A Novel Di-platinum(II) Octaphosphite Complex showing Metal–Metal Bonding and Intense Luminescence; a Potential Probe for Basic Proteins. *X*-Ray Crystal and Molecular Structure

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Summary *X*-Ray crystallography and ^{195}Pt and ^{31}P n.m.r. spectroscopy show that an intensely luminescent product from K_2PtCl_4–H_3PO_3 reactions is a dimer with close Pt atoms (2·925 Å) bridged by four P–O–P linkages from diphosphorous acid ligands; its reactions and uses are discussed.

ROUNDHILL *et al.*[1] have recently reported the existence of a Pt phosphite complex which displays a unique luminescence in aqueous solution. They attributed this to $Pt\{OP(OH)_2\}_2\{P(OH)_3\}_2$, (**1**), a complex which had previously been prepared by Troitskaya.[2] However, we did not observe the intense green luminescence during the alkaline hydrolysis of $Pt\{OP(OMe)_2\}_2\{HOP(OMe)_2\}_2$, (**2**), or from K_2PtCl_4–H_3PO_3 solutions,[2] even though our n.m.r. studies indicated that tetrakisphosphite species were present. We subsequently discovered that it was essential to heat crystals of (**2**) or K_2PtCl_4–H_3PO_3 solutions to dryness, and it is now apparent from our *X*-ray crystallographic and ^{195}Pt and ^{31}P n.m.r. studies that a solid-state condensation occurs to give a novel P–O–P bridged Pt^{II} dimer which is the luminescent species.

In our preparations, K_2PtCl_4 (0·8 g) and H_3PO_3 (2·8 g) in 4 ml of H_2O were heated on a steam bath for 2 h to give a pale brown solution. By ^{195}Pt n.m.r. spectroscopy, this contained approximately equal amounts of $Pt[P]_4$ (**3**),† (for n.m.r. data, see Table) $Pt[P]_3Cl$, and *cis*-$Pt[P]_2Cl_2$. Careful evaporation of the solution on Petri dishes at 110 °C led to the evolution of HCl, and the formation of green or purple solids which were washed with methanol and acetone to remove excess of H_3PO_3. Both solids have similar electronic absorption spectra in H_2O (λ_{max} at 345, 285, and 370 nm with $\epsilon = 3 \times 10^3$, $2·8 \times 10^3$, and 3×10^4 l mol^{-1} respectively) and exhibit the green luminescence. A purple sample was recrystallised from H_2O to give dark green prismatic needles (**4**).

TABLE. ^{195}Pt and ^{31}P n.m.r. chemical shifts and coupling constants[a]

Complex	δ (^{195}Pt)/p.p.m.[b]	δ(^{31}P)/p.p.m.[c]	^1J(Pt–P)/Hz
(**2**)	−5107	90·9	3460
(**3**)	−5103	86·3	3360
(**4**)	−5139	69·4	3075 (^3J, 17)
(**5**)	−5123	86·7	3248

[a] The high frequency (low field)-positive shift convention is used for both nuclei; measurements were made at 298 K. [b] Relative to external 1 M Na_2PtCl_6. [c] Relative to external 85% H_3PO_4–15% D_2O.

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† The state of ionisation of the ligand (P) was not determined, but is probably $P(OH)_3$ since the solution is highly acidic.

Crystal data: $K_4[Pt_2H_8P_8O_{20}]\cdot 2H_2O$ (**4**)‡ crystallises in the tetragonal space group $P\bar{4}b2$ with cell dimensions a = 13·335(1) and c = 7·989(1) Å, Z = 1. The structure was refined to R = 0·0356 for 1055 significant reflections [$I > 2{\cdot}5\sigma(I)$] collected on an Enraf–Nonius CAD4 diffractometer using Cu-K_α radiation. The asymmetric unit contains $\frac{1}{2}K_2[Pt(H_2P_2O_5)_2]\cdot H_2O$. The complex has several of its elements situated on two-fold axes. Thus the Pt atom is surrounded by four phosphite groups in two equivalent pairs. The space group symmetry is such as to relate a Pt tetraphosphite to a neighbour to form the dimeric unit shown in Figure 1. Viewed down the Pt–Pt axis, the complex has approximately 4-fold symmetry, with square-planar arrangements around Pt. The Pt–Pt distance in the dimer (2·925 Å) indicates a strong metal–metal bond,[3] but the Pt–Pt distance between adjacent dimers, Figure 2, is much longer (5·063 Å). The P–O distances are typical of phosphites and pyrophosphates,[4] and indicate that each phosphite group carries a single negative charge. The second one, P(2), probably involves substantial charge delocalisation. Overall, each dimeric complex presents a sphere of negative charge to its environment.

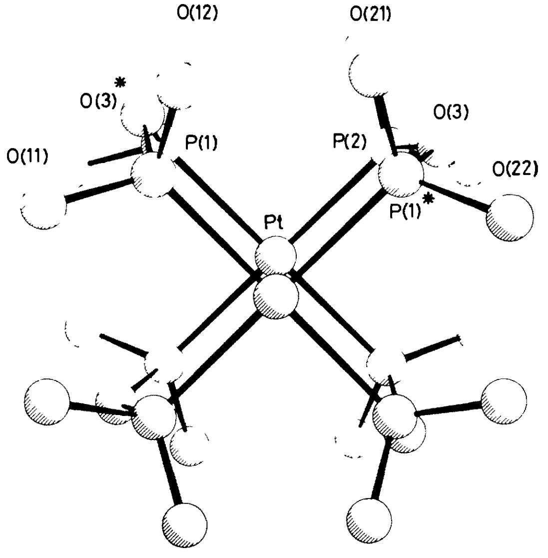

FIGURE 1. The molecular structure of the complex looking down a view slightly displaced from that down the Pt–Pt axis. Bond lengths: Pt–Pt 2·925(1); Pt–P(1) 2·334(4); Pt–P(2) 2·307(4); P(1)–O(11) 1·523(14); P(1)–O(12) 1·669(12); P(1)–O(3) 1·629(11); P(2)–O(21) 1·515(10); P(2)–O(22) 1·492(11); P(2)–O(3) 1·616(12) Å.

There are strong interactions between the phosphite oxygens and the K+ ions, and these are largely responsible for producing deviations from exact 4-fold symmetry for the complex. The K+ ions also bridge adjacent dimers in the crystal (Figure 2) ensuring the 5 Å separation. All the K+ ions are, somewhat unusually, tetrahedrally co-ordinated.

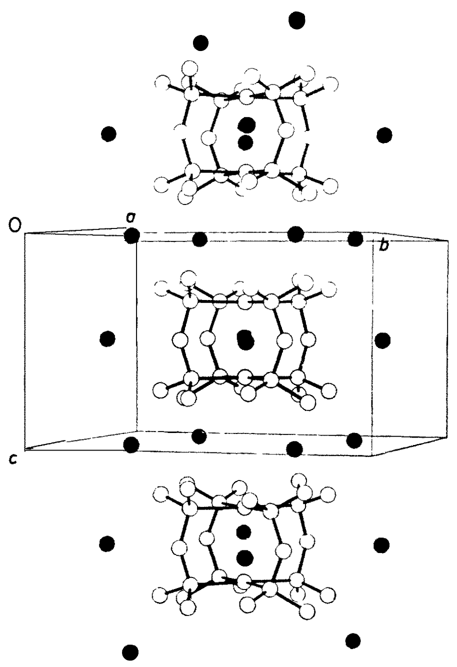

FIGURE 2. A view of a part of the crystal structure, showing three adjacent dimer units. The shaded circles indicate K+ ion positions.

The ^{195}Pt n.m.r. spectrum of (**4**), a quintet of quintets as shown in Figure 3, confirms the existence of the dimer in solution. Pt is coupled to four equivalent, directly bonded P atoms, and also to the four P atoms on the neighbouring Pt (^3J, if through bridge). The ^{31}P n.m.r. spectrum is a pseudo-triplet with broad satellites.§ Perhaps surprisingly, in view of the proximity of the Pt atoms, the ^{195}Pt chemical

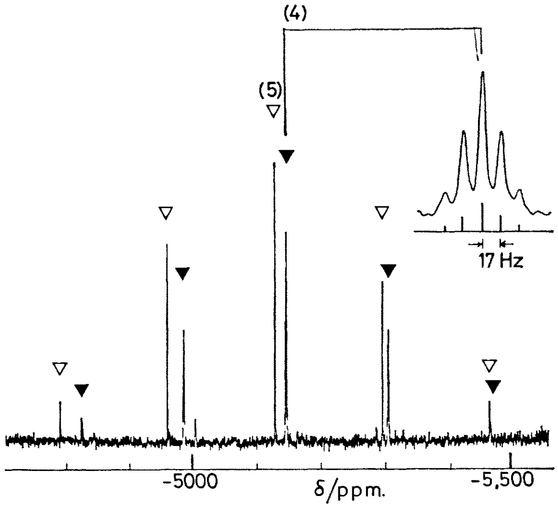

FIGURE 3. 19·2 MHz ^{195}Pt n.m.r. spectrum of unrecrystallised (**4**) (▼) in D_2O (250 mg/ml, 3000 pulses, 0·6 s interval); ▽, following partial hydrolysis to (**5**).

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‡ The atomic co-ordinates for this work are available on request from Prof Dr G Bergerhoff, Institut fur Anorganische Chemie der Universitat, Gerhard-Domagk-Str. 1, D5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

§ The spectrum is highly second order on account of the 33·8% natural abundance of ^{195}Pt.

shift and ${}^1J$(Pt–P) are comparable with those for the known Pt^{II} complex (**2**) (Table), but the ^{31}P resonance is shifted to high field by 21·5 p.p.m., explicable by the involvement of P in cross-linking. Traces of H_3PO_4 in unrecrystallised samples of (**4**) catalyse its hydrolysis, and the product, (**5**), has a quintet in the ^{195}Pt n.m.r. spectrum, see Figure 3, and a 1:4:1 triplet in the ^{31}P n.m.r. spectrum. Compound (**5**) is non-luminescent, and probably the same as the monomeric species (**1**).

The remarkable luminescence properties of (**4**) can therefore be attributed to the presence of Pt–Pt bonding in the dimer. This may also be required for luminescence in other Pt complexes: it is well recognised that the luminescence of $Pt(CN)_4^{2-}$, for example, in solution is highly concentration-dependent.[5,6] The luminescence of (**4**) is linear with concentration in the range 0·2—13 μM at which point quenching begins (excitation at 370 nm, emission at 514 nm). Compound (**4**) may be a useful probe for basic polypeptides since we find that they can enhance (polylysine) or decrease (histone) the luminescence. *cis*-$Pt(NH_3)_2Cl_2$ undergoes similar reactions with H_3PO_3, and the resulting luminescence may be used to detect ng quantities of this drug. These possibilities are being further investigated.

We thank Dr. C. D. Flint (Birkbeck College) for stimulating discussions, the S.R.C. for support and a studentship (M.A.F.D.R.P.), Johnson, Matthey Ltd. for the loan of Pt, the Cancer Research Campaign (S.N.), the S.R.C. and Roche Products Ltd for support (M.R.S.), Dr. M. B. Hursthouse and the S.R.C. for the use of the single-crystal data collection service at Queen Mary College, and Dr. P. J. Beynon (JEOL UK Ltd) for recording the 19 MHz ^{195}Pt n.m.r. spectrum.

(*Received*, 1*st August* 1979; *Com.* 840.)

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