

Chlorine Nuclear Quadrupole Coupling in Platinum and Palladium Dichlorides

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Nuclear quadrupole resonance studies confirm the existence of α -PdCl₂, β -PdCl₂, and β -PtCl₂, and show that whilst the β -PtCl₂ structure is distorted the β -PdCl₂ structure is regular. The magnitudes of the coupling constants show that the α - and β -structures have nearly identical electron distributions, all differences being due, presumably, to changes in the metal–chlorine–metal bond angle.

THE structure of the various forms of platinous and palladous chlorides has been the subject of discussion for some years. Unlike nickel chloride, which has a rutile structure and is paramagnetic with two unpaired electrons, as expected for a high-spin d^8 -configuration, PdCl₂ and PtCl₂ are both diamagnetic. As shown in Table 1, both PdCl₂ and PtCl₂ would be endothermic if they existed as ionic lattices.

TABLE 1

Heats of formation (kcal./mole) of dichlorides of Ni, Pd, and Pt

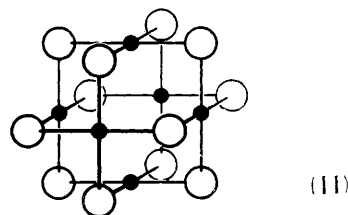
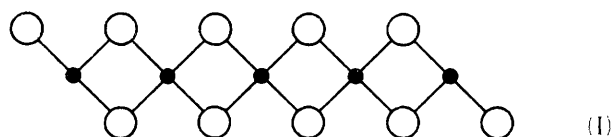
Compound	ΔH_f° (obs.) ¹	ΔH_f° (calc., if ionic)
NiCl ₂	−73	ca. −70
PdCl ₂	−43	+33 (estimated)
PtCl ₂	−35	+45 (estimated)

The large difference between the value of ΔH_f° observed (negative) and that calculated (positive) for the hypothetical ionic form indicates that the latter structure is untenable. The two obvious alternatives are a covalent halogen-bridged structure and one involving metal–metal bonding with two or more metal atoms in a cluster.

It was shown by Wells² that the α -form of PdCl₂, produced by treating palladium with chlorine at 550–575°, has the long-chain halogen-bridged structure (I) involving square co-ordinated Pd^{II}. More recently, Broderson, Thiele and Schnering³ have shown that the β -form of PtCl₂, formed by the chemical transport technique, is hexameric, having a multicentre bond structure (II) involving an octahedron of platinum atoms with a bridging chlorine atom along each edge.

Vapour pressure and mass spectrometric⁴ data on [PtCl₂]₆ indicate that the hexameric unit is largely retained in the gas phase. Studies on the vapour pressure of PdCl₂ reveal that this substance also apparently forms hexamers in the gas phase,⁵ presumably owing to a change of structure. However, it has been shown by Schafer *et al.*⁴ that the β -form of PtCl₂ is isomorphous with the corresponding (hexameric) β -form of PdCl₂, which can be produced either by preparing PdCl₂ at temperatures below 550° or by allowing α -PdCl₂ to revert to this on long standing.

Calculations of bond strengths by Kettle⁶ suggest that energetically there would be little difference between the thermodynamic stabilities of the two forms of PtCl₂. He assumes that in both the (unknown) long-chain form and the hexameric structure, metal–metal interaction is negligible, and that binding occurs wholly through bridging chlorine atoms. If this were so, the chlorine



atoms should be electronically equivalent in both forms. It is convenient to test this hypothesis by studying the nuclear quadrupole resonance of the chlorine atoms in crystals of both PdCl₂ and PtCl₂.

EXPERIMENTAL

The specimens of PtCl₂ and PdCl₂ obtained from Johnson Matthey and Co. were in the β -form, and the compounds were purified by sublimation. PdCl₂ in the α -form was prepared by the published method.⁴

Nuclear quadrupole resonance frequencies were obtained using a super regenerative oscillator of the Colpitts type, constructed in this laboratory, and phase-sensitive detection techniques. Frequencies were measured using a BC-221 frequency meter which gave an uncertainty of ± 0.005 MHz in the position of the observed resonances, fundamental and side-band frequencies being distinguished by variation of the quench frequency. A typical spectrum is shown in the Figure.

¹ 'Handbook of Chemistry and Physics,' Chemical Rubber Publishing Co., New York, 47th edn., 1966.

² A. F. Wells, *Z. Krist.*, 1938, **100**, 189.

³ K. Broderson, G. Thiele, and H. G. Schnering, *Z. anorg. Chem.*, 1965, **337**, 120.

⁴ H. Schafer, U. Wiese, K. Rinke, and K. Brendel, *Angew. Chem. Internat. Edn.*, 1967, **6**, 253.

⁵ W. E. Bell, U. Merton, and M. Tagami, *J. Phys. Chem.*, 1961, **65**, 510.

⁶ S. F. A. Kettle, *Nature*, 1956, **209**, 1021.

RESULTS AND DISCUSSION

The resonances obtained for α -PdCl₂, β -PdCl₂, and β -PtCl₂ were broad and weak, having half-widths of the order of 25 kHz and signal-to-noise ratios (peak-to-peak)



Nuclear quadrupole resonance spectrum of β -PdCl₂

of about 4. The resonances were obtained at 23°; no absorption was observed at liquid-nitrogen temperatures (Table 2).

TABLE 2
Observed ³⁵Cl frequencies for PtCl₂ and PdCl₂ at 23°

Compound	Frequency (MHz) †	η (calc.)	eqQ/h (MHz)
α -PdCl ₂	18.069	0.157	35.994
β -PdCl ₂	20.242	0	40.484
β -PtCl ₂ *	23.615	0	47.230
	23.035	0	46.070

* In one isolated sample of PtCl₂, only one resonance was found (23.033 MHz). As this result could not be repeated with other samples, no real inferences can be drawn from it. It could, however, have been due to either an undistorted β -PtCl₂ structure or α -PtCl₂. † The corresponding value for anhydrous NiCl₂ is not available and could not be determined with our instrument. However, it is unlikely to differ very much from that of anhydrous CoCl₂, which is 5.12 MHz (R. G. LeCander, *Bull. Amer. Phys. Soc.*, 1963, **8**, 260), *i.e.*, much less than that observed for the 'covalent' chlorines in platinum and palladium compounds. In both CoCl₂ and NiCl₂, the chlorine is essentially 'ionic,' and hence the low value; for chlorine in potassium chloride the even more 'ionic' chloride ion has a resonance at *ca.* 0.0 MHz (C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1955, **23**, 118).

The complete crystal structures have been published for α -PdCl₂,² and β -PtCl₂,³ and the number of resonance lines observed is in agreement with these. One line is expected for the regular α -PdCl₂ structure in which all chlorine atoms are equivalent, and two lines are expected for the distorted β -PtCl₂ structure in which two types of chlorine atom occur; one of these has a Pt-Cl distance of 2.35 Å, the other being 2.39 Å. The complete crystal structure of β -PdCl₂ is not available at

present but the one observed nuclear quadrupole resonance line indicates that all chlorine atoms are equivalent and that the structure is undistorted.

No resonance lines were found which could be unequivocally assigned to α -PtCl₂ (see footnote to Table 2), and all our efforts to prepare this form have been unsuccessful. The greater apparent stability of the hexameric form of PtCl₂(β) may be due to the fact that platinum has a much larger heat of atomisation (135 kcal./mole) than Pd (90 kcal./mole); this tends to favour cluster formation.

The data were interpreted using the Townes and Dailey approach:⁷

$$f = q_{\text{obs.}}/q_{\text{at.}} = [N_z - \frac{1}{2}(N_x + N_y)]$$

where q = effective electric field gradient, and N_x , N_y , and N_z are the electron occupancies of the p_x -, p_y -, and p_z -orbitals. For a bridging chlorine the unique axis is perpendicular to the plane of the bridge, and hence the p_x - and p_y -orbitals will be equivalent, the lone pair of electrons filling the p_z -orbital. The above equation assumes all bonds to involve pure p -chlorine orbitals (*i.e.*, bond angles 90°); this is not, however, the normal situation, and deviations were accounted for by use of the equations:

$$s\text{-Hybridisation } (a_s^2) = \cos 2\gamma/(1 - \cos 2\gamma), \quad (\text{ref. 8})$$

$$\text{Asymmetry parameter } (\eta) = 3 \cos 2\gamma, \quad (\text{ref. 9})$$

$$f = [N_z - \frac{1}{2}(N_x + N_y)]/2 \sin^2 \gamma, \quad (\text{ref. 10})$$

where 2γ is the inter-orbital angle (which was assumed to coincide with the interatomic angle).

The results so calculated are in Table 3, the charges

TABLE 3
Charge distribution in PtCl₂ and PdCl₂

Compound	Bond angle	s -Hybridisation (calc.)	Calc. charge on Cl	Charge on metal
α -PdCl ₂	93°	5%	-0.27	+0.54
β -PdCl ₂	90° *	0	-0.26	+0.52
β -PtCl ₂	90	0	-0.16	+0.29
	90	0	-0.13	

* Angle assumed to be 90° by analogy with β -PtCl₂.

on the metal being calculated to give zero charge per molecular entity. The results for α - and β -PdCl₂ are identical within the experimental accuracy, and an increase of 0.5° in the bond angle of β -PdCl₂ will render the results numerically identical.

The results as a whole are thus open to a simple interpretation. The charges associated with the chlorine and palladium atoms in the α - and β -forms of PdCl₂ are nearly identical, there being only small differences which arise from differences in the s -contributions to chlorine orbitals. β -PdCl₂, which is known to be isotypic with β -PtCl₂, has an undistorted structure, whilst β -PtCl₂ is distorted along one three-fold axis of the

⁷ C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1949, **17**, 782; 1955, **23**, 118.

⁸ A. Coulson, 'Valence, Oxford, 2nd edn., 1961.

⁹ T. P. Das and E. L. Hahn, 'Solid State Physics, Supplement 1,' Academic Press, 1958.

¹⁰ A. E. G. Lueken, personal communication.

metal octahedron. No evidence has been found for the existence of α -PtCl₂ as a stable room-temperature entity. The difference in the charges on the metal atoms (Pd — Pt = +0.2) is of the order, and in the direction, found for other square-planar platinum and palladium complexes (Pd — Pt = 0.1 for MBr₄²⁻);¹¹ if this were accepted, the valence-state electronegativity of platinum would be about 0.1 unit greater than that of palladium, a matter which has also been observed in the optical electronegativities calculated from charge transfer spectra.¹²

The assignment of the two resonance lines of β -PtCl₂ to the specific bond distances is not as simple, however,

¹¹ K. Ito, D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 1961, **83**, 4526.

and can be considered as follows. Since chlorine is more electronegative than platinum, then, as the platinum–chlorine distance increases, the chlorine will tend to take the platinum valence electrons with it, thereby increasing its *p*-electron density and hence decreasing its nuclear quadrupole resonance frequency. We hence tentatively assign the resonance line at 23.035 MHz to the chlorine involved in the longer bridge (2.39 Å), and the line at 23.615 MHz to the chlorine involved in the shorter bridge (2.35 Å).

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¹² C. K. Jørgensen, 'Orbitals in Atoms and Molecules,' Academic Press, 1962.