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The *cis*-Effect in *trans*-[$PtCl_2XY$] Compounds

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The *cis*-influence observed in chlorine NQR data of X, Y affecting the Pt–Cl bonds in compounds of type *trans*-[$PtCl_2XY$] is interpreted. σ-bonding differences in Pt–Cl bonds are suggested to account for the trends in NQR frequencies. Pt–Cl π-bonding is negligibly small for both $d_\pi(Pt) - p_\pi(Cl)$ and $p_\pi(Pt) - p_\pi(Cl)$ interactions.

Introduction

A number of weak ^{35}Cl nuclear quadrupole resonances have recently been reported [1] for compounds of type *trans*-[MCl_2XY], M = Pd or Pt. Data for Pt compounds are compiled in the Table. This *cis*-effect of X or Y influencing the M–Cl bond has been invoked before [1]. However, an explanation of how the effect is operative has not been offered. For example, the origin of the *cis*-effect at chlorine might arise through the σ-bonding and/or π-bonding in the M–Cl bonds, in the M–X, Y bonds, or in both bonds. Thus, a fundamental analysis of these possibilities appears in order. We report here an LCAO-MO interpretation of the *cis*-effect for planar d^8 compounds of type *trans*-[$PtCl_2XY$] based on experimental chlorine NQR data. The interpretation also relates to the entire electronic structure of these complex types.

The Pt compounds of the Table are arranged in the order of increasing resonance frequency, $\nu(^{35}Cl)$. The resonances are high when X, and/or Y, in [$PtCl_2XY$] is a potential π-acceptor and low when this is not the case. Therefore, we compared the bonding in $[PtCl_4]^{2-}$ and $[PtCl_3(C_2H_4)]^-$ in order to understand the differences in the Pt–Cl bonds.

Results and Discussion

NQR [2] and computational [3] results for K_2PtCl_4 have been obtained previously. Zeise's salt $K[PtCl_3(C_2H_4)] \cdot H_2O$ has been the subject of several investigations [4–6] which have partly illucidated the ground electronic state of this interesting anion, $[Pt(C_2H_4)Cl_3]^-$.

Semi-empirical LCAO-MO calculations with a full valence atomic orbital basis set (Pt: 5*d*, 6*s*, 6*p*; Cl: 3*s*, 3*p*; C: 2*s*, 2*p*; H: 1*s*) were carried out here for the Zeise anion using two sets of Pt–Cl bond distances. For the first calculation a slightly longer *trans* Pt–Cl bond than *cis* Pt–Cl bond was assumed. The 33 × 33 overlap matrix for the secular determinant $|F - \varepsilon S| = 0$ was constructed using STO's from

Table. ^{35}Cl NQR *frequencies in compounds, trans*-$[PtCl_2XY]$

X	Y	ν(MHz)	Temp. (°C)	Ref.
NH_3	NH_3	17.30	0	[1]
Cl	Cl	17.93	0	[2][a]
$NHMe_2$	$NHMe_2$	18.16	0	[1]
py	py	19.63	0	[1]
ethylene	Cl	20.09 20.29	23	this paper[b, c]
PEt_3	PEt_3	20.99	0	[1]
$P(n\text{–}Bu)_3$	$P(n\text{–}Bu)_3$	20.90 21.04 21.08	0	[1]

[a] K_2PtCl_4.

[b] $K[Pt(C_2H_4)Cl_3] \cdot H_2O$.

[c] One or both frequencies are ^{35}Cl resonances of atoms *cis* to ethylene in $K[PtCl_3(C_2H_4)] \cdot H_2O$. We have observed frequencies (MHz) for this salt at 20.29 ($S/N = 10:1$), 20.09 ($S/N = 6:1$), and at 16.02 ($S/N = 3:1$), 15.96 ($S/N = 7:1$), and 15.83 ($S/N = 3:1$). While the 20 MHz frequencies certainly belong to ^{35}Cl on the basis of intensity arguments, the 15.96 MHz signal may also be one of these. This was pointed out by Prof. T. L. Brown (Univ. of Illinois) who is currently investigating a number of Pt-olefin complexes containing both bromine and chlorine atoms in order to clarify this point in question.

the literature (Pt, Cl: Ref. [3]; C: Ref. [7]; and H: $1s = 1.2$). Diagonal Hamiltonian matrix elements for orbitals of neutral atoms were employed from Refs. [3] (Pt, Cl); [7] (C); and $1s(H) = -13.60$ eV. They were corrected 1 eV per unit charge. Off-diagonal elements were calculated using $F_{ij} = l/2\, S_{ij} K (F_{ii} + F_{jj})$ with $K = 1.9$. The eigenvalue-eigenvector computations were carried out repeatedly until self-consistent charges and orbital occupations resulted.

We obtained the following charge distribution when carrying out the complete population analysis [8] in the oblique basis: Pt + 0.617, Cl(*cis*) – 0.520, Cl(*trans*) – 0.540, C – 0.210, H + 0.095. Due to the equal division of bond overlap populations between atoms when calculating charges, it is more meaningful to compare overlap populations for this non-orthogonal basis. Bond overlap populations between Pt and *cis* and *trans* chlorine atoms are 0.511 and 0.432, respectively. These results indicate that Cl(*cis*) and Cl(*trans*) have different electronic environments, and that Cl(*trans*) is bound more ionically. A closer look at the overlap population results shows that only a negligible amount of π-bonding occurs in both the Pt–Cl(*cis*) and Pt–Cl(*trans*) bonds relative to the σ-bonding; (Pt–Cl(*cis*): $\sigma = 0.515$, $\pi = -0.004$; Pt–Cl(*trans*): $\sigma = 0.438$, $\pi = 0.006$). A similar observation regarding the negligibility of Pt–Cl π-bonding was made for the closely related tetrachloroplatinate (II) anion [3]. In passing, *we conclude, therefore, that the trans-effect of* C_2H_4 *in Zeise's anion is primilarily a σ-effect*[1]. It must be kept in mind, however, that the origin of bond *differences* in Pt–Cl(*cis*) and Pt–Cl(*trans*) relates to the nature of both the *trans*-effect as well as the *cis*-effect of ethylene.

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[1] A limited basis calculation has led to a π-effect interpretation of the *trans*-effect [Moore, J. W.: Acta chem. scand. **20**, 1154 (1966)].

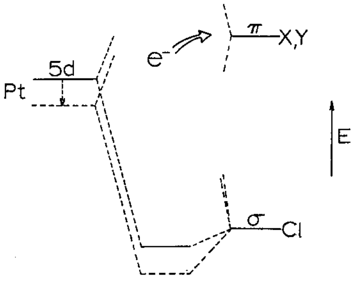

Fig. 1. The effect on the Pt–Cl covalency due to the presence of π-acceptor ligands X, Y in *trans*-[$PtCl_2XY$]. The dotted levels represent increasing Pt–Cl covalency in the presence of X, Y

For symmetry reasons alone the *cis*-effect of ethylene can arise here only through σ-bonding ($6p_\pi(Pt) - 3p_\pi(Cl)$ overlap population is negligible, i.e., about -0.001). On the basis of this and the computational results, both the *cis*-effect and the *trans*-effect of ethylene appear to arise through σ-bonding within the $PtCl_3$ part of the Zeise anion. Of course, both σ- and π-bonding are present in the Pt–C_2H_4 bond of the anion, which is reflected in our overlap populations.

The results for Zeise's anion may be compared with those of $[PtCl_4]^{2-}$ which lacks a π-acceptor such as C_2H_4. The Pt–Cl bonds are more ionic in the latter complex ion than in the Zeise anion based on the Pt–Cl overlap populations [3] (~0.4 for $[PtCl_4]^{=}$ and 0.511 for Pt–Cl(*cis*) of $[PtCl_3(C_2H_4)]^-$). From this comparison one predicts a qualitatively lower NQR frequency for Cl in $[PtCl_4]^{2-}$, which is consistent with the experimental observation [2] (Table).

Similar results for $[PtCl_3(C_2H_4)]^-$ were obtained from a second calculation in which all three Pt–Cl bond distances were taken to be the same (2.26 Å)[2]. Using bond overlap populations as a criterion again, both *cis* and *trans* Pt–Cl bonds were found to be more covalent than in $[PtCl_4]^{2-}$, which has no π-acceptor attached to Pt. The Pt–Cl(*cis*) bond overlap population is 0.504 and is again larger than the ~0.4 of $[PtCl_4]^{2-}$, but similar to the 0.511 of the calculation.

The above discussion and the data in the Table lead us to offer the following simple interpretation of the NQR results. First, the platinum atoms in compounds *trans*-[$PtCl_2XY$] with X and/or Y capable of π-bonding will suffer loss of Pt electron charge by $Pt(d_\pi) \rightarrow X, Y(\pi)$ bonding. This leaves Pt more positive, as is reflected in present results. In turn, this will cause the formation of more covalent Pt–Cl bonds through σ-bonding (see Fig. 1). Finally, the trend of ^{35}Cl resonance frequencies is expected to follow relative Pt–Cl covalency.

This interpretation is also expected to be operative for Pd analogs of the *trans*-[$PtCl_2XY$] ion. The limited available data confirm this anticipation [1].

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[2] For the first calculation these bond distances were employed: Pt–Cl (*cis*) = 2.26 Å, Pt–Cl (*trans*) = 2.40 Å; also, C–H = 1.08 Å, and < (HCH) = 120°; $PtCl_3$ is planer.

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