Contribution from the Pennsalt Chemicals Corporation,
Technological Center, King of Prussia, Pennsylvania

Phosphinylmethylphosphinates as Chelating Ligands

By J. P. King, B. P. Block, and I. C. Popoff

Received September 14, 1964

(Dimethylphosphinyl)-, (methylphenylphosphinyl)-, and (diphenylphosphinyl)methylphenylphosphinic acids have been prepared by hydrolysis of the Michaelis–Arbuzov reaction products of the appropriate chloromethylphosphine oxides and diethyl phenylphosphonite. They react with $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ and $Cr(C_5H_7O_2)_3$ under suitable conditions to yield the corresponding bis and tris chelates, except for the diphenyl–chromium(III) derivative, which was prepared in low yield *via* the chromium(II) derivative. The zinc derivatives are dimers, the chromium derivatives monomers. The metal chelates are more thermally stable than the corresponding acetylacetonates. Their infrared and ^1H n.m.r. spectra are discussed.

In order to prepare more stable analogs of $[Cr(CH_3COCHCOCH_3)(OP(C_6H_5)_2O)_2]_x$[1] we require chelating groups which will withstand higher temperatures than do the acetylacetonate and other organic groupings. The purpose of this report is to describe the synthesis of some phosphinylmethylphenylphosphinates and their evaluation as chelating groups.

Experimental

Reagents.—Reagent grade chemicals were used without purification except as otherwise indicated.

$(C_6H_5)_2P(O)CH_2Cl$ was prepared essentially as described by Kabachnik and Shepeleva[2] and recrystallized from benzene to a melting point of 135–136°.

Anal. Calcd. for $C_{13}H_{12}ClOP$: C, 62.29; H, 4.81; Cl, 14.14; P, 12.36. Found: C, 62.37; H, 5.05; Cl, 14.20; P, 11.90.

$(C_6H_5)(CH_3)P(O)CH_2Cl$.—A solution of 38 g. (0.32 mole) of CH_3MgBr in diethyl ether[3] was added with stirring to a solution of 66 g. (0.32 mole) of $C_6H_5P(O)(CH_2Cl)Cl$[4] in 300 ml. of diethyl ether chilled below 15° at such a rate that the reaction temperature never exceeded 25°. The mixture was then stirred for 2 hr. at room temperature, the ether was decanted, and the gummy residue was poured into a 750-ml. aqueous solution containing 66 g. of Na_2CO_3. The resulting mixture was extracted four times with 250-ml. portions of chloroform, and the combined extracts were evaporated almost to dryness on a steam bath. Addition of 80 ml. of petroleum ether (b.p. 30–60°) to the residue resulted in immediate precipitation of 28 g. (47% yield) of white solid which was recrystallized from benzene to a m.p. of 106–108°.

Anal. Calcd. for $C_8H_{10}ClOP$: C, 50.95; H, 5.34; Cl, 18.70; P, 16.42. Found: C, 50.30; H, 5.32; Cl, 17.89; P, 16.62.

$(CH_3)_2P(O)CH_2Cl$ was similarly prepared by a Grignard reaction. For its preparation 72 g. (0.43 mole) of $ClCH_2P(O)Cl_2$[5] in 250 ml. of diethyl ether was treated with 103 g. (0.862 mole) of CH_3MgBr in 450 ml. of diethyl ether at temperatures below 30°. Work-up as before yielded 15 g. (28% yield) of a white crystalline product, m.p. 69–72°.

Anal. Calcd. for C_3H_8ClOP: C, 28.48; H, 6.37; Cl, 28.02; P, 24.48. Found: C, 28.03; H, 6.06; Cl, 27.45; P, 23.58.

$RR'P(O)CH_2P(O)(C_6H_5)OH$.—The general procedure employed was to heat a 1:1 molar mixture of $RR'P(O)CH_2Cl$ and $C_6H_5P(OC_2H_5)_2$[6] carefully under nitrogen with stirring until C_2H_5Cl started evolving (care, reaction is exothermic) and then to maintain the temperature at 170–180° until C_2H_5Cl was no longer evolved (about 2 hr.). The cooled reaction product was washed with diethyl ether or *n*-hexane several times and then hydrolyzed in refluxing 2 *M* HCl. The HCl solution was distilled off, and traces of water were removed by azeotropic distillation from toluene. The crude product, recovered from the cooled toluene by filtration, was then recrystallized from toluene or acetonitrile. The results are summarized in Table I.

Zinc Chelates.—The general procedure used to prepare the zinc chelates was to reflux a mixture of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ and excess phosphinylmethylphosphinic acid in ethanol or benzene, evaporate off the solvent, convert the residual oil to a solid by trituration with diethyl ether or hexane, and recrystallize the product from ethanol–benzene or chloroform–diethyl ether. The results are given in Table II.

Chromium Chelates.—The procedure that was used for two of the chromium chelates was to reflux a mixture of $Cr(CH_3COCHCOCH_3)_3$[7] and a slight excess of the phosphinylmethylphosphinic acid in o-$C_6H_4Cl_2$ for 12–24 hr. until $CH_3COCH_2COCH_3$ was no longer evolved. Work-up then varied with the acid. The methylphenyl product was recovered by stripping off the solvent, dissolving the residue in benzene, and precipitating the product with petroleum ether. A chloroform solution of the product was then passed through an alumina column, and two products softening at 210–234 and 210–218° were eluted with chloroform and ethanol, respectively (see Table III). The dimethyl product, on the other hand, was filtered off, dissolved in chloroform, and precipitated from the concentrated solution with benzene. Azeotropic distillation from xylene removed the water of crystallization.

The third chelate, the chromium diphenyl derivative, could not be prepared by the foregoing procedure. It was made by refluxing a mixture of 2.7 g. (0.0144 mole) of $Cr(C_2H_3O_2)_2 \cdot H_2O$[8] and 12.2 g. (0.0309 mole) of $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OK$ in 80 ml. of water under nitrogen. The precipitate was washed with oxygen-free water and added to a solution of 5.48 g. (0.0154 mole) of $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OH$ in oxygen-free water and refluxed under nitrogen. The solid produced was washed with water, dissolved in chloroform, and reprecipitated by the addition of petroleum ether to the solution after it was concentrated. It was then separated into soluble and insoluble fractions by extraction with benzene in a Soxhlet extractor. The benzene-soluble fraction was recovered and purified by passing its chloroform solution through an alumina column. The benzene-insoluble fraction was purified in the same manner. During the

---

[1] B. P. Block, J. Simkin, and L. R. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

[2] M. I. Kabachnik and E. S. Shepeleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 862 (1953); from *Chem. Abstr.*, **49**, 843*f* (1955).

[3] Obtained from Arapahoe Chemicals, Inc., as an approximately 3 *M* solution.

[4] Prepared by the method of Kabachnik and Shepeleva.[2] M.p. 48–50° after solidification of liquid (refractive index 1.5170 at 28°) first collected.

[5] M. I. Kabachnik and E. S. Shepeleva, *Sintezy Org. Soedin. Sbornik*, **2**, 150 (1952).

[6] Prepared in the usual way from $C_6H_5PCl_2$ and C_2H_5OH; b.p. 63° at 0.3 mm. Kosolapoff lists 235–237° at atmospheric pressure and 110–111° at 10–13 mm. G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 147.

[7] Obtained from Mackenzie Chemical Works, Inc., and purified by the procedure of W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957).

[8] Prepared by a modification of the usual technique: L. R. Ocone and B. P. Block, *ibid.*, **8**, in press.

TABLE I

SYNTHESIS OF $RR'P(O)CH_2P(O)(C_6H_5)OH$ (0.05 MOLE SCALE)

				Calcd.				Found				
R	R′	Yield,[a] %	M.p.,[b] °C.	C, %	H, %	P, %	Form. wt.	C, %	H, %	P, %	Neut. equiv.	Mol.[c] wt.
C_6H_5	C_6H_5	47	130–131	64.05	5.09	17.39	356	63.91	5.31	17.45	355	550
C_6H_5	CH_3	52	206–208	57.15	5.48	21.05	294	56.86	6.10	21.13	292	. . .
CH_3	CH_3	78	143–145	46.56	6.08	26.68	232	46.70	6.16	26.89	230	400

[a] Crude product. [b] Recrystallized product. [c] In CH_3CN.

TABLE II

ZINC PHOSPHINYLMETHYLPHENYLPHOSPHINATES, $Zn[RR'P(O)CH_2P(O)(C_6H_5)O]_2$

				Calcd., %				Found, %			
R	R′	Yield, %	M.p.,[a] °C.	C	H	P	Zn	C	H	P	Zn
C_6H_5	C_6H_5	92	265–273	58.82	4.42	15.97	8.42	58.86	4.68	16.24	8.37[b]
C_6H_5	CH_3	95	135–160	51.60	4.64	19.01	10.03	51.61	5.10	18.69	10.5[c]
CH_3	CH_3	97	229–233	40.97	4.97	23.48	12.39	40.49	4.84	23.81	12.1[d]

[a] These chelates softened over a range and did not melt sharply. [b] Calcd. formula wt., 776; mol. wt. found in $CHCl_3$, 1401. [c] Calcd. formula wt., 652; mol. wt. found in acetone, 1200. [d] Calcd. formula wt., 528; mol. wt. found in $CHCl_3$, 1000.

TABLE III

CHROMIUM PHOSPHINYLMETHYLPHENYLPHOSPHINATES, $Cr[RR'P(O)CH_2P(O)(C_6H_5)O]_3$

				Calcd., %				Found, %			
R	R′	Yield, %	M.p., °C.	C	H	Cr	P	C	H	Cr	P
C_6H_5	C_6H_5	. . .[a]	200–220	61.24	4.60	4.65	16.63	60.96	4.78	. . .[a]	16.48
C_6H_5	CH_3	95	210–234[b]	54.15	4.87	5.58	19.95	53.88	5.38	5.5	17.37
			210–218[c]	54.15	4.87	5.58	19.95	54.02	5.62	5.1	19.48[d]
CH_3	CH_3	95	365–370 dec.	43.50	5.27	6.98	24.93	43.21	5.28	7.3	24.11[e]

[a] Benzene-soluble, yield and Cr content not determined. [b] Eluted with $CHCl_3$. [c] Eluted with C_2H_5OH. [d] Calcd. formula wt., 941; mol. wt. found in $CHCl_3$, 1000. [e] Calcd. formula wt., 745; mol. wt. found in $CHCl_3$, 680.

work-up of the benzene-soluble fraction additional products were obtained; however, their analyses did not correspond to any expected products.

The results for the chromium chelates are given in Table III.

The benzene-insoluble fraction of the diphenyl product proved to be $Cr(H_2O)(OH)[(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)O]_2$, softening at 270–290°.

Anal. Calcd. for $C_{38}H_{37}CrO_8P_4$: C, 57.23; H, 4.68; Cr, 6.52; P, 15.53. Found: C, 56.98; H, 4.66; Cr, 6.31; P, 14.91.

Thermogravimetric Analysis.—The chelates were subjected to thermogravimetric analysis by our usual procedure[9] in a nitrogen atmosphere at a heating rate of 5°/min. The weight–temperature curves are shown in Figure 1.

Infrared spectra were recorded with a Perkin-Elmer Model 221 instrument employing a sodium chloride prism in the 2–15 μ region and with a Perkin-Elmer Model 337 grating spectrometer in the 2–25 μ region. Spectra were obtained for Nujol mulls and acetonitrile solutions. The absorption bands are listed in tables available from the American Documentation Institute.[10]

Proton nuclear magnetic resonance spectra were recorded at 60 Mc. on a Varian Associates HR-60 spectrometer for $CDCl_3$ or $CDCl_3$–CH_3OH solutions. Tetramethylsilane (TMS) was used as an internal standard. Resonance frequencies are accurate to ±0.02 p.p.m. and resolution is about 1 c.p.s. Spectra are recorded in Table IV. In both the doublet and triplet J_{HP} was 14–16 cycles for all the compounds studied.

Molecular weights were determined for chloroform or acetonitrile solutions with a Mechrolab vapor pressure osmometer by extrapolating measurements made at a series of concentrations to zero concentration.

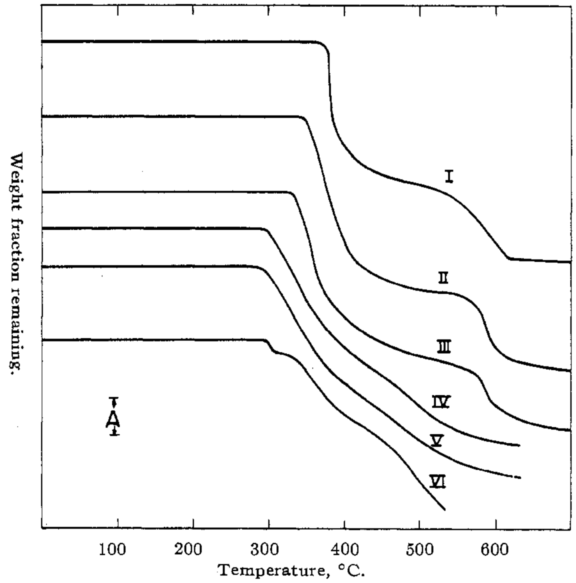


Figure 1.—TGA of $Cr(RR'P(O)CH_2P(O)(C_6H_5)O)_3$ [R and R′ = CH_3 (curve I), R = C_6H_5 and R′ = CH_3 (curve II), and R and R′ = C_6H_5 (curve III)] and of $[Zn(RR'P(O)CH_2P(O)(C_6H_5)O)_2]_2$ [R = C_6H_5 and R′ = CH_3 (curve IV), R and R′ = CH_3 (curve V), and R and R′ = C_6H_5 (curve VI)] in nitrogen with a heating rate of 5°/min. The ordinate distance *A* corresponds to 10% of the sample weight for each curve.

Discussion

Other investigators have found that phosphinylmethylphosphine oxides function as neutral bidentate ligands but are not sufficiently enolic to be effective analogs of β-diketones.[11,12] Consequently we turned to the consideration of phosphinylmethylphosphinic acids as the source of bidentate ligands bearing a charge of −1

---

[9] J. R. Soulen and I. Mockrin, *Anal. Chem.*, **33**, 1909 (1961).

[10] Order Document No. 8161 from the Chief, Photoduplication Service, Library of Congress, Washington 25, D. C., Auxiliary Publications Project, remitting $1.25 for microfilm (35-mm.) or $1.25 for photocopies.

[11] J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, *J. Am. Chem. Soc.*, **83**, 1722 (1961).

[12] J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, **2**, 312 (1963).

TABLE IV

^{1}H N.M.R. SPECTRA OF $M[RR'P(O)CH_2P(O)(C_6H_5)O]_n$ IN $CDCl_3$ (P.P.M. BELOW TMS)

M	R	R′	n	CH_3 doublet	CH_2 triplet	Aromatic CH	Acidic H
H[a]	CH_3	CH_3	1	1.58	2.51	7.29–8.01	12.84
H[a]	C_6H_5	CH_3	1	1.97	2.76	7.29–7.98	...
H	C_6H_5	C_6H_5	1	...	3.25	6.98–7.87	12.32
Zn[a]	CH_3	CH_3	2	1.57	2.51	7.17–8.05	...
Zn[a]	C_6H_5	CH_3	2	1.85	2 77	7.00–8.01	...
Zn	C_6H_5	C_6H_5	2	...	3.28	6.77–7.92	...

[a] Spectra recorded in $CDCl_3$–CH_3OH.

and capable of forming $\underbrace{M{-}O{-}P{-}C{-}P{-}O}$ chelate rings.

A logical route to disubstituted phosphinylmethylphosphinic acids is *via* a Michaelis–Arbuzov reaction between $RR'P(O)CH_2Cl$ and $R''P(OR''')_2$, *i.e.*

$$RR'P(O)CH_2Cl + R''P(OR''')_2 \rightarrow RR'P(O)CH_2P(O)(R'')OR''' + R'''Cl$$

Although difficulties were recently reported in the synthesis of one of the starting materials of choice, chloromethylphosphine oxides,[13] we found the procedure of Kabachnik and Shepeleva,[2] the reaction between the appropriate R_nPCl_{3-n} and $(CH_2O)_3$ in a bomb, to be quite satisfactory for the preparation of $(C_6H_5)_2P(O)CH_2Cl$ and $(C_6H_5)P(O)(CH_2Cl)Cl$. The latter compound and $ClCH_2P(O)Cl_2$ both react readily with CH_3MgBr in the proper stoichiometric ratio to give $(C_6H_5)(CH_3)P(O)CH_2Cl$ and $(CH_3)_2P(O)CH_2Cl$[14] in 47 and 28% yields, respectively. The chlorine in the chloromethyl group is thus, as expected, less reactive than the chlorines bonded directly to the phosphorus. The chloromethylphosphine oxides were found to react with $C_6H_5P(OC_2H_5)_2$ at elevated temperatures in the expected manner to yield the ethyl esters of the desired phosphinylmethylphenylphosphinic acids. Hydrolysis with 3 M HCl led to the acids.

The synthesis of the zinc chelates of the three phosphinylmethylphenylphosphinic acids was straightforward and merely required the treatment of $Zn(C_2H_3O_2)_2{\cdot}2H_2O$ with an excess of the acid in ethanol or benzene. Yields were quantitative. The synthesis of the chromium chelates of $(C_6H_5)(CH_3)P(O)CH_2P(O)(C_6H_5)OH$ and $(CH_3)_2P(O)CH_2P(O)(C_6H_5)OH$ was also routine although a somewhat different type of reaction, the displacement of $(CH_3COCHCOCH_3)^-$ from $Cr(CH_3COCHCOCH_3)_3$ by treatment with the appropriate acid in refluxing *o*-dichlorobenzene, was used. In the dimethyl case the yield was quantitative, but in the methylphenyl case two forms were isolated during the work-up. It thus appears that there are geometric somers in this case, as is to be expected; however, this aspect was not studied in detail.

The preparation of the chromium chelate of the diphenyl acid was much more difficult, apparently because of steric problems, and the 3:1 chelate could only be obtained indirectly. Reactions of the acid or its potassium salt with $Cr(C_2H_3O_2)_3{\cdot}xH_2O$, $Cr(CH_3COCHCOCH_3)_3$, or $CrCl_3(THF)_3$ under a variety of conditions did not yield the desired chelate. A small amount of the 3:1 chelate was obtained by first treating $Cr(C_2H_3O_2)_2{\cdot}H_2O$ with $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OK$ to form the chromium(II) derivative and then oxidizing with $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OH$. Most of the product, however, was $Cr(H_2O)(OH)[(C_6H_5)_2P(O)CH_2(PO)(C_6H_5)O]_2$ and unidentified material. This suggests that there was extensive oxidation of the chromium(II) intermediate by water at 100° in the inert atmosphere to give a product analogous to the $Cr(H_2O)(OH)[OP(C_6H_5)_2O]_2$ polymer obtained by air oxidation of chromium(II) diphenylphosphinate.[15]

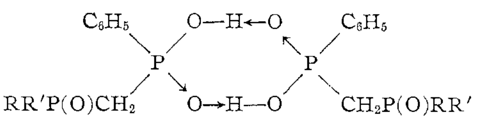
Infrared Spectra.—The stretching frequencies of phosphoryl groups usually occur between 1350 and 1170 cm.$^{-1}$.[16,17] The assignment of the highest P–O band, 1225 cm.$^{-1}$, in $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OC_2H_5$ to the P(O) in the $-P(O)(C_6H_5)OC_2H_5$ group is based on the consideration that P(O) stretching frequencies shift toward higher frequencies with increasing electronegativity of the other groups bonded to the phosphorus. This effect has been clearly shown for $C_6H_5P(O)(OC_2H_5)_2$, 1257 cm.$^{-1}$, and $(C_6H_5)_3PO$, 1190 cm.$^{-1}$.[18]

The assignment of the stretching frequencies to the two phosphoryl groups in the phosphinylmethylphenylphosphinic acids was made by comparing the frequencies in Nujol mulls and dilute solutions in acetonitrile (Table V). In the solid state both phosphoryl groups can readily participate in hydrogen bonding by intermolecular association, whereas in solution discrete dimers are expected, in analogy to other phosphinic acids.[19] The molecular weights (see Table I) of the acids included in Table V indicate degrees of polymerization of 1.5 and 1.7 in acetonitrile in support of this thesis. Consequently we conclude that the bands that increase in frequency are to be assigned to the phosphoryl in the RR′P(O) end of the molecule since they are not hydrogen bonded in the dimer

TABLE V

P(O) ABSORPTION BANDS IN NUJOL MULLS AND IN ACETONITRILE SOLUTION (CM.$^{-1}$)

$(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OH$		$(CH_3)_2P(O)CH_2P(O)(C_6H_5)OH$	
Nujol	Acetonitrile	Nujol	Acetonitrile
1220	1236	1208	1220
1185	1198		
1147	1149	1176	1176
1124	1124	1124	1124



It is interesting to note that the bands assigned to phosphoryl in the RR′P(O) groups do not change in the manner expected from consideration of the electro-

---

(13) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 2423 (1961).

(14) These two compounds were included in a study of P-31 n.m.r. spectra [K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962)], but details of their preparation are not available in the literature.

(15) A. J. Saraceno and B. P. Block, *J. Am. Chem. Soc.*, **85**, 2018 (1963).

(16) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1958.

(17) L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961).

(18) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(19) G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

negativities of R and R′. Hydrogen bonding appears to be an overriding factor in this case.

The bonded OH bands present in the acids at 2700–2200 cm.$^{-1}$ are absent, as expected, in the zinc and chromium complexes. Again it is interesting to attempt to assign the proper absorption bands to the two different phosphoryl groups. The substitution of a metal ion for hydrogen and the concomitant formation of a chelate should lower the frequency of the phosphoryl in the RR′P(O) group and increase the frequency of the phosphoryl in the $P(O)(C_6H_5)O^-$ group because of the complete elimination of hydrogen bonding in the chelate. The assignments on this basis are in good agreement with those made for the acids and serve to support the formation of chelate rings.

Table VI summarizes the average stretching frequencies assigned to each type of phosphoryl group and gives the shifts observed in going from the acids to the chelates.

TABLE VI
AVERAGE P(O) STRETCHING FREQUENCIES AND SHIFTS FOR $M(RR'P(O)CH_2P(O)(C_6H_5)O)_n$ (CM.$^{-1}$)

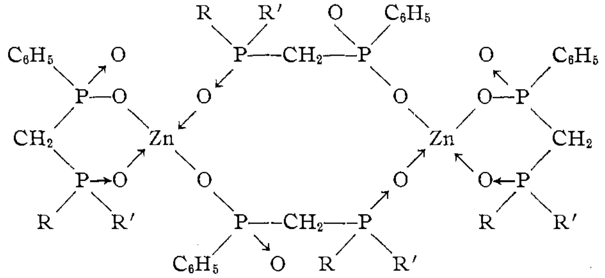
M	R	R′	n	ν_{PO} for RR′P(O)	Shifts from acids	ν_{PO} for $P(O)(C_6H_5)O$	Shifts from acids
H	C_6H_5	C_6H_5	1	1203	...	1136	...
Zn	C_6H_5	C_6H_5	2	1146	−57	1192	+56
Cr	C_6H_5	C_6H_5	3	1125	−78	1208	+72
H	C_6H_5	CH_3	1	1200	...	1137	...
Zn	C_6H_5	CH_3	2	1136	−64	1170	+33
Cr	C_6H_5	CH_3	3	1130	−70	1198	+61
H	CH_3	CH_3	1	1208	...	1171	...
Zn	CH_3	CH_3	2	1150	−58	1198	+27
Cr	CH_3	CH_3	3	1139	−69	1203	+32

All the shifts for P(O) in the RR′P(O) group are in the range −57 to −78 cm.$^{-1}$ and for P(O) in the $P(O)(C_6H_5)O$ group from +27 to +72 cm.$^{-1}$. The decreases in the former clearly indicate the effect of coordination on these groups and are comparable to the effects noted by Cotton and Schunn[20] for metal derivatives of $(RO)_2P(O)CH_2COCH_3$. The consistently greater shift for the chromium complexes than for the corresponding zinc complexes suggests that the P(O) bond order is lower in them than in the zinc chelates. This difference, the broadening of the bands, and the larger number of peaks in the zinc chelate spectra are consistent with the structures proposed for them later. It is interesting to note that all the phosphinylmethylphenylphosphinate compounds examined have strong absorption bands near 800 cm.$^{-1}$, a region assigned to PCP by previous investigators.[11,21]

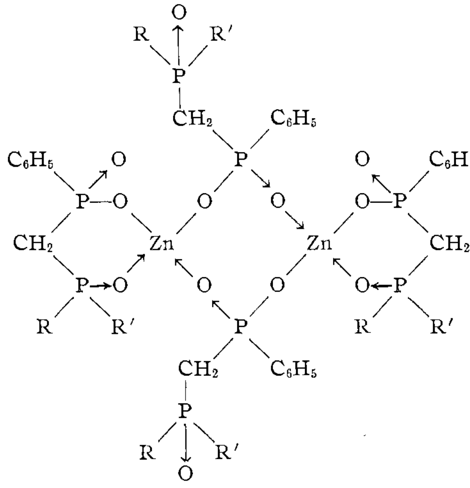
N.m.r. Spectra.—The ^1H n.m.r. spectra of the phosphinylmethylphenylphosphinic acids show the lines and splitting patterns expected. All exhibit a triplet due to the methylene group adjacent to two phosphorus atoms and a broad band due to phenyl protons, not separately resolved. There is a doublet for the two acids containing methyl groups adjacent to one phosphorus atom. A single line is found for the proton in the dimethyl and diphenyl acids, but the corresponding resonance could not be detected for $(C_6H_5)(CH_3)P(O)CH_2P(O)(C_6H_5)OH$ in the mixed solvent $CH_3OH–CDCl_3$.

The spectra of the zinc complexes are in all cases nearly identical with those of the acids. Only small differences in line positions, considered negligible, are observed, except for the CH_3 doublet in $Zn[(C_6H_5)(CH_3)P(O)CH_2P(O)(C_6H_5)O]_2$. This difference may be due to the acid not the chelate, for the melting point of $(C_6H_5)(CH_3)P(O)CH_2P(O)(C_6H_5)OH$, 208°, is out of line with the melting points of the dimethyl and diphenyl analogs, 146 and 131°, respectively.

Because the zinc chelates were found to be dimeric in chloroform, their most probable structures are II and III. There is precedent in the literature for both types of bridges.[1,12] Although from consideration of ring size III is more attractive, what little evidence n.m.r. affords would appear to support II, in that two kinds of CH_3 protons are not observed and all the CH_3 groups are more equivalent in II than in III. It is true, however, that the differences in environment in III are two to three atoms removed from the CH_3 and may not be significant. The large number of phosphoryl absorption bands in the infrared suggests that, in fact, both structures may be present.



II



III

Thermal Stability.—Although the phosphinylmethylphenylphosphinates do not exhibit outstanding thermal stability as judged by the inception of weight loss at about 300° for the zinc chelates and 330 to 360° for the chromium(III) chelates, they are significantly more stable than the corresponding acetylacetonates, *i.e.*,

---

(20) F. A. Cotton and R. A. Schunn, *J. Am. Chem. Soc.*, **85**, 2394 (1963).
(21) K. Moedritzer and R. R. Irani, *J. Inorg. Nucl. Chem.*, **22**, 297 (1961).

$Zn(C_5H_7O_2)_2$, 190°,[22] and $Cr(C_5H_7O_2)_3$, 250°.[23] Consequently, in view of their demonstrated chelating ability, they may prove of value in improving the thermal stability of our chelated coordination polymers.[1]

Acknowledgment.—This work was supported in part by the Office of Naval Research. We are indebted to Miss Ruth Kossatz for the infrared spectral data and assistance in their interpretation and to Dr. G. R. Leader for the n.m.r. data and assistance in their interpretation. The thermogravimetric data were supplied by Dr. J. R. Soulen and the analyses and molecular weights by our Analytical Department. Dr. L. K. Huber first prepared $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)OC_2H_5$, and W. E. Smith provided experimental assistance.

[22] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

[23] J. von Hoene, R. G. Charles, and W. W. Hickam, *ibid.*, **62**, 1098 (1958).

CONTRIBUTION FROM W. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Optical Activity of Pseudotetragonal Coordination Compounds. The Dissymmetric Ligand Field in Diacidobis(*l*-propylenediamine)cobalt Complexes

BY R. A. D. WENTWORTH AND T. S. PIPER

Received September 14, 1964

The circular dichroism and absorption spectra of $Co(l\text{-pn})_2Cl_2^+$ and $Co(l\text{-pn})_2(NO_2)_2^+$ are reported. The assignments are discussed. Point charge and molecular orbital models are proposed for the molecules. Electric moments calculated from the circular dichroism indicate that virtually all of the intensity in the absorption spectra is vibronic in origin.

Optical activity and in particular circular dichroism is beginning to provide new information about molecular and electronic structure of coordination compounds. Recent attention has centered on predominantly d–d transitions of trigonal complexes such as $Co(en)_3Cl_3$ in both experimental studies[1,2] and theoretical analyses.[2,3] Complexes with pseudotetragonal symmetry are relatively unstudied but for the early experimental work of Mathieu[4] and a recent proposal of assignments for electronic transitions of *trans*-$Co(l\text{-pn})_2Cl_3$ based on circular dichroism and magnetic selection rules.[5]

Experimental

Preparation of Compounds. *l*-Propylenediamine.—Propylenediamine was resolved by recrystallization of the *d*-tartrate[6] until there was no appreciable change in the optical rotation; $[\alpha]_D$ −30.1°.

Anal. Calcd. for $C_{11}H_{22}N_2O_{12}\cdot 2H_2O$: C, 32.20; H, 6.39; N, 6.83. Found: C, 31.95; H, 6.33; N, 6.91.

Solutions of *l*-pn were prepared by reaction of the dihydrate with the calculated amount of $Ba(OH)_2\cdot 8H_2O$ in a minimum amount of water, followed by cooling at ice temperature and filtering.

trans-$[Co(l\text{-pn})_2Cl_2]ClO_4$ was prepared by dropwise addition of concentrated perchloric acid to a cold, concentrated, aqueous solution of crude *trans*-$[Co(l\text{-pn})_2Cl_2]Cl\cdot HCl\cdot 2H_2O$,[7] followed by filtration and a rapid recrystallization by the same procedure.

Anal. Calcd. for $[Co(C_3H_{10}N_2)_2Cl_2]ClO_4$: C, 19.09; H, 5.30; total Cl, 28.18. Found: C, 18.89; H, 5.39; total Cl, 28.37.

trans-$[Co(l\text{-pn})_2(NO_2)_2]ClO_4$ was prepared by the method of O'Brien, McReynolds, and Bailar.[8]

trans-$[Co(l\text{-pn})(d\text{-pn})Cl_2]ClO_4$ was prepared by treating a saturated methyl alcohol solution of the racemic chloride[7] with concentrated $HClO_4$ and washing with methyl alcohol and then ether. A second crop was obtained by cooling the filtrate to 0°. Interestingly, the recrystallization procedure used with the optically active compound was not useful because of lower solubility. Instead, the perchlorate was converted to the chloride by shaking with an excess of Dowex 2 anion-exchange resin in the chloride form, followed by reprecipitation of the perchlorate with concentrated perchloric acid and washing with methyl alcohol and then ether.

Anal. Found: C, 18.97; H, 5.38.

Spectral Measurements.—Visible and ultraviolet spectra were determined using a Cary Model 14 spectrophotometer. The circular dichroism was determined using a Roussel–Jouan Dichrographe with a spectral range of 2000–6000 Å. Methanol was used as a solvent. The spectra are given in Figures 1 and 2. The decadic extinction coefficient in M^{-1} cm.$^{-1}$ (ϵ) is used. $\Delta\epsilon$ is the circular dichroism $\epsilon_l - \epsilon_r$.

Assignments

Before making assignments, we need to be certain our recorded spectra were obtained from solutions free of solvolysis products. We used methanol solutions because such solutions of *trans*-$Co(en)_2Cl_2^+$ are known to be stable to solvolysis and isomerization.[9] In water this cation hydrolyzes with isomerization; the half-time is 3.57 hr. at 30°.[10] We have followed the hydrolysis of *trans*-$Co(l\text{-pn})_2Cl_2^+$ at 27° using the circular dichroism at 6000 Å.; this cation disappears with a half-life of 3.5 hr., in good accord with Mathieu's result.[11] Our

---

[1] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

[2] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

[3] A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

[4] J.-P. Mathieu, *Ann. Phys.*, [11] **19**, 335 (1944).

[5] J. H. Dunlop and R. D. Gillard, *Mol. Phys.*, **7**, 493 (1964).

[6] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

[7] A. Werner and A. Frohlich, *Ber.*, **40**, 2228 (1907).

[8] T. D. O'Brien, J. P. McReynolds, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **70**, 749 (1948).

[9] D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

[10] J.-P. Mathieu, *Bull. soc. chim. France*, **3**, 2152 (1936).

[11] As the hydrolysis proceeds a new band appears at 4780 Å. which may be assigned to *cis* hydrolysis products. At no point in the hydrolysis could we reproduce the results of ref. 5; see Figure 1.