Polyhedron Vol. 3, No. 3, pp. 325–329, 1984
Printed in Great Britain.

0277–5387/84 \$3.00 + .00
Pergamon Press Ltd.

2,2,3,4,4-PENTAMETHYLPHOSPHETANIC ACID, $C_8H_{16}PO_2H$: SALTS, COMPLEXES AND A HYDROGEN BONDED AMINE ADDUCT

JOHN EMSLEY,* AMANDA P. DUNNING, ROBERT J. PARKER
and JOHN K. WILLIAMS
Department of Chemistry, King's College, Strand, London WC2R 2LS, England

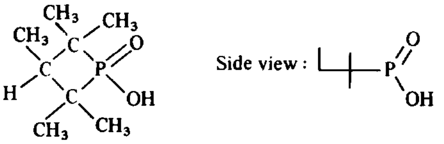
SHIRLEY BROWN, STELLA EARNSHAW and DAVID S. MOORE†
Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, England

(*Received* 1 *July* 1983; *accepted* 25 *July* 1983)

Abstract—The conjugate base of the title acid, i.e. $C_8H_{16}PO_2^-$, has been investigated as its simple salts, as a ligand in transition metal complexes of cobalt and ruthenium, and as a secondary amonium salt in which hydrogen bonding between anion and cation occurs.

1-Chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}POCl$, can be easily synthesized from 2,4,4-trimethylpent-2-ene and PCl_3 in the presence of Al_2Cl_6.[1,2] This chloride is slowly hydrolysed in air. The products of hydrolysis may be the acid, a phosphetanic acid, $C_8H_{16}PO_2H$, or the anhydride, $C_8H_{16}P(O)OP(O)C_8H_{16}$, depending on conditions.[3] The latter is rapidly formed[4] and is remarkably stable to further hydrolysis.[3]

Little has been written about $C_8H_{16}PO_2H$ beyond reporting a few basic physical properties and spectra.[5] It is a fairly strong acid, pK_a 2.85.[1] Its structure is assumed to be (I), based on that of other phosphetans.[6]



(I)

Whereas for the chloride there are two non-interconverting isomers, *cis* and *trans*, defined for the ring H and PO groups with respect to the plane of the ring, there can be only one form of the acid. The conjugate base, $C_8H_{16}PO_2^-$, has a plane of symmetry bisecting the phosphetan ring. Because of the similarity of R_2PO_2H and $R_2PO_2^-$ to RCO_2H and RCO_2^-, it was thought likely that this phosphinic acid might also display some of the properties of a typical carboxylic acid in its ability (i) to act as a ligand, and (ii) to involve itself in hydrogen bonding including possibly very strong hydrogen bonding.[7] These hopes have been realized and in this communication we present evidence of $C_8H_{16}PO_2^-$ acting as a ligand towards certain transition metals and of $C_8H_{16}PO_2H$ forming an adduct with secondary amines in which a cyclic hydrogen bonding system is suspected.

EXPERIMENTAL

Instruments. IR spectra as KBr discs were run on PE457 and PE580 machines. Nuclear magnetic spectra were taken on JEOL PMX60 SI, Bruker HFX90 and Bruker WM250 spectrometers. ^{31}P NMR spectra at 36.4 MHz are referenced to external H_3PO_4. UV spectra were taken on a UNICAM SP800 spectrometer

Preparation of 2,2,3,4,4-*pentamethylphosphetanic acid*, $C_8H_{16}PO_2H$

$C_8H_{16}POCl$, made by the reported methods,[1,2] is hygroscopic. On exposure it the atmosphere for *ca.*

---

*Author to whom correspondence should be addressed.

†Present address: Priory House, Dover College, 6 Waterloo Crescent, Dover, Kent CT16 1LA, England.

1 week it is converted to the acid. Refluxing a mixture of $C_8H_{16}POCl$ and water for 3 hr produces a mixture of the acid and the anhydride $C_8H_{16}P(O)OP(O)C_8H_{16}$. Aqueous 2M NaOH solution and $C_8H_{16}POCl$ react to give the same mixture, although with less anhydride, from which the acid can be recovered by treatment with 2M HCl. The acid is only slightly soluble in water (1.33 g/100 cm^3 H_2O at 20°C).

The ^{31}P NMR spectrum of $C_8H_{16}PO_2H$ in $CDCl_3$ consists of a multiplet of 13 peaks (3747 scans), with $^3J_{PCCH_3}$ 18.55 Hz, split into doublets due to $^3J_{PCCH}$, 5.86 Hz. Further fine structure from $^4J_{PCCH_3}$ was evident but not resolvable. No evidence of J_{POH} coupling shows that rapid exchange in this solvent is occurring probably via hydrogen bonding. The proton decoupled spectrum has δ 59.04 ppm. In D_2O the decoupled signal is at δ 59.18 ppm.

SALTS

Preparation of lithium 2,2,3,4,4-*pentamethylphosphetanate*. To a solution of lithium hydroxide monohydrate (0.42 g, 10 mmol) in water (10 cm^3) was added $C_8H_{16}PO_2H$ (1.76 g, 10 mmol). The solution was evaporated to yield $C_8H_{16}PO_2Li$ which was dried at 130°C. The ^1H NMR spectrum of a solution in D_2O gave signals at 1.50 (1H, CH, dq, $J_{HCCH_3} = 4.5$ Hz), 1.03 (12H, CH_3, dd, $J_{PCCH_3} = 17.5$ Hz) 0.78 ppm (3H, CH_3, dd, J_{PCCH_3} 1.5 Hz). The calcium salt was made likewise.

In a similar reaction, but using metal carbonate, the following salts were made: Na, K, Rb, Cs, Sr, Ba and Ag. The silver salt darkened on exposure to light. The ammonium salt was made from $C_8H_{16}PO_2H$ and liquid NH_3 in toluene. All the salts gave similar IR spectra showing the characteristic phosphetan vibration absorptions. The $\nu_{as}(PO_2^-)$ and $\nu_s(PO_2^-)$ modes were recognizable as a pair of strong bands at 1160–1130 cm^{-1} and 1050–1030 cm^{-1} respectively. The ^{31}P NMR signal of $C_8H_{16}PO_2K$ in D_2O gave a spectrum like that of the acid (2521 scans) from which $^3J_{PCCH_3} = 17.63$ Hz and $^3J_{PCCH_3} = 3.42$ Hz. The proton decoupled signal appeared at δ 49.1 ppm.

$C_{18}H_{16}PO_2K$ *and* $C_8H_{16}PO_2H$. An aqueous solution of $C_8H_{16}PO_2K$ is capable of dissolving more acid than the same volume of water. Thus a 0.187 M solution of $C_8H_{16}PO_2K$ was stirred for several hours with excess $C_8H_{16}PO_2H$ and the latter dissolved to give a solution of 0.204 M in acid; the mole ratio of salt: acid is 1:1.09. The ^{31}P NMR spectrum of the resulting solution showed only a 13 peak multiplet with $^3J_{PCCH_3} = 16.85$ Hz (5343 scans). The fine structure due to $^3J_{PCCH}$ was not evident but unresolved substructure was present. The proton decoupled signal was at δ 48.97 ppm.

COMPLEXES

Reaction of $C_8H_{16}PO_2H$ *and cobalt(II) carbonate*. Cobalt(II) carbonate (2.0 g, 16 mmol) was added to a solution of $C_8H_{16}PO_2H$ (7.0 g, 40 mmol) dissolved in hot water; CO_2 was evolved. When all the $CoCO_3$ had reacted the pink solution was heated to boiling and a blue precipitate formed which was filtered hot. This was *bis*(2,2,3,4,4-pentamethylphosphetanato) cobalt(II), $Co(C_8H_{16}PO_2)_2$ (6.2 g, 12 mmol, 60%), m.p. > 360°C. The complex was stable in air. Found: C, 46.93; H, 7.82; P, 15.13. $C_{16}H_{32}CoO_4P_2$ requires: C, 46.94; H, 7.82; P, 15.16%.

$Co(C_8H_{16}PO_2)_2$ gave an IR spectrum with absorptions at 2975–2861 s (CH_3), 1460 m (CH_3, 1393–1370 w (CH_3), 1240 w (P), 1208 w, 1143 s (P), 1092 s (PO_2), 1062 s (PO_2), 1020 m (CH_3), 940 w (P), 760 w (P), 730 sh (P), 657 m (P), 545 m (CoOP), 534 sh (P), 418 w, 410 w (P), 312 m cm^{-1}, where P refers to the mode being a recognized phosphetan ring absorption.[5]

The UV spectrum of a $CHCl_3$ solution (blue) has λ_{max} 500 nm (118,000 mol^{-1} cm^2), 580 nm (138,000 mol^{-1} cm^2), 626 nm (147,000 mol^{-1} cm^2).

An aqueous solution (pink) has λ_{max} 500 nm (1680 mol^{-1} cm^2).

The blue crystals of $Co(C_8H_{16}PO_2)_2$ are soluble in cold water to form a pink solution which on heating to 79°C precipitates the blue complex. This in turn redissolves as the solution is allowed to cool. The blue complex is also soluble in $CHCl_3$ but can be extracted from this solvent into water as a pink solution. This technique can be used to remove unreacted $C_8H_{16}PO_2H$.

The blue complex can also be prepared by heating $Co(NO_3)_2$ and an excess of $C_8H_{16}PO_2H$ in an acetone solution for 2 hr.

From a cold aqueous solution of $Co(C_8H_{16}PO_2)_2$ pink crystals grow on evaporation of the solvent. On standing these slowly revert to the blue form, rapidly at 40°C or on being left in a desiccator.

The magnetic susceptibility of the blue complex was measured by the Gouy method at 19960×10^{-12} m^3 mol^{-1} from which a magnetic moment of 6.1 Bohr magnetons was calculated. The diamagnetic correction factor for $C_8H_{16}PO_2H$ was calculated as -2561×10^{-12} m^3 mol^{-1}.

Reaction of $C_8H_{16}PO_2H$ *and maganese(II) nitrate*. Manganese(II) nitrate (1.78 g, 10 mmol) and $C_8H_{16}PO_2H$ (5.0 g, 28 mmol) were refluxed together in acetone (20 cm^3) for 2 hr. On cooling, white microcrystalline needles of the complex *bis*(2,2,3,4,4-pentamethylphosphetanato) manganese(II) formed (2.9 g, 7.1 mol, 71%), m.p. > 360°C. Found: C, 46.81; H, 7.84; P, 14.75. Calculated for $C_{16}H_{32}MnO_4P_2$: C, 47.41; H, 7.90; P, 15.31%. The IR spectrum (Nujol mull) showed absorptions: 1239 m (P), 1147 s (P), 1089 m (PO_2), 1056 m (PO_2), 1019 m (CH_3), 989 w, 934 m (P), 758 m (P), 672 s (P), 641 m (P), 560 w (P), 540 s (P), 521 sh (MnOP) cm^{-1}.

Preparation of RuX_2Y_2 *(phosphetanato) complexes* [X = Cl, Br; Y = PPh_3, $AsPh_3$, $PpyPh_2$]

The RuX_2Y_3 complex, made by published methods,[8,9] was dissolved in benzene under aerobic conditions in the presence of $C_8H_{16}PO_2H$. The mixture was stirred for 3 hr, the solvent removed and the oily product crystallized from petroleum spirit (60/80°). The following compounds were prepared by this method: *dichloro*(2,2,3,4,4 - *pentamethylphosphetanato*) - *bis*(*triphenylphosphine*)*ruthenium*, dark green crystals m.p. 130°C, yield 31%, [Found: C, 59.40; H, 5.22; P, 10.29; $C_{44}H_{46}Cl_2O_2P_3Ru$ requires: C, 60.62; H, 5.28; P, 10.68%]; *dibromo*(2,2,3, 4,4-*pentamethylphosphetanato*)*bis*(*triphenylphosphine*)*ruthenium*, brown crystals, m.p. 142°C, yield 46% [Found: C, 54.86; H, 4.60; P, 9.62, $C_{44}H_{46}Br_2O_2P_3Ru$ requires: C, 55.00; H, 4.79; P, 9.69%]; *dichloro*(2,2,3,4,4-*pentamethylphosphetanato*)*bis*(*tripyrridinodiphenylphosphine*)*ruthenium*, orange–brown crystals, m.p. 118°C, yield 11%; [Found: C, 56.90; H, 5.02; P, 10.47; N, 3.15; $C_{42}H_{46}Cl_2N_2O_2P_3Ru$ requires: C, 57.60; H, 5.26; P, 10.63; N, 3.20%]; *dibromo*(2,2,3,4,4-*pentamethylphosphetanato*)*bis*(*pyridinodiphenylphosphine*)-*ruthenium*, pale yellow crystals, m.p. 102°C, yield 11%; [Found: C, 52.17; H, 4.67; P, 9.58; N, 2.85; $C_{42}H_{46}Br_2N_2O_2P_3Ru$ requires: C, 52.28; H, 4.77; P, 9.65; N, 2.90%]; and *dichloro*(2,2,3,4,4-*pentamethylphosphetanato*)*bis*(*triphenylarsine*)*ruthenium*, *ruthenium*, brown crystals, m.p. > 230°C, yield 20%; [Found: C, 55.00; H, 4.73; P, 2.98; $C_{44}H_{46}As_2Cl_2O_2PRu$ requires: C, 55.05; H, 4.79; P, 3.23%].

ADDUCTS

Reaction of $C_8H_{16}PO_2H$ *and diethylamine*. Diethylamine (0.73 g, 10 mmol) was mixed with water (5 cm^3) and $C_8H_{16}PO_2H$ (1.76 g, 10 mmol) added. This slowly dissolved and the solution was evaporated to dryness on a steam bath to yield 2.49 g of a solid that was recrystallized from benzene to yield the adduct $C_8H_{16}PO_2H.NEt_2H$, m.p. 153–156°. Found: C, 55.7; H, 11.25; N, 5.43. $C_{12}H_{28}NO_2P$ requires: C, 57.8; H, 11.24; N, 5.62%. The IR spectrum has absorbances at 3450 vw br (trace of free amine), 3000–2860 s (CH_3), 2700 sbr (NH_2), 2520 sbr (NH_2), 2410 sbr (NH_2), 2345 s (NH_2), 1942 wbr, 1717 wbr, 1627 m, 1514 m, 1465 s (CH_3), 1453 s (CH_3), 1333 w (CH_3), 1231 w (P) 1217 w (P), 1143 s (P), 1079 s (PO_2), 1037 s (PO_2), 1010 s, 982 w (CH_3), 932 w (P), 870 w, 813 s (P), 764 w, 756 w (P), 722 vw, 660 s (P), 634 m (P), 532 s (P), 503 w, 450 vw (P), 418 m (P), 384 m (P), 330 m cm^{-1}.

The ^1H NMR spectrum run in $CDCl_3$ has resonances at 0.83 (3H, ring CH_3, dd, ${}^4J_{PCCCH_3} = 1.61$, ${}^3J_{HCCCH_3} = 7.11$ Hz), 1.10 (6H, ring CH_3, d, ${}^3J_{PCCH_3} = 17.0$ Hz), 1.13 (6H, ring CH_3, d, ${}^3J_{PCCH_3} = 17.0$ Hz), 1.36 (6H, amine CH_3, t, ${}^3J_{H_2CCH_3} = 7.34$ Hz), 1.50 (1H, CH, dq, ${}^3J_{PCCH} = 5.28$ Hz, ${}^3J_{HCCH_3} = 7.11$ Hz); 2.90 (4H, CH_2, q, ${}^3J_{H_2CCH_3} = 7.34$ Hz), 10.5 (2H, NH_2, very broad) ppm. The δ(NH) was sensitive to concentration. At infinite dilution this was projected to have a chemical shift of 9.75 ppm.

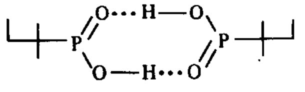
The ^{13}P NMR spectrum, proton decoupled, had $\delta = 49.05$ ppm in D_2O and 37.38 ppm in $CDCl_3$. In an undecoupled spectrum (30307 scans) the 13 multiplet clearly showed ${}^3J_{PCCH_3}$ coupling (16.18 Hz) but the finer coupling could not be resolved.

DISCUSSION

The physical and spectral features of 2,2,3,4,4-pentamethylphosphetanic acid, $C_8H_{16}PO_2H$, are given in Refs. 1 and 5 respectively. This acid is a phosphinic acid that, unlike most of this type, is easily made and is stable to hydrolysis. Moreover the phosphetan ring itself is very stable towards chemical attack. To date little has been said of its chemical behaviour as an acid and in this paper we report on the formation of some salts, complexes and an amine adduct.

$C_8H_{16}PO_2H$ is not very soluble in water. The hydrophobic tendency of the five methyl groups is enough to cancel the hydrophilicity of the acid centre. It is soluble in organic solvents. The metal salts of the acid are water soluble.

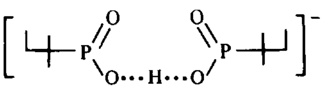
In some respects the behaviour of $C_8H_{16}PO_2H$ is expected to parallel that of carboxylic acids so that mutual hydrogen bond formation to give cyclic dimers would be anticipated, i.e. (II).[10] The ν_{OH} signal at *ca.* 3500 cm^{-1} is not observed but two very broad and strong peaks at 2250 and 2600 cm^{-1} can be attributed to ν(OH ·· O) of (II) by analogy with carboxylic acid dimers. Other broad bands at 955 and



(II)

500 cm^{-1} are the corresponding in-plane and out-of-plane OH··O bending modes. Dilution of $C_8H_{16}PO_2H$ in CCl_4 down to 0.001 M concentration failed to produce a signal in the spectrum at *ca.* 3500 cm^{-1} that could arise from the monomeric acid species. This seems to be evidence that the hydrogen bonding of (**II**) is stronger than that of $(RCO_2H)_2$ where dilution disturbs the equilibrium towards the monomer sufficiently for the latter's OH bond vibration to be observed.

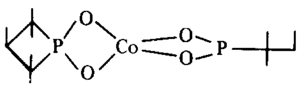
If the hydrogen bonding of acids is strong then that between an acid and its conjugate base is generally very strong.[7] Examples of this are the hydrogen bonds between the following combinations: $CH_3CO_2H + CH_3CO_2^-$;[11,12] $HNO_3 + NO_3^-$;[13] and even between $HSO_4^- + SO_4^{2-}$.[14] Indeed the first of these combinations, carboxylic acid and carboxylate, has yielded a large number of very strongly hydrogen bonded adducts.[15] Few examples of phosphorus acids interacting in this way are known but in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$ there is a polymeric arrangement of $H_2PO_4^- + HPO_4^{2-}$.[16] There is thus high expectation that $C_8H_{16}PO_2H + C_8H_{16}PO_2^-$ would interact in this manner to form an adduct (III).



(III)

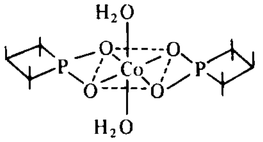
That this may occur is supported by the salting-in effect which occurs when $C_8H_{16}PO_2K$ is dissolved in water and the fact that this produces a solution that is approximately of the right composition for (**III**). Unfortunately crystals which grew from slow evaporation of such solutions were unsuitable for X-ray investigation. However the IR spectrum showed a high water content and a continuum in the region 850–450 cm^{-1} which may arise from a very strong hydrogen bond of the OHO type. Moreover the chemical shift of the phosphorus is not a weighted average of the acid and the anion, being almost the same as that of the anion. This suggests that both phosphetan parts have a deprotonated environment such as would be expected for (**III**) with the proton centred in the strong hydrogen bond.

The ability of the conjugate base $C_8H_{16}PO_2^-$ to act as a ligand was demonstrated by the formation of several complexes and in particular the cobalt (II) complex. This occurs in two forms which interconvert at 79° in solution. Above this temperature the tetrahedra complex is favoured and the structure (**IV**) is proposed as the most likely form based on the IR and UV evidence.[17] This form is stable at room temperature in the solid state but in aqueous solution it dissolves to form a pink solution, although in $CHCl_3$ it retains the tetrahedral configuration as shown by its colour and UV spectrum. Changes in the vibrational frequencies for the ν_s and $\nu_{as}(PO_2)$ modes are not dramatically different as compared to those of the salts except the $\nu_{as}(PO_2)$ is at a lower and $\nu_{as}(PO_2)$ at a slightly higher frequency than expected. A band in the IR spectrum at 545 cm^{-1} is not a phosphetan vibration and is tentatively assigned to a Co–O vibration.



(IV)

The pink crystals which can be grown from aqueous solution at room temperature are presumably octahedral and structure (V) is a reasonable assumption which would explain their colour and spectra. These crystals readily lose water and turn blue which suggest that it is the coordinated water molecules that are lost.



(V)

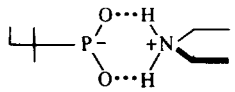
Whether this complex holds together in solution as V or exists in equilibrium with $Co(H_2O)_6^{2+}$ could not be determined conclusively from the UV spectrum; the λ_{max} of 500 nm may overlap the λ_{max} of $Co(H_2O)_6^{2+}$ at 530 nm, but the band was a single maximum with no suggestion of a second species so that V would appear to persist in aqueous solution.

The manganese complex of composition $Mn(C_8H_{16}PO_2)_2$ is insoluble in all solvents and may well be polymeric.

A selection of complexes were made of ruthenium showing that this ligand is capable of behaving in a manner analogous to carboxylic acids with $RuX_2(PPh_3)_3$.[18] The complexes $RuX_2(C_8H_{16}PO_2)(PPh_3)_2$, where X = Cl or Br, showed the expected IR bands associated with the phosphetan ligand. Yields of these and similar complexes were low due to higher solubility in the acetone used as solvent.

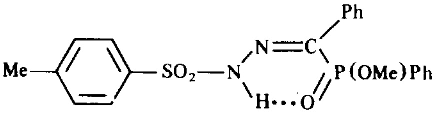
The combination of $C_8H_{16}PO_2H$ and diethylamine gave a material that analysed as the diethylammonium phosphetanate and in D_2O the ^{31}P NMR spectrum showed the anion to be $C_8H_{16}PO_2^-$ by comparison with the potassium salt's spectrum.

In $CDCl_3$ the signal shifts to 37.4 ppm. This, and especially the IR spectrum of this material, suggests that there is close association between the cation and the anion, maybe in the formation of a cyclic hydrogen bonded structure (**VI**).[19] Because of the dimensions



(VI)

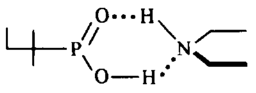
of the PO_2^- moiety and the tetrahedral angle at nitrogen, it would not be feasible for linear OHN bonds to form. An intramolecular NHOP hydrogen bond that is non-linear ($\angle$143°) has been reported in **VII**.[20]



(VII)

The δ(NH) chemical shift of the amine adduct is very downfield, again suggesting strong hydrogen bonding. In the system $CF_3CO_2H + Et_3N$ δ(NH) varies from 7.5 to 10.5 ppm and separate signals can be distinguished for the two forms $CF_3CO_2H \cdot\cdot NEt_3$ and $CF_3CO_2^- \cdot\cdot H\overset{+}{N}Et_3$, even at 40°C.[21]

The combination RCO_2H + imidazole[22] also has an IR spectrum in the region 3000–2000 cm^{-1} like that reported here for $C_8H_{16}CO_2H + Et_2NH$, i.e. a hydrogen bonding continuum with several sub-maxima. Whether this is solely due to **VII** or involves contributions from (**VIII**) cannot be decided



(VIII)

at this stage. The ^{31}P chemical shift of **VIII** would resemble that of $C_8H_{16}PO_2H$ in $CDCl_3$ ($\delta = 59.0$ ppm) but is much further upfield suggesting that contributions from **VIII** are small. In aqueous solution there is no evidence for **VIII** but a polar solvent would in any case favour the **VI** form. Yet type **VIII** structures have been postulated for adducts of RCO_2H + amines.[19]

It has also been shown by matrix IR spectroscopy that whereas $CF_3CO_2H + Me_3N$ is of the proton-transfer/hydrogen bond type, as is **VI**, the combination $CH_3CO_2H + Me_3N$ is a molecular adduct, as is **VIII**.[23] Further investigation into the amine adducts of $C_8H_{16}PO_2H$ is being carried out.

Acknowledgement—The authors thank the SERC for a research grant for R. J. P.

REFERENCES

1. E. Jugermann, J. McBride, R. Clutter and A. Mais, *J. Org. Chem.* 1962, **27**, 606 and 1833.
2. J. Emsley, T. B. Middleton and J. K. Williams, *J. Chem. Soc. Dalton* 1976, 979.
3. M. F. Crook, J. Emsley, T. B. Middleton and J. K. Williams, *Phosphorus* 1973, **3**, 45.
4. J. Emsley and J. K. Williams, *J. Chem. Soc. Dalton* 1973, 1756.
5. J. Emsley, T. B. Middleton and J. K. Williams, *J. Chem. Soc. Dalton* 1973, 2701.
6. D. D. Swank and C. N. Caughlan, *J. Chem. Soc. Chem. Commun* 1968, 1051; Mazhar-ul-Haque and C. N. Caughlan, *ibid*, 1968, 1228; Mazhar-ul-Haque, *J. Chem. Soc. B* 1970, 934; 1971, 117.
7. J. Emsley, *Chem. Soc. Revs.* 1980, **9**, 91.
8. T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.* 1966, **28**, 945.
9. L. Vaska, *Chem. Ind.* (*London*) 1961, 1402.
10. D. F. Peppard, J. R. Ferraro and B. W. Mason, *J. Inorg. Nucl. Chem.* 1960, **16**, 246.
11. J. Emsley, O. P. A. Hoyte and R. E. Overill, *J. Am. Chem. Soc.* 1978, **100**, 3303.
12. M. Currie, *J. Chem. Soc. Perkin II* 1972, 832.
13. J. M. Williams, J. Rozière and M. T. Rozière-Bories, *Inorg. Chem.* 1976, **15**, 2490.
14. M. Calti, G. Ferraris and G. Ivaldi, *Acta Cryst.* 1979, **B35**, 525.
15. J. C. Speakman, *Structure and Bonding* 1972, **12**, 141.
16. S. Tagaki, M. Mathew and W. E. Brown, *Acta Cryst.* 1980, **B36**, 766.
17. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* 4th Edn, p. 769. (1980).
18. D. S. Moore and S. D. Robinson, *Inorg. Chem.* 1979, **18**, 2307.
19. G. S. Denisov and N. S. Golubev, *J. Mol. Struct.* 1981, **75**, 311.
20. G. Mass and R. Hodge, *Acta Cryst.* 1980, **B36**, 499.
21. F. Kohler, R. Gopal, G. Götze, H. Atrops, M. A. Demiriz, E. Libermann, E. Wilhelm, F. Ratkovics and B. Palagyl, *J. Phys. Chem.* 1981, **85**, 2524.
22. R. Lindemann and G. Zundel, *J. Chem. Soc. Faraday II* 1977, **73**, 788.
23. M. Wierzejewska-Hnat, Z. Mielke and H. Ratajczak, *J. Chem. Soc. Faraday II* 1980, **76**, 834.