	0.030	0.128	0.233	0.257	a
	$F_{2\,2}$*	1.334	1.336	1.267	1.299	1.280	1.330	a
	$F_{1\,3}$	0.138	0.163	0.177	0.100	0.159	0.175	b
	$F_{1\,4}$	−0.138	−0.163	−0.177	−0.100	−0.159	−0.175	b
	$F_{2\,3}$	−0.144	−0.166	−0.179	−0.103	−0.160	−0.179	b
	$F_{2\,4}$*	−0.091	0.131	0.179†	0.083	0.133	0.179	b
	$F_{3\,3}$	1.382	1.174	0.988	1.472	1.469	1.480	c
	$F_{3\,4}$	0.354	0.255	0.170	0.240	0.281	0.338	c
	$F_{4\,4}$*	1.463	1.252	1.015†	1.822	1.684	1.480	c
B_{1g}	$F_{6\,6}$*	1.705	1.395	1.163	2.003	1.666	1.460	a
	$F_{6\,7}$*	0.062	0.002	0.020	0.223	0.044	0.030	a
	$F_{7\,7}$*	1.031	1.196	1.171	1.345	1.439	1.350	a
	$F_{6\,8}$	0.196	0.230	0.250	0.142	0.224	0.247	b
	$F_{7\,8}$	−0.203	−0.234	−0.256	−0.145	−0.226	−0.252	b
	$F_{8\,8}$	1.061	0.932	0.831	1.253	1.195	1.163	c
B_{2u}	$F_{12\,12}$*	1.705	1.395	1.163	2.003	1.666	1.460	a
	$F_{12\,13}$*	0.062	0.002	0.020	0.223	0.044	0.030	a
	$F_{13\,13}$*	1.113	1.262	1.203	1.479	1.367	1.190	a
	$F_{12\,14}$	0.196	0.230	0.250	0.142	0.224	0.247	b
	$F_{13\,14}$	−0.203	−0.234	−0.256	−0.145	−0.226	−0.252	b
	$F_{14\,14}$	1.061	0.932	0.831	1.253	1.195	1.163	c
B_{3u}	$F_{16\,16}$*	1.999	1.531	1.293	2.132	1.978	1.640	a
	$F_{16\,17}$*	0.458	0.158	0.125	0.187	0.325	0.351	a
	$F_{17\,17}$*	1.583	1.535	1.347	1.791	1.704	1.490	a
	$F_{16\,18}$	0.138	0.163	0.177	0.100	0.159	0.175	b
	$F_{17\,18}$	−0.348	−0.311	−0.268	−0.243	−0.322	−0.356	b
	$F_{18\,18}$	1.382	1.174	0.988	1.472	1.469	1.480	c

*Refined force constants – see text. a = 10^2 N m^{-1}; b = 10^{-8} N rad^{-1}; c = 10^{-18} N m rad^{-2}. †Additional constraints for $[Pd_2I_6]^{2-}$.

(c) *trans* stretch–stretch interaction, $f_{Rr'}$; (d) bending, f_α, f_β, f_γ, and f_δ; (e) stretch–bend interactions, $f_{R\alpha}$, $f_{R\beta}$ and $f_{r\delta}$; (f) bend–bend interactions, $f_{\alpha\beta}$ and $f_{\beta\delta}$. The interactions $f_{r\gamma}$ and those between non-adjacent internal coordinates have been ignored. The correlation between the force constants in internal coordinates and in symmetry coordinates is shown in Table IV. The force constants $F_{13\,13}$, $F_{16\,17}$, $F_{17\,17}$ and $F_{17\,18}$ are the linear combination of stretching and bending internal coordinate force constants in accordance with the cyclic redundancy in the B_{2u} and B_{3u} symmetry species.

Except of $[Pd_2I_6]^{2-}$, ten of the thirteen in-plane modes have been assigned. Thus it is necessary to restrict the number of force constants to be refined. We have assumed $f_\beta = f_\alpha$, $f_{r\beta} = f_{R\alpha} = f_{R\beta}$, and $f_{\alpha\beta} = f_{\beta\delta}$, and have constrained them to values that we have previously computed [13] for the corresponding $[MX_4]^{2-}$ ions. We have also arbitrarily set $f_\delta = ½f_\beta$. In the absence of long distance interactions $F_{1\,1} = F_{16\,16}$, $F_{6\,6} = F_{12\,12}$, $F_{6\,7} = F_{12\,13}$, and $F_{1\,2} = F_{16\,17}$ + a constrained constant.

For $[Pd_2I_6]^{2-}$ we have only assignments for the eight stretching vibrations, and we have no force constants for $[PdI_4]^{2-}$. The constrained force constants $f_\beta = f_\alpha$ are assigned a value based on the trend to heavier halide in the $[PtX_4]^{2-}$ series, scaled to the chloride to bromide trend in $[PdX_4]^{2-}$. Additional

TABLE VI. Experimental and Calculated Fundamental Wavenumbers for Planar $[M_2X_6]^{2-}$ Anions.

		$[Pd_2Cl_6]^{2-}$		$[Pd_2Br_6]^{2-}$		$[Pd_2I_6]^{2-}$		$[Pt_2Cl_6]^{2-}$		$[Pt_2Br_6]^{2-}$		$[Pt_2I_6]^{2-}$	
		obs	calcd	obs	calcd	obs	calcd	obs	calcd	obs	calcd	obs	calcd
A_g	ν_1	346	345.1	262	262.2	219	225.7	349	345.5	241	238.5	196	190.1
	ν_2	302	298.9	194	193.0	143	144.0	316	315.4	211	210.5	160	163.9
	ν_3	169	169.0	115	110.1	–	82.9	162	171.3	116	116.4	93	90.5
	ν_4	119	118.8	83	78.1	–	55.3	108	100.1	84	79.9	60	62.3
B_{1g}	ν_6	328	331.2	253	252.1	219	213.7	333	331.9	238	238.0	196	199.0
	ν_7	265	263.9	173	174.3	130	130.8	294	293.4	193	193.0	145	145.2
	ν_8	–	146.1	–	105.4	–	78.8	–	143.1	–	107.4	–	85.6
B_{2u}	ν_{12}	335	332.0	257	255.1	218	213.9	330	332.0	236	235.0	196	193.3
	ν_{13}	262	263.1	178	173.6	133[a]	131.2	300	302.4	192	188.1	147	139.9
	ν_{14}	–	101.4	–	64.3	–	72.2	–	106.2	–	69.5	–	74.1
B_{3u}	ν_{16}	343	344.7	264	261.0	218	222.9	341	345.9	239	239.7	196	187.0
	ν_{17}	297	299.4	192	189.7	140	139.1	312	311.3	210	210.5	157	158.9
	ν_{18}	–	171.2	–	105.6	–	73.1	–	171.5	–	114.2	–	87.2

[a] Taken from mull spectra.

TABLE VII. Internal Coordinate Force Constants for In-Plane Coordinates in 10^2 N m^{-1}.

	$[Pd_2X_6]^{2-}$			$[Pt_2X_6]^{2-}$		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
f_R	1.852	1.463	1.228	2.067	1.822	1.550
f_r	1.038	1.264	1.199	1.363	1.328	1.222
f_{RR}	0.147	0.068	0.065	0.065	0.156	0.090
f_{rr}	0.210	0.126	0.120	0.078	0.093	0.150
$f_{Rr'}$	0.219	0.033	0.025	0.175	0.138	0.143
f_{Rr}	0.157	0.031	0.005	−0.047	0.094	0.113
$f_{rr'}$	0.086	−0.054	−0.051	−0.142	−0.140	−0.042
$f_\beta = f_\alpha$	(0.193)	(0.159)	(0.122)	(0.227)	(0.204)	(0.172)
f_γ	0.099	0.089	(0.061)	0.168	0.136	0.080
f_δ $(=\frac{1}{2}f_\beta)$	(0.096)	(0.079)	(0.061)	(0.113)	(0.102)	(0.086)
$f_{r\beta} = f_{R\alpha} = f_{R\beta}$	(0.085)	(0.096)	(0.096)	(0.061)	(0.093)	(0.096)
$f_{r\delta}$	0.016	0.086	(0.096)	0.055	0.085	0.096
$f_{\alpha\beta} = f_{\beta\delta}$	(0.016)	(0.018)	(0.018)	(0.035)	(0.027)	(0.018)

constraints $f_\gamma = f_\delta$ $(= \frac{1}{2}f_\beta)$, and $f_{r\delta} = f_{r\beta}$ have been added, and the values derived for $[Pd_2Br_6]^{2-}$ have been utilised as estimates for $f_{r\beta}$ and $f_{\alpha\beta}$. It is appreciated that some of these assumptions are rather arbitrary and this calculation is much less firmly founded than for the other complexes.

The starting set for the refinements is based on the values of the $[MX_4]^{2-}$ force constants [13] (or for $[Pd_2I_6]^{2-}$ a reasonable estimate of them). The force constants which gave the best fit of the experimental frequencies are listed in Table V and the wavenumber agreement shown in Table VI. The average percentage difference between observed and calculated wavenumbers is 1.53, and is 1.12 for stretching vibrations alone; the agreement is best for the chlorides and worst for the iodides. The force constants expressed in terms of the internal coordinates are listed in Table VII.

Discussion

The present work shows a greater difference between terminal and bridging bond force constants than did the previous, limited study [6]. This is in part due to the different wavenumbers from solution measurements, and from the reversal of the assignments of ν_{13} and ν_{17}. It also reflects the more extended form of $F_{13\ 13}$ and $F_{17\ 17}$ used here which leads to a lower dominance of the bridge-bond stretching force constant on these terms.

TABLE VIII. Potential Energy Distribution of Stretching Coordinates for $[Pd_2I_6]^{2-}$ and $[Pt_2Cl_6]^{2-}$ Anions.

Species	Frequency No.	Symmetry Coordinates			
		$[Pd_2I_6]^{2-}$		$[Pt_2Cl_6]^{2-}$	
		S_1	S_2	S_1	S_2
A_g	ν_1	0.45	0.56	0.99	0.04
	ν_2	0.33	0.58	0.01	0.65
		S_6	S_7	S_6	S_7
B_{1g}	ν_6	0.50	0.56	1.02	0.01
	ν_7	0.37	0.64	0.00_4	0.83
		S_{12}	S_{13}	S_{12}	S_{13}
B_{2u}	ν_{12}	0.48	0.56	1.03	0.00_2
	ν_{13}	0.41	0.61	0.01	0.89
		S_{16}	S_{17}	S_{16}	S_{17}
B_{3u}	ν_{16}	0.46	0.58	0.98	0.08
	ν_{17}	0.45	0.62	0.03	0.94

TABLE IX. Comparison between the Stretching Force Constants of Planar $[MX_4]$ Anions [13] and the Mean Stretching Force Constants of Related $[M_2X_6]$ (10^2 N m^{-1}).

	X = Cl	X = Br	X = I
$[PdX_4]^{2-}$	1.534	1.378	1.214
$[Pd_2X_6]^{2-}$	1.445	1.364	
Ratio	1.06	1.01	
$[PtX_4]^{2-}$	1.814	1.637	1.406
$[Pt_2X_6]^{2-}$	1.715	1.575	1.386
Ratio	1.06	1.04	1.01
$[AuX_4]^-$	2.206		
$[Au_2X_6]$	1.951 [4]		
Ratio	1.13		

TABLE X. Terminal (f_t) and Bridge (f_b) Stretching Force Constants of Some M_2X_6 Molecules where M is in a Tetrahedral Environment [4, 17] (10^2 N m^{-1}).

		X = Cl	X = Br	X = I
Al_2X_6	f_t:	2.35	1.767	1.313
	f_b:	1.05	0.801	0.826
Ga_2X_6	f_t:	2.467	1.965	1.237
	f_b:	0.974	0.814	0.813
In_2X_6	f_t:			1.424
	f_b:			0.616

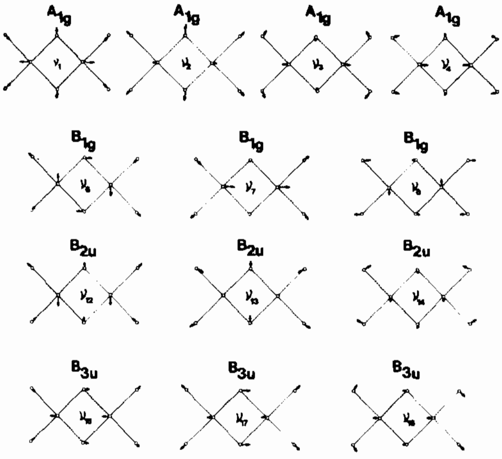

Figure 2. Calculated in-plane normal modes for $[Pd_2Br_6]^{2-}$.

The previous report compared the separations of terminal and bridging frequencies within this series in terms of lower coupling across the heavier metal. However, lower separations would be expected for the platinum systems merely as a result of the greater metal mass.

We have computed potential energy distributions and find that, for a given halide, mixing of the terminal and bridging stretches is less in the platinum complexes, but increases with halide mass in both metal series. For $[Pt_2Cl_6]^{2-}$ there is practically no mixing and assignment of bands as arising from 'terminal' and 'bridging' modes is reasonably valid, whereas in $[Pd_2I_6]^{2-}$ mixing is so substantial that such terms are essentially meaningless; these two cases are compared in Table VIII. Mass weighted Cartesian displacements have also been calculated and these are shown diagrammatically for $[Pd_2Br_6]^{2-}$ in Figure 2. It can be seen that the terminal and bridge bond displacements are similar in a given stretching mode whereas for the chlorides their contributions were quite different. The displacements of the metal atoms are higher for the terminal stretches but the distinction decreases as the halide becomes heavier.

For both the platinum and palladium series the terminal and bridging stretching force constants become closer to each other. Previously, on the basis of relative terminal and bridging stretching frequencies in platinum complexes where ligating atoms carry lone pairs of electrons, we have suggested that a major factor in differentiating terminal and bridging bond strengths is repulsion between the ligating atom lone pairs and filled interaxial d-orbitals of the metal [14, 15]. The force constant trends suggest that the repulsions are less important when the halide becomes larger and its lone pairs more diffuse. In the $[Pt_2X_6]^{2-}$ series, the bridge stretching force constants decrease much less than the terminal ones with increased halide mass.

The terminal stretching force constants of the platinum compounds are 12, 25 and 26 per cent higher than those of the palladium anions for chloride, bromide and iodide respectively, and these differences are broadly comparable with those in $[MCl_4]^{2-}$ and $[MBr_4]^{2-}$ counterparts for which the platinum force constants were 18 and 19 per cent higher respectively.

In the five cases where we can compare stretching force constants in $[MX_4]^{2-}$ and $[M_2X_6]^{2-}$, the former always lie between the terminal and bridging values of the latter. It is of interest to note that where the $[MX_4]^{2-}$ values are significantly above the mean of the terminal and bridging values of $[M_2X_6]^{2-}$ (the PdCl, PtCl and PtBr systems) (Table IX), there were no preparative restrictions on the formation of $[MX_4]^{2-}$ systems. For the palladium bromide and platinum iodide cases, where the $[MX_4]^{2-}$ values are close to the means of $[M_2X_6]^{2-}$, $[MX_4]^{2-}$ anions cannot be formed from $[M_2X_6]^{2-}$ in organic solvents such as acetone or dichloromethane even in the presence of a large excess of $[NBu^n_4]X$. There are numerous other reactions in which the resistance of heavier halide bridges to rupture is greater than lighter halide bridges and one good parallel with the behaviour described above is the reaction of $[M_2X_6]^{2-}$ with trimethylamine where the anions $[MX_3NMe_3]^-$ are formed for PtCl, PtBr, and PdCl systems but not for PtI, PdBr or PdI [16].

Tetrahedral bridged systems Al_2X_6, Ga_2X_6 (X = Cl, Br or I) and In_2I_6 have been studied in some detail [4, 17]. Comparison (Table X) with our results shows that whilst in all the sets the ratio of terminal to bridge stretching decreases as the halide gets more massive, the distinction between terminal and bridging bonds is mostly much greater for the tetrahedral systems.

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