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Force Constant Calculations for the In-Plane Vibrations of Anions $[MX_3CO]^-$ (where MX is PdCl, PdBr, PtCl, PtBr or PtI)

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Force constants for planar complexes $[MX_3CO]^-$ (MX = PdCl, PdBr, PtCl, PtBr and PtI) have been calculated using a modified valence force field, with constrained off-diagonal force constants based on results of $[MX_4]^{2-}$ systems. The resulting stretching force constants are shown to have little dependence on choice of skeletal deformation assignments. The stretching force constants to palladium are lower than to platinum. The difference is more marked for the MC bonds than for MX bonds demonstrating the much weaker π-donor ability of 4d orbitals of Pd(II) than 5d of Pt(II). The relationship between MX force constants in $[MX_4]^{2-}$, $[M_2X_6]^{2-}$ and $[MX_3CO]^-$ is discussed.

Introduction

We have recently recalculated force constants for the square planar $[MX_4]^{2-}$ ions (where MX = PdCl, PdBr, PtCl, PtBr and PtI) using data from solution studies of infrared and Raman spectra in most instances [1]. We have also studied force constants in the dimeric anions $[M_2X_6]^{2-}$ (where M = Pd or Pt, X = Cl, Br or I) on a similar basis [2]. We have just completed a detailed study of the vibrational spectra of the closely related complexes $[MX_3CO]^-$ (where MX = PdCl, PdBr, PtCl, PtBr or PtI) in solution [3] and now present force constant calculations for these species. The main interest lies in the way in which stretching force constants vary between closely related compounds and we confine our attention to studies of the in-plane vibrations.

Normal Coordinate Calculations

The internal coordinates used are shown in the Figure. The G matrix calculations and force constant refinement procedures used have been outlined previously [4–6]. The non-redundant valence symmetry coordinates are listed in Table I. The relationship between force constants in symmetry coordinate terms and those in internal coordinate terms is shown in Table II.

There are nine in-plane vibrations for these complexes, $5A_1 + 4B_1$ and we are restricted to determining the nine diagonal force constants in the symmetry coordinate representation, and are forced to

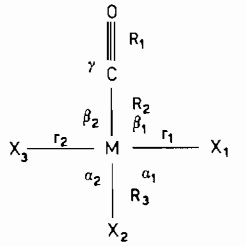

Figure. Internal coordinates for planar $[MX_3CO]^-$ anions.

TABLE I. Internal Valence Symmetry Coordinates for In-Plane Vibrations of Planar $[MX_3CO]^-$ Species.

A_1	$S_1 = \Delta R_1$	B_1	$S_6 = \Delta\gamma$
	$S_2 = \Delta R_2$		$S_7 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$
	$S_3 = \Delta R_3$		
	$S_4 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$		$S_8 = \frac{1}{2}(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\beta_1 - \Delta\beta_2)$
	$S_5 = \frac{1}{2}(\Delta\alpha_1 + \Delta\alpha_2 - \Delta\beta_1 - \Delta\beta_2)$		$S_9 = \frac{1}{2}(\Delta\alpha_1 - \Delta\alpha_2 - \Delta\beta_1 + \Delta\beta_2)$

TABLE II. Relationships between Force Constants in Symmetry Coordinate Representation and Those in Internal Coordinate Representation.

A_1 *Species*	B_1 *Species*
$F_{11} = f_{R_1}$	$F_{66} = R_1R_2f_\gamma$
$F_{22} = f_{R_2}$	$F_{77} = f_r - f_{rr}$
$F_{23} = f_{R_2R_3}$†	$F_{78} = \frac{1}{\sqrt{2}} r(f_{r\alpha} + f_{r\beta})$†
$F_{24} = \sqrt{2} f_{R_2r}$†	$F_{79} = \frac{1}{\sqrt{2}} r(f_{r\alpha} - f_{r\beta})$†
$F_{25} = -R_2f_{R_2\beta}$†	$F_{88} = \frac{1}{2} [rR_3f_\alpha + rR_2f_\beta - rR_3f_{\alpha\alpha} - R_2^2f_{\beta\beta} + 2r^2f_{\alpha\beta}]$
$F_{33} = f_{R_3}$	$F_{89} = \frac{1}{2} [rR_3f_\alpha - rR_2f_\beta - rR_3f_{\alpha\alpha} + R_2^2f_{\beta\beta}]$†
$F_{34} = \sqrt{2} f_{R_3r}$†	$F_{99} = \frac{1}{2} [rR_3f_\alpha + rR_2f_\beta - rR_3f_{\alpha\alpha} - R_2^2f_{\beta\beta} - 2r^2f_{\alpha\beta}]$
$F_{35} = R_3f_{R_3\alpha}$†	
$F_{44} = f_r + f_{rr}$	
$F_{45} = \frac{1}{\sqrt{2}} r(f_{r\alpha} - f_{r\beta})$†	
$F_{55} = \frac{1}{2} [rR_3f_\alpha + rR_2f_\beta + rR_3f_{\alpha\alpha} + R_2^2f_{\beta\beta} - 2r^2f_{\alpha\beta}]$	

TABLE III. In-Plane Force Constants of $[MX_3CO]^-$ Anions (where MX = PtCl, PtBr, PtI, PdCl and PdBr) in Symmetry Coordinate Representation.

Species	*Force Constant*	*MX = PdCl*	*PtBr*	*PtI*	*PdCl*	*PdBr*	
A_1	F_{11}	16.45	16.33	16.13	17.58	17.36	a
	F_{22}	3.90	3.90	3.83	2.36	2.37	a
	F_{23}	0.28	0.22	0.19	0.17	0.15	a†
	F_{24}	0.11	0.09	0.10	0.13	0.10	a†
	F_{25}	−0.11	−0.16	−0.17	−0.15	−0.17	b†
	F_{33}	2.13	1.83	1.56	1.83	1.64	a
	F_{34}	0.11	0.09	0.10	0.13	0.10	a†
	F_{35}	0.14	0.22	0.25	0.20	0.23	b†
	F_{44}	2.21	1.98	1.72	1.96	1.70	a
	F_{55}	0.98	0.88	0.92	0.83	0.64	c
B_1	F_{66}	0.60	0.63	0.62	0.43	0.48	c
	F_{77}	1.83	1.68	1.49	1.62	1.51	a
	F_{78}	0.20	0.31	0.35	0.28	0.33	b†
	F_{88}	0.90	0.69	0.58	0.97	0.57	c
	F_{89}	0.11	0.12	0.15	0.11	0.10	c†
	F_{99}	0.92	0.55	0.49	0.77	0.43	c
Bond lengths used (pm).							
	R_1	114	114	114	114	114	
	R_2	176	176	176	176	176	
	R_3	232	241	259	232	242	
	r	230	239	257	230	240	

Units: a = 10^2N m^{-1}; b = 10^{-18}N m rad^{-2}; c = 10^{-8}N rad^{-1}.
† Constrained values, see text.

constrain all the non-diagonal terms. We have ignored all interaction constants to the CO group and thus entries F_{12}, F_{13}, F_{14}, F_{15}, F_{67}, F_{68}, and F_{69} are set to zero. In order to constrain F_{23}, we have assigned $F_{R_2R_3}$ the value of the *trans* stretch–stretch interaction constant [1] of $[MX_4]^{2-}$ except in the case of $[PtI_4]^{2-}$ where an arbitrary value of 0.19 was chosen because the calculations on $[PtI_4]^{2-}$ had been forced to rely on solid as well as solution state data and this had led to a slight discontinuity in the trend between the different halides. This constraint is admittedly not ideal since the nature of the bonds involved is not the same. We have constrained f_{R_2r} and f_{R_3r} to the value of the *cis* stretch–stretch interaction constant of $[MX_4]^{2-}$. The values of $f_{r\alpha} - f_{r\alpha'}$ of $[MX_4]^{2-}$ have been adopted for all the stretch–bend interactions about the metal, $f_{R_2\beta}$, $f_{R_3\alpha}$, $f_{r\alpha}$ and $f_{r\beta}$; this means that F_{45} and F_{79} become zero.

The above assumptions cater for all off-diagonal terms except F_{89}. To get a reasonably realistic estimate for this term we have used the values of $f_\alpha - f_{\alpha\alpha'}$ from $[MX_4]^{2-}$ for both f_α and f_β, and $f_{\alpha\alpha} - f_{\alpha\alpha'}$ from $[MX_4]^{2-}$ for both $f_{\alpha\alpha}$ and $f_{\beta\beta}$; it should be noted that the equalities $f_\alpha = f_\beta$ and $f_{\alpha\alpha} = f_{\beta\beta}$ have not been assumed when these terms appear in diagonal elements. Reasonable bond lengths were assumed on the basis of the range of values published for comparable bonds, and the MX (*trans* to CO) bond assigned a value 2 pm greater than that assigned to the MX bonds *trans* to each other; the values are listed in Table III.

Initial values for the force constant refinements were taken from the $[MX_4]^{2-}$ results and, for terms involving thc CO groups, from a previous study on these complexes [7]. The final refined values in symmetry coordinate terms are listed in Table III.

The assignment of ν_9 [3] is not regarded as conclusive and in the refinement it was given a weighting of 0.2 relative to the other modes to avoid distorting the whole calculation if it is in error. In arriving at a final result for the CO stretching force constant we have used both the ^{12}CO and ^{13}CO stretching wavenumbers, and the result represents the compromise least squares fit of the calculated and observed wavenumbers when ν_1 is the only mode sensitive to the carbon mass. The agreement between the wavenumbers calculated from the force constants and the experimental assignments [3] is given in Table IV. It is seen that the wavenumber correspondance is good except for the two B_1 deformation modes about the metal, ν_8 and ν_9, which cannot be calculated as close together as this assignment requires. Because this problem could be the result of erroneous assignments and since it is of interest to examine the extent to which the stretching force constants depend on the wavenumber assignments of deformations, we have examined $[PtCl_3CO]^-$ using different deformation assignments. We have used $\nu_5 = 152$, $\nu_8 = 166$, $\nu_9 = 131$ and $\nu_5 = 166$, $\nu_8 = 152$ and $\nu_9 = 131$ cm^{-1}. The symmetry coordinate force constants and calculated frequency results are given in Table V and it is clear that the overall wavenumber agreement is best for the first of these two alternative assignments. However there is little doubt that the infrared intensity associated with the lowest frequency primarily arises from an out-of-plane vibration and in most of the other cases there are so few deformation frequencies observed that such choice in assign-

TABLE IV. Assignment Used and Wavenumbers Calculated in Force Constant Studies on Planar $[MX_3CO]^-$ Anions.

		Pt–Cl		Pt–Br		Pt–I	
	Species	*Ass.*	*Calc.*	*Ass.*	*Calc.*	*Ass.*	*Calc.*
ν_1	A_1	2096.5	2099	2089.5	2092	2078	2079
ν_1*		2050	2047	2043	2040	2029	2028
ν_2		497	497	496	496	492	492
ν_3		345	345	227	227	178	178
ν_4		322	321.5	204	204	150	150
ν_5		152	150.5	100	100	80	80
ν_6	B_1	540	542.5	525	525	510	510
ν_7		344	344	246	246	202	202
ν_8		166	178	100	102	80	88
ν_9		152	129	100	96	80	67
		Pd–Cl		Pd–Br			
		Ass.	*Calc.*	*Ass.*	*Calc.*		
ν_1	A_1	2131	2133	2119	2121		
ν_1*		2084	2082	2072	2070		
ν_2		416	416	413	413		
ν_3		331	331	230	230		
ν_4		300	300	189	189		
ν_5		146	146	90	90		
ν_6	B_1	475	478	462	463		
ν_7		350	350	267	267		
ν_8		157	171	90	92		
ν_9		146	129	90	87.5		

$\nu_1^* = \nu_{^{13}CO}$ stretch.

TABLE V. Diagonal Force Constants for In-Plane Modes of $[PtCl_3CO]^-$ in Symmetry Coordinate Representation, Based on Different Skeletal Bending Assignments.

		Set 1	*Set 2*	
A_1	F_{11}	16.45	16.45	a
	F_{22}	3.90	3.90	a
	F_{33}	2.13	2.12	a
	F_{44}	2.21	2.21	a
	F_{55}	0.98	1.18	c
B_1	F_{66}	0.59	0.61	a
	F_{77}	1.83	1.83	a
	F_{88}	0.70	0.54	c
	F_{99}	1.07	1.06	c

Assigned Wavenumbers

		Expt.	*Calc.*	*Expt.*	*Calc.*
A_1	ν_1	2096.5	2099.2	2096.5	2099.2
	ν_1*	2050	2047.3	2050	2047.3
	ν_2	497	497	497	497
	ν_3	345	345	345	345
	ν_4	322	321.5	322	321.5
	ν_5	152	150.5	166	165.2
B_1	ν_6	540	540	540	540.6
	ν_7	344	344	344	344
	ν_8	166	166	152	156.8
	ν_9	131	131	131	122.7

Units: a = 10^2N m^{-1}; c = 10^{-8}N rad^{-1}. Constrained off-diagonal force constants are as in Table III.

TABLE VI. Some In-Plane Force Constants (10^2N m^{-1}) of $[MX_3CO]^-$ Anions in Internal Coordinate Representation.

	MX = PtCl	*PtBr*	*PtI*	*PdCl*	*PdBr*
f_{R_1}	16.45	16.33	16.13	17.58	17.36
f_{R_2}	3.90	3.90	3.83	2.36	2.37
f_{R_3}	2.13	1.83	1.56	1.83	1.64
f_r	2.02	1.83	1.60	1.79	1.61
f_{rr}	0.19	0.15	0.11	0.17	0.10
$f_{\alpha\beta}$	0.00	0.01	0.01	0.02	0.01
f_γ	0.30	0.31	0.31	0.22	0.24
Constrained values					
$f_{R_2R_3}$	0.28	0.22	0.19	0.17	0.15
$f_{R_2r} = f_{R_3r}$	0.08	0.06	0.07	0.09	0.07
$f_{R_2\beta} = f_{R_3\alpha} = f_{r\alpha} = f_{r\beta}$	0.06	0.09	0.10	0.09	0.10
Values constrained in F_{89} of Table III only					
$f_\alpha = f_\beta$	0.23	0.20	0.17	0.19	0.16
$f_{\alpha\alpha} = f_{\beta\beta}$	0.04	0.03	0.02	0.02	0.02

ment is not possible; the ease of fitting one of the choices of deformation assignment may be a reflection on the constrained values of the interaction constants (to angles) that it has been necessary to use. What is certainly more interesting and important is that the terms involving stretching force constants (F_{11}, F_{22}, F_{33}, F_{44} and F_{77}) are not sensitive to the choice of deformation assignments in these cases where the deformation wavenumbers are no more than about half those associated with the stretching modes.

From the form of the expressions in Table II it will be seen that it is not possible to obtain values for all the individual internal coordinate force constants concerned with bending about the metal, indeed only $f_{\alpha\beta}$ may be determined. Table VI lists those internal coordinate force constants which may be evaluated together with the constrained values employed in the calculation.

Discussion

As appears usual from our studies of $[MX_4]^{2-}$ and $[M_2X_6]^{2-}$, stretching force constants [1, 2] for bonds from platinum(II) to a given halide are significantly larger than those from palladium(II). In $[MX_3CO]^-$ the mutually *trans* MX bonds have values 16 and 12 percent higher, and those *trans* to CO 13 and 14 percent higher for the chloride and bromide respectively. These differences are of similar order to those between platinum and palladium anions $[MX_4]^{2-}$ and $[M_2X_6]^{2-}$ where they ranged from 2 to 32 percent. Since bond lengths in corresponding species of the two metals are similar, this must largely be due to better overlap of the 5d orbital than the 4d in its contribution to σ-bonding, resulting in increases covalency.

The Pt–C stretching force constants are some 65 percent greater than Pd–C. The behaviour of the CO stretching force constant demonstrates the greater degree of π donation from the metal in the platinum case, but the much greater proportionate change in the M–C force constant must be the result of both the increased σ covalency and the increased degree of π bonding in the Pt–C bond.

In the platinum series the relationship between the two types of bond to halide shows a reversal from chloride to iodide, and implies that CO displays a *trans* influence [8] comparable with bromide.

With one exception for $PdCl_3CO^-$, our calculations show a stretching force constant relationship $[MX_4]^{2-}$ < terminal MX in $[M_2X_6]^{2-}$ < *trans* MX_2 in $[MX_3CO]^-$. The increase with decreasing overall negative charge is hardly surprising, and the relationship between $[Pt_2X_6]^{2-}$ and $[PtX_3CO]^-$ is consistent with the CO ligand being a net abstractor of electronic charge leaving the metal somewhat more positive.

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