ESCA Studies of Square-planar Platinum Complexes; Correlations with Nuclear Quadrupole Resonance Studies

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A correlation has been established between the molecular core binding energy of chlorine in square-planar platinum chlorides and their ^{35}Cl n.q.r. frequencies. This is used, together with measured core binding energies, to discuss structure and bonding in Zeise's salt and its analogues.

In a communication of preliminary results from studies of platinum and palladium complexes[1] we illustrated the usefulness of ESCA or X-ray photoelectron spectroscopy (x.p.s.) in obtaining information concerning the overall charge distribution in such molecules. One aspect of this, measurement of shifts in liganded chlorine binding energies, gave information on the *trans*-influence in square-planar complexes and indicated how bridging and terminal chlorines in dinuclear species could be distinguished. In assigning the binding energies to bridging and terminal chlorines we used the fact that a qualitative correlation between Cl binding energies and ^{35}Cl n.q.r. frequencies is expected (see below). It is of interest, therefore, to examine this correlation more closely.

^{35}Cl N.q.r. frequencies have recently been reported[2,3] for a number of complexes of the type L_2MCl_2 ($M =$ Ni^{II}, Pd^{II}, and Pt^{II}) and for various dimeric Pt^{II} complexes with chlorine in terminal and bridging situations. We have obtained ESCA data on many of these complexes, in most cases using the same samples.

Spectra were measured on an A.E.I. ES100 electron spectrometer by use of Mg-$K_{\alpha1,2}$ radiation. Samples were studied as thin films on a gold backing when solubilities in suitable solvents ($CHCl_3$ or CH_2Cl_2) were satisfactory and/or as powders pressed on Scotch tape. Relative binding energies obtained in either case were always within the estimated experimental error ($\pm$0·20 eV) but sample charging had considerable and variable effect on the 'absolute' binding energies.

Previous studies in this laboratory have shown that sample charging effects can effectively be eliminated by studying samples as very thin films on a conducting backing such as gold. This is only the case, however, for films sufficiently thin for a signal still to be observed from the gold $4f$ core levels and, from published data on escape depths, the required film thicknesses are almost certainly $<$40 Å.[4] In this situation with the sample having a high surface area sufficient charge carriers are obviously available from the gold backing to ensure overall electroneutrality of the sample under the conditions of the measurement, and sample charging effects are thereby obviated. With thicker films (produced from both involatile samples by deposition from solution or by melting directly on gold, and from volatile samples condensed on gold on a cryogenic tip), we have found quite substantial charging effects.

In this discussion, therefore, we confine our attention to those complexes which can be compared directly through use of an 'internal reference level'. The C(1s) level from alkyl or aryl groups on polyatomic ligands (*e.g.*, R_2S or R_3P) can be used in this capacity since charge migration to or from the ligand has little effect on any individual carbon atom (it being spread over many centres) and within experimental error the binding energy can be taken to be constant at 284·7 eV.

Chlorine binding energies [from the Cl($2p_{2/3}$) level] and associated ^{35}Cl n.q.r. frequencies are shown in Table 1. Results for some of these complexes have been quoted previously.[1] Owing to an arithmetic error the Cl($2p_{3/2}$) binding energies in ref. 1 are 1 eV too high; this does not affect the results discussed therein since these depend upon differences in binding energies. Improvements in sensitivity and resolution have allowed us to make more accurate measurements of chlorine binding energies and these updated results are shown in Table I.

TABLE 1

Complex	$^{35}\nu$ [a] / MHz	Cl($2p_{3/2}$) B.E.[e] / eV
β-$(Pr^n{}_3P)_2Pt_2Cl_4$	22·36 [a]	198·2
	15·46 [c]	197·0
β-$(Pr^n{}_3P)_2Pt_2(SCN)_2Cl_2$	21·50	198·0
cis-$(Bu^n{}_3P)_2PtCl_2$	17·84	197·4
trans-$(Bu^n{}_3P)_2PtCl_2$	21·0	197·8
cis-$(Et_2S)_2PtCl_2$	19·2 [d]	197·6
trans-$(Et_2S)_2PtCl_2$	20·3 [d]	197·8
(bipy)$PtCl_2$	18·98	197·5
cis-$(Ph_3P)_2PtCl_2$	19·8 [d]	197·6
trans-$(py)_2PtCl_2$	19·62	197·6
trans-$(Ph_3P)_2Pt$,HCl		197·0
trans-$(PhMe_2P)_2Ph$,HCl	14·43	

[a] Data from refs. 2 and 3 unless otherwise stated. [b] Terminal chlorine. [c] Bridging chlorine. [d] C. W. Fryer (unpublished results). [e] Estimated accurate to $\pm$0·20 eV.

In the electrostatic potential model developed by Siegbahn and his co-workers,[5] shifts in core binding energies can be related to the charge distribution by equation (1) where $E_0{}^i$ is a reference level and the

$$E^i = E_0{}^i + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}} \qquad (1)$$

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[1] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.

[2] C. W. Fryer and J. A. S. Smith, *J. Chem. Soc.* (*A*), 1970, **7**, 1029.

[3] C. W. Fryer, *Chem. Comm.*, 1970, 907.

[4] Y. Baer, P. F. Heden, J. Hedman, M. Klasson, and C. Nordling, *Solid State Comm.*, 1970, **8**, 1479.

[5] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and T. Baer, 'ESCA Applied to Free Molecules,' North Holland, Amsterdam, 1969.

second term represents the potential from the charge at the atom considered. The third term is an intramolecular Madelung-type potential and accounts for the potential from charges in the rest of the molecule. In general the shift in binding energy of a given core level [*e.g.*, Cl($2p_{3/2}$) considered here] is dominated by the charge on the atom concerned, the potential from other atoms being much smaller and opposite in sign. In the closely related series of molecules described here, therefore, the shifts in a given core level will in some measure reflect differences in charge distribution.

The Townes–Dailey approximation[6,7] leads to an expression for the ^{35}Cl n.q.r. frequency of the form (2)

$$^{35}\nu = [(1 - S)\sigma - \tfrac{1}{2}\pi]e^2Qq_{At}/2h \qquad (2)$$

where chlorine employs a $3p_z$ orbital in a σ bond of covalent character σ and its $3p_x$ and $3p_y$ orbitals in π bonds of covalent character π. S is the degree of hybridisation of the 3s with the $3p_z$ orbital and e^2Qq_{At}/h is the quadrupole coupling constant for the free chlorine atom. If it is assumed that chlorine hybridisation changes for closely related complexes can be neglected (ref. 2 and refs. therein) [*i.e.*, $\Delta(1 - S) = 0$] and participation by chlorine in π-bonding is not significant (*i.e.*, $\pi = 0$) then equation (2) reduces to (3) where c is a

$$^{35}\nu = c\sigma \qquad (3)$$

constant. Thus, decreasing population of the $3p_z$ orbital on chlorine (decreasing negative charge; increasing σ) gives increasing n.q.r. frequencies and, from equation (1) increasing binding energies. In this series of complexes, therefore, a relationship might be expected between $^{35}\nu$ and Cl($2p_{3/2}$) binding energy. Figure 1 shows a plot of n.q.r. frequency against binding energy.

The expected increase of $^{35}\nu$ with increase in Cl($2p_{3/2}$) binding energy is clearly shown even though the change in binding energy is <1·5 eV. The many simplifications introduced in the above theory being borne in mind, the correlation is surprisingly good ($R^2 = 0{\cdot}96$).

The two n.q.r. frequencies observed for *trans*-$(Et_3P)_2$-Pt_2Cl_4 fall at the extremes of the curve. It is reasonable to assign the higher frequency to the terminal Cl since this is in the same region as other terminal chlorines in dinuclear species. Also Fryer's correlation[3] between $^{35}\nu$ and Pt–Cl bond length suggests that the higher-frequency signal corresponds to the terminal Cl. This means that the bridging chlorines have lower binding energy (higher negative charge) which implies that attachment to two Pt centres increases the electron drift towards chlorine. A study of some palladium bromide systems has recently[8] led to the opposite general conclusion with regard to electron densities at terminal and bridging bromines: the binding energy for bromine in $PdBr_2$ (assumed polymeric; all bridging bromines) was found to be *ca.* 0·5 eV higher than for terminal bromine in $(Ph_3P)_2PdBr_2$. This comparison, however, may not be strictly valid since n.q.r. data[9] show that the bridge frequencies in polymeric α-$PdCl_2$ and β-$PtCl_2$ are 6—8 MHz higher than those in corresponding dimeric complexes; the latter give lower values of $^{35}\nu$ than terminal chlorines as described above.

In general, then, these results show that within this closely related series of complexes, the chlorine binding energy gives a good indication of the effect of changes in overall electron density on the Pt–Cl bond (as paralleled in a more sensitive fashion by n.q.r. frequencies). The advantage of ESCA is that it gives information, in principle, on all other atoms in the molecule.

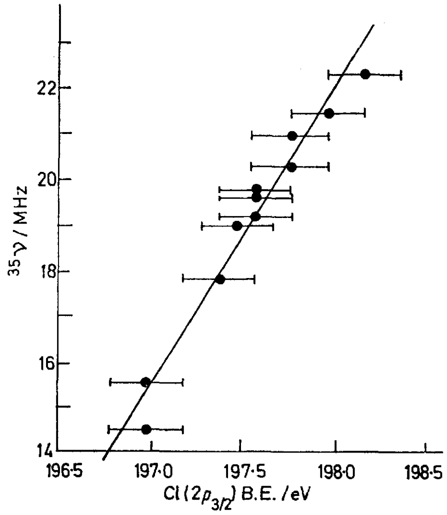

FIGURE 1 Correlation of n.q.r. frequency ($^{35}\nu$) with binding energy [Cl($2p_{3/2}$) B.E.]. Error bars indicate ±0·2 eV B.E. Slope of line 6·4 ± 0·4

We turn now to data which we have obtained from a study of Zeise's salt and related anionic complexes of the type $[LPtCl_3]^-$.

The structure of, and electronic distribution in, Zeise's salt have been debated for many years. Apart from its historical significance, this complex is important because it demonstrates the high *trans*-effect of the ethylene ligand. The kinetic *trans*-effect in a large number of complexes can be correlated with the *trans*-influence which ligands exert in the ground state. It can reasonably be argued that a Syrkin-type description[10] of the *trans*-influence in terms of σ-donation and rehybridisation of metal orbitals adequately accounts for the mass of data available for these complexes, even when ligands capable of π-bonding (*e.g.*, phosphines)[11] are involved. In general the labilisation of the *trans*-

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[6] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1949, **17**, 782.

[7] (*a*) M. Kubo and D. Nakamura, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 257; (*b*) *Cf.* H. Sillescu, in ' Physical Methods in Advanced Inorganic Chemistry,' ed. H. A. O. Hill and P. Day, Interscience, London, 1968.

[8] Gomid Kumar, T. R. Blackburn, R. G. Albridge, W. E. Moddeman, and M. M. Jones, *Inorg. Chem.*, 1972, **11**, 296.

[9] W. von Bronswyk and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1968, 204.

[10] Y. K. Syrkin, *Bull. Acad. Sci. U.R.S.S., Classe Sci. chim.*, 1948, **69**.

[11] L. M. Venanzi, *Chem. in Britain*, 1968, **4**, 162.

ligand is a result of bond weakening in the ground state. This is nicely shown by the n.q.r. work noted above and is supported by our own results.

Ethylene does not appear[12] to cause weakening of the Pt–N bond in *trans*-$PtCl_2(Me_2NH)(C_2H_4)$ but its *trans*-effect is high. Thus previous attempts have been made to observe a ground-state effect in Zeise's salt $\{K[PtCl_3(C_2H_4)],H_2O\}$ as evidenced by some difference in the *cis*- and *trans*-Pt–Cl bonds. Until recently *X*-ray crystal structure data were inconclusive but it has now been shown[13] that the previously assumed space group was incorrect. The redetermined structure[13] gives the average length of the *cis*-Pt–Cl bonds to be 2·305(7) Å which is equal to the Pt–Cl bond length in K_2PtCl_4.[14] The *trans*-Pt–Cl bond length is 2·327(5) Å, *i.e.*, longer by *ca.* 4σ. This could be indicative of *trans*-weakening but the *trans*-Cl interacts with four K^+ ions (albeit with one only weakly) while the *cis*-chlorines interact with one K^+ ion and one H_2O molecule. The difference in environment of the *trans*-Cl may account for some of this lengthening relative to the other two P–Cl bonds.

The n.q.r. spectrum of Zeise's salt has been reported[3,15,16] to consist of three main signals at *ca.* 20·4, 20·2, and 16·0 MHz (depending on temperature). The tentative conclusion[16] that these represent the *cis* (*ca.* 20 MHz) and *trans* (16 MHz) chlorines respectively is strengthened by recent data[17] from related complexes with substituted olefins all of which exhibit signals in these two regions. Lattice effects (which cause the two signals at *ca.* 20 MHz) are not usually greater than 0·5 MHz. Since these two types of signal differ by *ca.* 4 MHz it is not unreasonable, on the basis of the above correlation, to expect a difference in the binding energies of the *cis*- and *trans*-chlorines (of *ca.* 0·6 eV), if the n.q.r. data reflect a difference in electron population on the chlorines. We have, therefore, investigated by ESCA the complexes $M^+[LPtCl_3^-]$ ($M^+ = K^+$ and Pr_4N^+; $L = C_2H_4$, C_3H_6, Me_3P, and Me_3As) and $[M^+]_2[PtCl_4^{2-}]$ ($M^+ = K^+$ and Me_4N^+) to check this and also to obtain a picture of the overall electron distributions.

All the samples were studied as powders on Scotch tape. The binding energy data are in Table 2. Complex peaks were deconvoluted by use of a Dupont 310 Curve Resolver. In examining these data a number of important points should be borne in mind. As discussed above, charging effects demand caution in making comparisons between different complexes, especially since it is our experience that sample charging can be more severe for ionic solids than for molecular ones. Thus each triplet of complexes is internally referenced either to the $K(2p_{3/2})$ level or to the N(1*s*) level, from the respective cation, since it is assumed (with some experimental justification) that these will not be greatly affected by the relatively small changes in the structure of the anion. In an attempt to reference both sets of complexes to the same binding energy scale an intimately ground mixture of K_2PtCl_4 and $(Me_4N)_2PtCl_4$ was studied so as to directly relate the K(2*p*) and N(1*s*) levels. The results of this experiment are noteworthy.

The chlorine 2*p* peak was broad and not resolved into the component $2p_{1/2,3/2}$ peaks (in contrast to the peaks from each complex investigated singly) and the $Pt(4f_{5/2,7/2})$ doublet was likewise significantly broadened. By relating the integrated peak areas from spectra of the mixture and the individual components it was possible to show that the surface was stoicheiometric (*i.e.*, composed of an intimate mixture of microcrystallites of the two components) and to obtain the fraction of $PtCl_4^{2-}$ ions present from each salt (f_1 and f_2). Using linewidths and separations from the K_2PtCl_4 spectra the broad Pt(4*f*) and Cl(2*p*) spectra obtained from the mixture could be deconvoluted. The area ratios obtained were in very good agreement with f_1 and f_2 while the shifts indicated the Pt and Cl binding energies in K_2PtCl_4 to be higher than in $(Me_4N)_2PtCl_4$ by *ca* 0·7 and 0·9 eV respectively. The internal check of calculating the Pt(4*f*) and Cl(2*p*) binding energies of each component in the mixture from a knowledge of the relative binding energies of the reference N(1*s*) and K(2*p*) levels (of the cations) in the mixture and separately led to the same conclusion. A possible explanation of this effect is that the Madelung correction in equation (1), which in ionic crystals should be summed over the entire lattice, differs significantly for the two crystal lattices and thus has increased importance.

Any difference in the binding energies of the *cis*- and *trans*-chlorines in $[LPtCl_3^-]$ will be manifested as a change in the line shape of the $Cl(2p_{1/2,3/2})$ spin–orbit split doublet owing to overlap of the two sets of peaks, as we have found, for example, in the dinuclear complexes with terminal and bridged chlorines[1] and also in *cis*-$(Et_3P)_2PtCl_4$[18] which has two distinct types of chlorine (*trans* to chlorine and phosphorus respectively). Differences in binding energy are expected to be less than in these cases, however, so it is important that the line shape for a single chlorine be well characterised. Since all the samples were highly pure and crystalline we do not consider line-broadening effects due to sample inhomogeneity to make any contribution. Figure 2(a) shows the deconvoluted $Cl(2p_{1/2,3/2})$ double (area ratio 1 : 2) from K_2PtCl_4 (powder sample) in which all chlorines are equivalent; the separation is 1·65 (±0·05) eV. As a check the same peaks were used to fit the $Cl(2p_{1/2,3/2})$ doublet from *cis*-$(Bu^n{}_3P)_2PtCl_2$ studied as a very thin film on gold (under these conditions sample charging and inhomogeneity are minimised). No change in peak

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[12] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 149.

[13] J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Cryst.*, 1971, *B*, **27**, 366.

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[16] T. L. Brown, *Discuss. Faraday Soc.*, 1969, **47**, 200.

[17] T. L. Brown and T. P. Yesinowski, *Inorg. Chem.*, 1971, **10**, 1097.

[18] D. T. Clark and D. Briggs, unpublished results.

widths or separation was required to give an exact 1 : 2 match. This line shape is, therefore, taken as standard for a single chlorine.

All the [$LPtCl_3^-$] complexes studied gave Cl(2*p*) spectra which could not be fitted by a single doublet of standard line shape. The deconvolution procedure adopted was to take two sets of standard doublets and fit these to the experimental peak shape. Only one fit in every case gave standard $2p_{1/2,3/2}$ separations in each doublet (1·7 eV) and a consistent separation of the two $2p_{1/2}$ and $2p_{3/2}$ peaks while at the same time satisfying the criteria of correct area ratios (1 : 2 in each doublet; overall 2 : 1 doublets for the two types). The consistent result for all four complexes indicates that the single chlorine has a lower binding energy than the other two chlorines. Two examples of the deconvoluted Cl(2*p*) peak are shown in Figure 2.

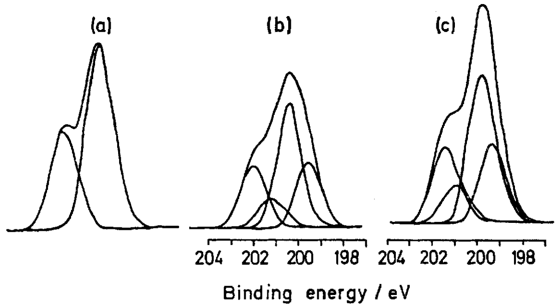

FIGURE 2 (a), Standard Cl(2*p*) line shape deconvoluted into $2p_{1/2,3/2}$ components. From K_2PtCl_4 or *cis*-$(Bu^n{}_3P)_2PtCl_2$; (b), Deconvoluted Cl(2*p*) peak from K[$(C_3H_6)PtCl_3$]; (c), Deconvoluted Cl(2*p*) peak from [Pr_4N][$Me_3AsPtCl_3$]

As indicated above a comparison cannot be meaningfully made between the absolute values of the data in the two halves of Table 2. However, the following points arise from a consideration of relative shifts where direct comparison can be safely made: (i) The effect of replacing one Cl^- ligand in [$PtCl_4{}^{2-}$] by a neutral ligand L to give [$LPtCl_3^-$] is to split the remaining chlorine ligands into two differing types in the ratio 2 : 1 and these can, therefore, be assigned to the *cis*- and *trans*-positions respectively. Hence ESCA detects a ground-state influence of L on the remaining ligands. (ii) There is evidence that relative to $PtCl_4{}^{2-}$ the binding energy of the *cis*-chlorines is raised (decrease in negative charge) and that of the *trans*-chlorine is lowered. This is in agreement with other ground-state phenomena which relate to the *trans*-effect: increase in Pt–Cl bond length is accompanied by electron drift to chlorine.[2] The correlation of chlorine binding energy with $^{35}\nu$ is again apparent since the single n.q.r. signal from K_2PtCl_4 is at 17·93 MHz while the two types of signal in K[(olefin)$PtCl_3$] are in the region of 16 and 20 MHz respectively.[17] Interestingly, these changes in electron density at chlorine are accompanied by a slight increase in binding energy of the central platinum which can only indicate some degree of Pt ⟶ L back donation. Significantly this effect is more noticeable when L = olefin and is greatest of all for ethylene.

TABLE 2

	$K(2p_{3/2})$	$Pt(4f_{7/2})$	$Cl(2p_{3/2})$	
K_2PtCl_4	294·8 [a]	73·9	200·3 [b]	
$K[C_2H_4)PtCl_3]$	294·8	74·5	200·4(2)	200·1(1) [c]
$K[(C_3H_6)PtCl_3]$	294·8	74·3	200·4(2)	199·6(1) [c]
	N(1*s*)	$Pt(4f_{7/2})$	$Cl(2p_{7/2})$	
$[Me_4N]PtCl_4$	404·1 [a]	73·5	199·5	
$[Pr_4N][Me_3PPtCl_3]$	404·1	73·7	199·8(2)	199·3(1) [c]
$[Pr_4N][Me_3AsPtCl_3]$	404·1	73·7	199·7(2)	199·3(1) [c]

[a] Relative binding energies from a mixture of K_2PtCl_4 and $(Me_4N)_2PtCl_4$; see text. [b] Estimated errors between samples ±0·2 eV. [c] Estimated errors within chlorine levels for a single complex ±0·1 eV.

In connection with the last point it is of interest to gain some additional information on the electron distribution in the Pt–olefin bond. The C(1*s*) peak from Zeise's salt comes mainly from the Scotch tape backing but a definite shoulder can confidently be assigned to the ethylenic carbons on the basis of its area ratio relative to the chlorine peak. The binding energy of these carbons is 283·4 eV which compares with an expected value of 284·9 eV for the free ligand. These figures reveal a considerable electron transfer from metal to olefin, which is understandable in terms of the Dewar–Chatt–Duncanson model[19] where the dominating feature is back donation from filled Pt *d*-orbitals into π^* anti-bonding orbitals of the olefin. The 0·6 eV increase in Pt(4*f*) binding energy in going from $[PtCl_4]^{2-}$ to $[PtCl_3(C_2H_4)]^-$ is confirmatory information. The olefinic carbon binding energy is similar to that reported previously[1] for the neutral complex $(Ph_3P)_2Pt(C_2H_4)$. The extra methyl carbons in $K[PtCl_3(C_3H_6)]$ are an additional contribution to the C(1*s*) peak from this complex and consequently no shoulder due to olefinic carbons is apparent although the breadth of the peak indicates that a qualitatively similar situation holds as for Zeise's salt.

In summary the *cis*- and *trans*-chlorines in $[LPtCl_3]^-$ have different electronic environments, the *trans*-chlorine having the higher negative charge. Both *cis*- and *trans*-effects of L are discernible and the correlations with n.q.r. data indicate that these most probably arise through σ bonding mechanisms. Back-bonding to the potential π-acceptors appears to occur, especially for olefinic ligands. These conclusions are in general agreement with those arrived at from semi-empirical LCAO-MO calculations on Zeise' salt itself.[15]

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