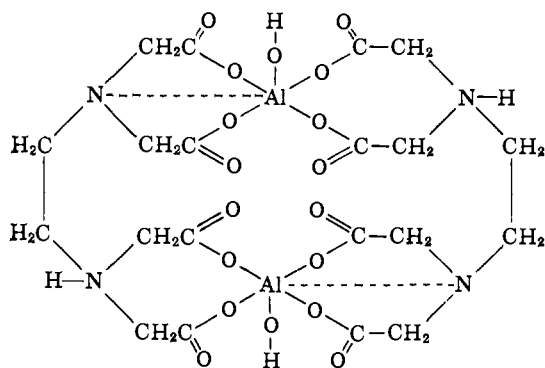


and somewhat more plausible, explanation of the two peaks observed for aluminum-EDTA would be that the area measurements are in error or that the molar absorptivities are different for the two species and that the ratio of concentrations for the two species is unity. Making this assumption, a possible structure for the complex would be $\text{AlHY}(\text{OH})^-$ with a proton attached to one of the nitrogen atoms. This, plus strong coordination with the two attached carboxylate groups, might account for the 1640 cm.^{-1} peak, while the other two carboxylates could bring about the 1580 cm.^{-1} peak. Studies of the n.m.r. spectra for the protons in the aluminum-EDTA complex¹⁰ tend to support this latter conclusion. A dimeric form of the chelate may be the actual species in solution with a structure represented by



Such a structure would explain in part the slow equilibria observed for the aluminum-EDTA complex

(10) D. T. Sawyer, R. J. Kula, C. M. Finley, and S. Chan, unpublished results, in preparation (1962).

and the resulting difficulties when titrating aluminum ions with EDTA. An alternative, but comparable structure would be a linear polymer. The infrared data (Fig. 5) indicate that at about pD 10 the complex becomes unstable and aluminum hydroxide precipitates, leaving the EDTA anion. The n.m.r. data also support this conclusion.¹⁰

The cerium(III)-EDTA complex has peaks only at 1610 and 1590 cm.^{-1} above pD 2.3. Since the peak areas are difficult to measure, further conclusions concerning the structure are not justified.

For the vanadium(IV)-EDTA complex there is a 1720 cm.^{-1} peak up to pD 3.6. There also is a 1620 cm.^{-1} peak which reaches its maximum area at pD 3.6 and then decreases in area as a 1580 cm.^{-1} peak increases in area. The areas of these two peaks are equal at pD 7.1. At this condition the chelate species may have the structure $\text{VOHY}(\text{OH})^-$ with the proton on one of the nitrogen atoms. As the pD is increased, this proton would be removed causing all four carboxylates to absorb at 1580 cm.^{-1} .

From pD 1 to pD 12 the bismuth-EDTA complex gives a single peak at 1605 cm.^{-1} which would indicate a single chelate species of the form BiY^- without protons on the nitrogen atoms. Because the frequency for this chelate is above 1580 cm.^{-1} , which is characteristic of the free carboxylate group, the strong coordinate bonding is indicated with some possibility that the nitrogen atoms are also strongly coordinated. The same remarks are applicable for the thorium(IV)-EDTA complex except that it has a single peak at 1605 cm.^{-1} from pD 0.4 to pD 12. Again, strong coordinate bonding is indicated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Metal Salts and Complexes of Dialkoxyphosphonylacetylmethanide Ions¹

By F. A. COTTON² AND R. A. SCHUNN

RECEIVED FEBRUARY 27, 1963

The preparation and characterization of some compounds containing the anions $\{[(\text{RO})_2\text{P}(\text{O})\text{CHCOCH}_3]^-$ are reported. Denoting the anion with $\text{R} = \text{C}_2\text{H}_5$ as L , the compounds prepared are: NaL , CrL_3 , $(\text{CoL}_2)_x$, and ZnL_2 . The cobalt complex is a pale pink solid containing octahedrally coordinated cobalt and evidently involves association of CoL_2 molecules. Association persists in various organic solutions at high concentrations and low temperatures, but dissociation to give a blue species, which may be a tetrahedral monomer, has been observed. The analog of CrL_3 in which $\text{L} = \text{CH}_3$ has also been prepared as have $\{[(\text{EtO})_2\text{P}(\text{O})]_2\text{CH}\} \text{K}$ and $\{[(\text{EtO})_2\text{P}(\text{O})]_2\text{CHCH}_3\}$, the latter by reaction of methyl iodide with the sodium salt $\{[(\text{EtO})_2\text{P}(\text{O})]_2\text{CH}\} \text{Na}$. The postulated structures of all diamagnetic compounds have been confirmed by high resolution proton magnetic resonance spectroscopy. Finally, it is shown that several lines of physical evidence leave little doubt that resonance similar to that in β -ketoenolate anions occurs in both the $\{[(\text{EtO})_2\text{P}(\text{O})]_2\text{CH}\}^-$ and $\{[(\text{EtO})_2\text{P}(\text{O})\text{CHCOCH}_3]^-$ anions.

Introduction

A considerable amount of work has been reported in the early literature on the existence of enol forms of β -ketophosphonates, $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{COR}'$. However, in 1952, Perkow³ showed that many of the β -ketophosphonates believed to exist in enol as well as keto forms were in reality mixtures of the β -ketophosphonates and the isomeric vinyl phosphates, $(\text{RO})_2\text{P}(\text{O})\text{OCR}'=\text{CR}_2$. This subject has recently been reviewed by Lichtenthaler.⁴

In many cases the two isomers can be cleanly separated and such is the case for the dialkoxyphosphonylacetylmethanes, $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{COCH}_3$, where $\text{R} = \text{CH}_3$ or CH_2CH_3 . Pudovik,⁵ in 1957, reported the reaction of diethoxyphosphonylacetylmethane with sodium metal and subsequent reaction of the mixture with various organic halides to give products of the type $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHRCOCH}_3$. The intermediate sodium compound was not isolated. The intermediate position of diethoxyphosphonylacetylmethane between acetylacetone and bis-(diethoxyphosphonyl)-methane, which we have recently investigated,⁶ made it appear

(1) This work has been supported by the U. S. Army Research Office (Durham).

(2) Fellow of the Alfred P. Sloan Foundation.

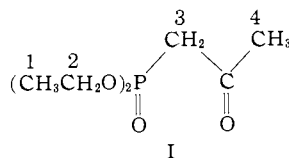
(3) W. Perkow, K. Ullerick, and F. Meyer, *Naturwissenschaften*, **39**, 353 (1952).

(4) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(5) A. N. Pudovik, et al., *Zhur. Obschei. Khim.*, **27**, 2367 (1957); *Chem. Abstr.*, **52**, 71341 (1958).

interesting enough to study the intermediate enolate ion in more detail. We have also extended our study of the bis-(diethoxyphosphonyl)-methane anion in some directions and the new results are reported here.

Preparation and Characterization of Compounds. Diethoxyphosphonylacetyl methane Compounds. The Free Ligand.—This molecule should have the structure I



and this is confirmed by the proton resonance spectrum (Table I) which can be satisfactorily assigned to it. The triplet resonance at 1.09 p.p.m. is assigned to H_1 with $J_{H_1H_2} = 7.0$ c.p.s. The resonance at 2.12 p.p.m. is assigned to H_4 and that at 2.93 p.p.m. to H_3 with $J_{PH_3} = 23.0$ c.p.s. The complicated resonance at 3.98 p.p.m. consists of a quintet with the three inner-most components further split and is assigned to H_2 with $J_{H_2H_1} = 7.0$ c.p.s. and $J_{PH_2} \approx 8$ c.p.s. This value is to be compared with that of 8.3 c.p.s. accurately measured for the P-O- CH_2 couplings in bis-(diethoxyphosphonyl)-methane.⁶

TABLE I
PROTON RESONANCE SPECTRA OF DIETHOXYPHOSPHONYLACETYL-
METHANE AND DERIVATIVES

Com- pound ^a	P.p.m. from (CH ₃) ₄ Si	Inte- grated intensity ^c	Structure	Observed resonances ^b	
				Splitting, c.p.s.	
LH	1.09	6.0*	Triplet	7.0	
	2.12	2.8	Singlet	..	
	2.93	1.8	Doublet	23.0	
	3.98	4.0	Quintet, further split	7	
LNa	1.28	6.0*	Triplet	7.0	
	2.16	2.6	Doublet	2.0	
	3.86	0.9 ^d	Doublet	20	} over- lap
	4.05	4.3 ^e	Quintet, further split	7	
LZn	1.08	6.0*	Triplet	7.5	
	2.08	2.9	Doublet	2.0	
	3.92(?)		Doublet	14.0(?)	} over- lap
		4.7 ^f	Quintet, further split	7	

^a L stands for $[(C_2H_5O)_2P(O)CHCOCH_3]^-$. ^b The spectra were recorded in benzene solution using (CH₃)₄Si as an internal standard. ^c For each compound, the starred number is assumed and the other numbers stand in the correct experimental ratios to the assumed one. ^d This is the value for the component of smallest δ -value multiplied by 2. ^e This was obtained after correction for the contribution from the overlapping doublet centered at 3.86 p.p.m. ^f This is the sum of the two overlapping multiplets.

The infrared spectrum, shown in Fig. 1 and summarized in Table II, is entirely consistent with structure I. It will be discussed more fully below in connection with the changes that occur when the salts and complexes are formed.

There are no features of either the proton magnetic resonance or the infrared spectra to suggest the presence of any enol form. As will be shown later, studies of the ultraviolet spectra confirm this and show that the mole fraction of enol present cannot exceed about 0.001.

(6) J. D. Baldeschwieler, F. A. Cotton, B. D. Nageswara Rao, and R. A. Schunn, *J. Am. Chem. Soc.*, **84**, 4454 (1962).

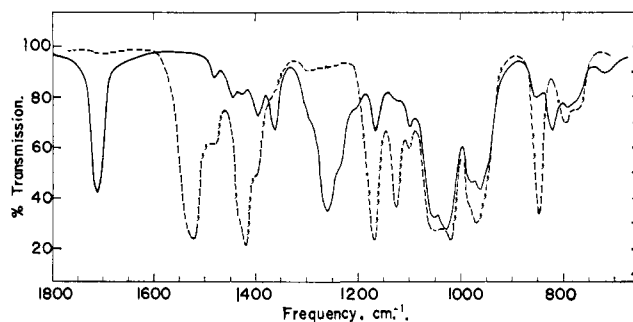
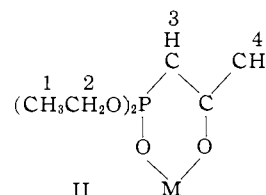


Fig. 1.—Infrared spectra of diethoxyphosphonylacetyl methane as a liquid film (—) and bis-(diethoxyphosphonylacetyl-methano)-zinc(II) as a 5% w/v. solution in benzene (---).

The Sodium and Zinc Salts.—Diethoxyphosphonylacetyl methane reacts smoothly with sodium in benzene at 25° to give the sodium salt $[(EtO)_2P(O)CHCOCH_3]^-Na^+$, which is a white crystalline solid, very soluble in certain organic liquids and extremely hygroscopic. It might be expected to have the structure



and this is substantiated by the following unambiguous assignment of the observed proton magnetic resonances (see Table I). The triplet resonance at 1.28 p.p.m. is again assigned to H_1 with $J_{H_1H_2} = 7.0$ c.p.s. and the doublet occurring at 2.16 c.p.s. is assigned to H_4 with $J_{PH_4} = 2$ c.p.s. The H_3 resonance is the doublet centered at 3.86 p.p.m. ($J_{PH_3} = 20$ c.p.s.), one component of which overlaps the quintet of H_2 occurring at 4.05 c.p.s. $J_{H_1H_2}$ is again 7.0 c.p.s. and $J_{PH_2} \approx 8$ c.p.s. Although the H_3 and H_2 resonances overlap, the components can be clearly recognized and assigned. All observed intensities fit the above assignments within experimental accuracy. The splitting of the resonance at 2.16 c.p.s. is interesting. It is evidently caused by coupling to the phosphorus since the resonance of H_3 shows no similar splitting. No such splitting is observed in the free ligand nor is the phosphorus coupled observably to the H_1 protons in either the free ligand or any of its compounds. It is tempting to suggest that the presence of a π -orbital extending over the ring (evidence for which is presented later) makes possible this relatively long range coupling, but such a conclusion remains tenuous.

Diethoxyphosphonylacetyl methanosodium reacts smoothly with zinc chloride in tetrahydrofuran at room temperature to afford bis-(diethoxyphosphonylacetyl-methano)-zinc, a white, crystalline solid soluble in various organic liquids and also very hygroscopic. It would be expected to contain two equivalent chelate rings each with the structure II, and this is substantiated by the proton magnetic resonance spectrum (Table I). The H_1 resonance occurs at 1.08 p.p.m. as a triplet with $J_{H_1H_2} = 7.5$ c.p.s. The doublet at 2.08 p.p.m. is assigned to H_4 with $J_{PH_4} = 2$ c.p.s. The quintet H_2 resonance occurs at 4.05 p.p.m. with $J_{H_1H_2} = 7.5$ c.p.s. and $J_{PH_2} \approx 8$ c.p.s. The H_3 resonance overlaps the H_2 resonance in such a way that unambiguous identification of one of the components of the H_3 resonance is impossible. The assignment of 3.92 p.p.m. for H_3 with $J_{PH_3} = 14$ c.p.s. must be considered tentative. All observed intensities agree with these assignments.

TABLE II
 INFRARED SPECTRA OF PHOSPHONYLACETYL METHANE DERIVATIVES^a

LH ^{b,c}	LNa ^d	L ₂ Zn ^d	L ₂ Co ^d	L ₃ Cr ^d	MH ^{b,e}	M ₃ Cr ^d	Bis-(β-chloroethyl)-vinyl phosphonate ^f
2960(62)	2960(74)	2970(71)	2960(72)	2960(70)	3000(90)	2980(83)	
2900(81)	2900(70)	2910(78)	2910(84)	2920(sh)	2950(82)	2940(76)	2950(85)
1710(42)					2850(83)	2840(88)	2880(92)
			1544(22)	1545(sh)	1717(38)		1612(91)
	1530(32)	1522(24)		1525(41)	1560(85)	1550(sh)	
1486(92)	1477(83)	1477(81)	1470(82)	1482(74)		1525(21)	
1445(80)			1442(55)			1476(63)	1459(87)
1425(82)	1425(32)	1418(22)		1418(41)	1425(85)	1423(19)	1433(83)
			1403(27)		1400(85)		1402(74)
1395(73)	1390(78)	1398(49)		1398(sh)	1362(73)		1388(88)
1362(67)	1362(88)		1359(78)		1275(sh)		1308(73)
1295(sh)		1299(89)			1265(28)		1264(sh)
1260(35)					1230(60)		1253(37)
1205(75)	1193(45)				1190(71)	1190(sh)	1173(34)
			1185(30)			1162(23)	
1165(67)	1160(sh)	1167(23)		1160(40)	1120(85)	1132(31)	
		1124(36)					
1100(68)	1095(63)	1098(60)	1100(75)	1099(67)	1060(20)	1060(29)	
1055(32)	1050(30)	1048(27)	1058(38)	1060(48)	1037(12)		1038(sh)
1027(28)		1018(23)	1022(34)	1027(38)		1025(26)	1018(24)
	1002(66)				973(78)	982(63)	988(50)
980(46)		980(sh)	982(60)	980(54)			966(49)
962(43)	950(37)	965(30)	957(35)	965(39)			930(63)
855(80)	845(67)	847(34)	847(40)	861(55)	860(72)	870(25)	
823(67)						832(44)	
790(76)	786(62)	797(70)	792(67)			802(55)	
		772(75)	773(69)			785(58)	

^a Figures are band maxima in cm.⁻¹; figures in parentheses are per cent transmission. ^b L stands for [(C₂H₅O)₂P(O)CHCOCH₃]⁻; M stands for [(CH₃O)₂P(O)CHCOCH₃]⁻. ^c This spectrum was recorded using a pure liquid film. ^d These spectra were recorded using a benzene solution, 5% w./v. ^e The solution used was 4% w./v. in CCl₄. ^f The solution used was 5% w./v. in CCl₄.

The Chromium(III) Complex.—Tris-(diethoxyphosphonylacetyl-methano)-chromium(III), an emerald-green oil which has not yet been induced to crystallize,^{6a} can be prepared by either of two methods. On refluxing chromium carbonyl with diethoxyphosphonylacetyl-methane in approximately 1:3 mole ratio, gas is evolved and the solution gradually becomes dark green. The product can be isolated in a slightly impure state. It is, however, difficult to remove the impurities, whatever they are, and the alternative method of preparation, namely by reaction of diethoxyphosphonylacetyl-methane with CrCl₃·3THF in THF at room temperature, is to be preferred. The compound is soluble in a great many organic liquids, both polar and nonpolar.

This complex has been further characterized by both magnetic data and its visible spectrum. As indicated in Table III, the magnetic moment in benzene solution is 3.85 ± 0.15 B.M., which is consistent with formulation of the compound as a tris-chelate species with the chromium present as Cr(III) surrounded by an approximately octahedral array of six oxygen atoms.

The visible spectrum (Table IV) is what would be expected for such a molecule. The bands at 16,100 and 22,500 cm.⁻¹, with molar extinction coefficients of ~40, can be assigned to the ⁴A₂ → ⁴T₂ and ⁴A₂ → ⁴T₁(F) transitions and it can be deduced that the octahedral ligand field splitting parameter, Δ_o, is 16,100 cm.⁻¹, which may be compared with values of 17,400 cm.⁻¹ for the hexaquo ion⁷ and the trisoxalato complex⁸ and 17,900 for the trisacetylacetonato complex.⁹

The Cobalt(II) complex is obtained as a pink, crystalline solid upon reaction of anhydrous cobalt(II)

(6a) NOTE ADDED IN PROOF.—A sample which had been maintained for several months at ~5° crystallized.

(7) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(8) C. K. Jørgensen, Rept. to the Xth Solvay Council, 1956, pp. 8–10.

(9) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).

 TABLE III
 MAGNETIC DATA FOR THE CHROMIUM AND COBALT
 PHOSPHONYLACETYL METHANE COMPLEXES

Complex	Concn. in benzene, moles/l.	Δf, ^a c.p.s.	χ _g × 10 ⁶ , c.g.s. units	χ _M ^{corb} × 10 ⁶	μ _{eff} , B.M.
[(C ₂ H ₅ O) ₂ P(O)-CHCOCH ₃] ₃ Cr	0.0432	56	8.99	6022	3.85 ± 0.15
[(CH ₃ O) ₂ P(O)-CHCOCH ₃] ₃ Cr	.0468	63	10.09	5790	3.78 ± .15
[(C ₂ H ₅ O) ₂ P(O)-CHCOCH ₃] ₂ Co	.0179	56	24.17	10990	5.21 ± .15
[(C ₂ H ₅ O) ₂ P(O)-CHCOCH ₃] ₂ Co	Solid ^c		24.39	11091	5.15 ± .05

^a Δf is the difference in the frequency of the proton resonance of benzene in the reference and sample compartments at 306°K.

^b The corrections for ligand diamagnetism are: [(C₂H₅O)₂P(O)-CHCOCH₃]⁻ = -115 × 10⁻⁶ c.g.s. units; [(CH₃O)₂P(O)-CHCOCH₃]⁻ = -91.4 × 10⁻⁶ c.g.s. units. ^c This moment was measured by the Gouy method and is the average of 3 packings at 297°K.

bromide with diethoxyphosphonylacetyl-methane in THF at room temperature. As indicated in the Experimental section, it is crucial that the reaction mixture never be heated during the reaction or during work-up of the product if parasitic reactions leading to other, as yet unidentified, products are to be avoided.

The pale pink color of the complex suggests that it contains octahedrally coordinated Co(II). This idea receives strong support¹⁰ from the magnetic moments, 5.1–5.2 B.M., which the compound has in the solid state and as a 0.02 M solution in benzene (Table III). Furthermore, the visible and near-infrared spectra of benzene solutions in the concentration range 10⁻²–10⁻³ M as well as the reflectance spectrum of the solid in the

(10) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

TABLE IV
VISIBLE AND NEAR-INFRARED SPECTRA FOR
PHOSPHONYLACETYL METHANO CHROMIUM AND COBALT
COMPLEXES

Compound	Concn., moles/l.	Absorption, $m\mu$	Maxima, cm^{-1}	ϵ_{max} , l. mole $^{-1}$ cm^{-1}
[(C ₂ H ₅ O) ₂ P(O)-CHCOCH ₃] ₃ Cr	0.0146 ^a	621	16,100	41
		444	22,500	42
[(CH ₃ O) ₂ P(O)-CHCOCH ₃] ₃ Cr	.0208 ^a	621	16,100	47
		444	22,500	47
[(C ₂ H ₅ O) ₂ P(O)-CHCOCH ₃] ₂ Co	.0382 ^a	1350	7,410	3.4
		536	18,700	15
.00382 ^a	.00382 ^a	484	20,700	sh
		1335	7,490	2.8
		631	15,800	sh
		536	18,650	16
.295 ^b	.295 ^b	479	20,900	sh
		1350	7,410	3.0
		538	18,600	15
.0379 ^b	.0379 ^b	482	20,700	sh
		1350	7,410	3.2
		543	18,400	17
.00303 ^b	.00303 ^b	484	20,700	sh
		1356	7,380	6.3
		609	16,400	sh
		568	17,600	29
Solid	Solid	515	19,400	sh
		548	18,200	..
		500	20,000	sh

^a In C₆H₆. ^b In CHCl₃.

visible (Fig. 2, Table IV) are very similar to the spectrum of the hexaaquocobalt(II) ion.¹¹ If, then, we assume that the cobalt ion is octahedrally coordinated, and we recognize that the ligands bound to the cobalt cannot span more than two coordination positions each, it becomes necessary to propose that this compound exists not as monomeric molecules but in some polymeric form.

That this is in fact the case is shown first by some molecular weight measurements. In freezing benzene the molecular weight is 1280 ± 65 (calcd. for a trimer 1335) and appears to be independent of concentration in the range 0.03–0.06 *M*. It will be noted in Fig. 3 that the spectrum in benzene is slightly but definitely concentration sensitive. This phenomenon is much more prominent, however, in other solvents, for instance, chloroform. Finally, the temperature sensitivity of the spectrum is also remarkable. When solutions which are pink at or below room temperature are heated they become violet, purple, or even deep blue, depending on solvent and temperature. They recover the pink color on cooling and the process can be repeated many times before decomposition becomes noticeable.

It is not yet known whether this system exists in a simple monomer-trimer equilibrium as seems likely in the nickel(II) β -ketoenolate systems¹² or in a more complicated set of equilibria as in cobalt(II) acetylacetonate,¹³ but detailed investigations now in progress should soon provide an answer. The data reported here as well as some further observations suggest that the species being formed at high temperature and/or low concentration is a tetrahedral monomer. The structural nature of the polymer is of interest and an X-ray investigation will be commenced soon.

Dimethoxyphosphonylacetyl methane Compounds.—Work in this area has not been extensive since, as de-

(11) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(12) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818, 3775 (1961).

(13) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, in press.

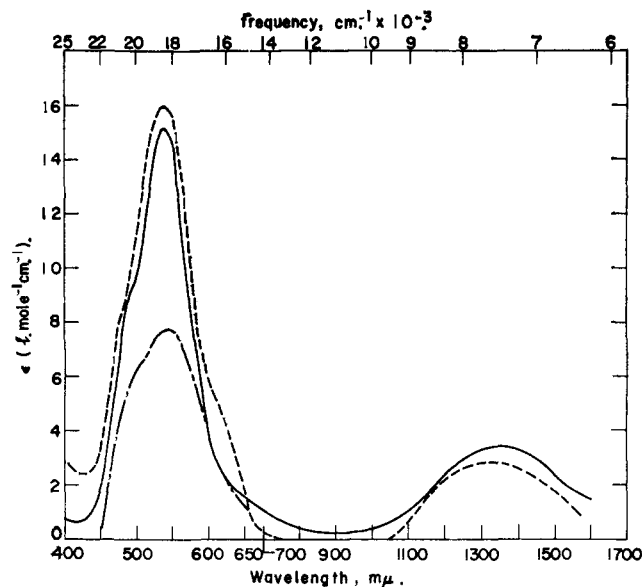


Fig. 2.—Visible and near-infrared spectra of bis-(diethoxyphosphonylacetyl methane)-cobalt(II) in C₆H₆ and as a solid: —, 3.82×10^{-2} *M*; ---, 3.82×10^{-3} *M*; - · -, solid, by reflectance.

scribed in the Experimental section, the alkali metal salts were insoluble and difficult to purify and thus not very appealing as preparative reagents. However, since the chromium complex of the diethoxy ligand could not be obtained in a crystalline form, a chromium derivative of the dimethoxy ligand was prepared in the hope that it would be crystalline.

Because of the unsuitability of the sodium and potassium salts, preparation was carried out by the reaction of the free ligand with Cr(CO)₆. In this way we were successful in isolating tris-(dimethoxyphosphonylacetyl methane)-chromium(III) as a dark green crystalline substance, soluble in various organic liquids. As seen in Table II its infrared spectrum compares with that of the free ligand in the same way as does that of the analogous diethoxy compound with the free diethoxy ligand. The magnetic moment (Table III) and the visible spectrum (Table IV) are essentially the same as those of the diethoxy compound and it may be concluded that the two complexes have similar structures, though they could be different geometrical isomers.

Bis-(diethoxyphosphonyl)-methane Compounds.—Studies in this area have been extended and are continuing. The potassium salt has now been prepared and characterized. It is a white crystalline solid, similar in general to the sodium salt but more reactive and correspondingly more difficult to handle. The sodium salt is preferable as a preparative reagent. In benzene at the freezing point the potassium salt, like the sodium salt, is highly associated. The molecular weights measured were in the neighborhood of the value for a hexamer, but reproducible values were not obtained, presumably because of the extreme hygroscopicity of the compound.

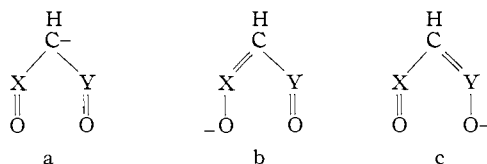
Kosolapoff¹⁴ treated [(EtO)₂P(O)]CH₂ with potassium, then added *n*-butyl bromide and from this reaction mixture isolated a liquid assumed to be [(EtO)₂P(O)]₂CHC₄H₉. This was hydrolyzed to afford an acid whose neutralization equivalent corresponded with that expected for C₄H₉CH(PO₃H₂)₂. Although these results, despite their circumstantial character, leave little doubt that alkylation occurs at the bridging carbon atom, we considered it worthwhile to obtain some more direct evidence on this point. [(EtO)₂P(O)]₂-

(14) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

CHNa was therefore prepared and treated *in situ* with methyl iodide; a high-boiling liquid was obtained which gave satisfactory C and H analyses.

A direct proof of its constitution was obtained by high resolution proton magnetic resonance spectroscopy. The group of peaks (centered at $\tau = 5.87$) arising from the methylene protons of the ethoxy groups is almost identical with the corresponding group of peaks in the unmethylated compound (centered at $\tau = 5.95$). There is also a 1-2-1 triplet ($J = 7.1$ c.p.s., $\tau = 8.69$) arising from the methyl protons of the ethoxy groups which is practically identical with the corresponding triplet ($J = 6.9$ c.p.s.; $\tau = 8.67$) in the unmethylated compound. In addition there are no less than 13 additional peaks, all weak or very weak relative to those in the groups already discussed, and ranging in position from $\tau \approx 9.2$ to $\tau \approx 7.15$. This is entirely consistent with the presence of an AB_3X_2 (P_2CHCH_3) group with comparable magnitudes for J_{AB} , J_{AX} , and J_{BX} , although the observed spectrum is so complex that it could not be analyzed. Had methylation occurred elsewhere, or had rearrangement of the molecular skeleton occurred, it is difficult to see how the observed spectrum could be explained. In particular, methylation at a phosphoryl oxygen is definitely ruled out. Like Kosolapoff, we obtained a very poor yield (11%) of alkylated product.

The Nature of the Anions and Chelate Rings.—Having now established that anions of the types $\{[(RO)_2P(O)]_2CH\}^-$ and $\{[(RO)_2P(O)CHCOCH_3]\}^-$ do exist and that they function as bidentate ligands, we turn to the question of the bonding within these anions. At least in preliminary and qualitative stages, the discussion of this question can most conveniently be conducted in terms of valence bond theory, *i.e.*, by considering the various possible canonical forms and attempting to assess their relative contributions. For this purpose, the sets of canonical structures III, IV, and V are relevant.



III, X = Y = $P(OC_2H_5)_2$

IV, X = $P(OC_2H_5)_2$; Y = CCH_3

V, X = Y = CCH_3

We shall utilize three kinds of physical evidence in attempting to determine the relative weights of these canonical forms in III and IV.

I. Nuclear Magnetic Resonance Data.—The positions of the H_3 proton resonances in the sodium and zinc compounds of diethoxyphosphonylacetylmethane are at lower fields than is the CH_2 resonance in the free ligand molecule. They are, in fact, about midway between the resonance for the analogous proton in acetylacetonate¹⁵ complexes (5.1 p.p.m.) and those in the sodium and potassium salts of bis-(diethoxyphosphonyl)-methane (0.7 p.p.m.). This would indicate that the environment of the CH group in $[(EtO)_2P(O)CHCOCH_3]^-$ is intermediate between those it has in $\{[(EtO)_2P(O)]_2CH\}^-$ and $[CH_3COCHCOCH_3]^-$. This is not inconsistent with the idea that the a, b, and c forms are of about the same relative importance in all three cases.

More cogent in this respect, however, are the P^{31} chemical shift data shown in Table V. From these data it seems quite evident that the phosphorus atoms in both the mono- and diphosphorus compounds, both the neu-

tral molecules and the anions, have quite similar surroundings.

Finally, if in IV the contribution of b were negligible, nonplanarity of the anion would be possible, and this might lead to nonequivalence of the ethoxy groups. The proton magnetic resonance spectra show no evidence of such nonequivalence, but the possibility of rapid interconversion of conformational isomers renders this result inconclusive.

2. Infrared Data.—Having shown with the phosphorus nuclear resonance data that the relative contributions of the corresponding canonical forms in III and IV are comparable, we now consider some data showing that a similar relationship exists between the canonical structures in IV and V. Results are recorded in Table II and characteristic spectra in the 1800-700 cm^{-1} region are shown in Fig. 1.

The absorptions occurring at about 2900 cm^{-1} are assigned to the various C-H stretching vibrations and the weak bands at 1420 to 1490 cm^{-1} to the C-H deformation frequencies. The very intense bands occurring below about 1100 cm^{-1} seem to be characteristic of organophosphorus compounds containing P-O-alkyl groups^{16a} but the precise assignment of these bands is uncertain. However, they are quite useful as a means of identifying the P-O-alkyl group in an organophosphorus compound. In the ethoxyphosphonyl compounds, the weak absorption at about 1160 cm^{-1} can be assigned to the P-O-ethyl vibration and that at about 1190 cm^{-1} in the methoxyphosphonyl compounds to the P-O-methyl vibrations.^{16a}

TABLE V
PHOSPHORUS NUCLEAR RESONANCE DATA

Compound	Chemical shift, ^a p.p.m. from 85% H_3PO_4
$[(EtO)_2P(O)]_2CH_2$	-25 ^b
$(EtO)_2P(O)CH_2COCH_3$	-23 ^b
$(EtO)_2P(O)CH_2C\equiv$	-20 ^b
$(ClCH_2CH_2O)_2P(O)CH=CH_2$	-22 ^b
$(EtO)_2PCHP(OEt)_2$	-45 ^c
$(EtO)_2PCHCCH_3$ O-K-O	-38 ^c
$(EtO)_2PCHCCH_3$ O-Zn-O 2	-38 ^c
$(EtO)_2PCHCCH_3$ O-Na-O	-38 ^c

^a Probable accuracy ± 0.5 p.p.m. ^b Run as pure liquid. ^c Run as solution in tetrahydrofuran.

The C=O stretching frequency in diethoxyphosphonylacetylmethane occurs at 1710 cm^{-1} and in the methyl analog at 1717 cm^{-1} . This is in the region expected for a nonconjugated aliphatic ketone.^{16b} The P=O stretching vibration is found at about 1260 cm^{-1} in both phosphonylacetylmethane esters and is in the region expected for uncomplexed P=O groups in dialkylphosphonates.^{16c}

It is obvious that the pure C=O and P=O stretching frequencies found in the free ligand have disappeared in the metal complexes while simultaneously three strong bands occur in all of the complexes at frequencies of about 1530, 1415, and 1170 cm^{-1} . The 1170 cm^{-1} band may be assigned to the P=O stretching frequency which has dropped by 90 cm^{-1} . For comparison, simply coordinated phosphine oxide complexes of the type R_3POM show decreases in the P=O stretching frequencies of only about 50 cm^{-1} (average of 14 com-

(15) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, New York, N. Y., 1958: (a) pp. 315-317; (b) p. 134; (c) p. 312.

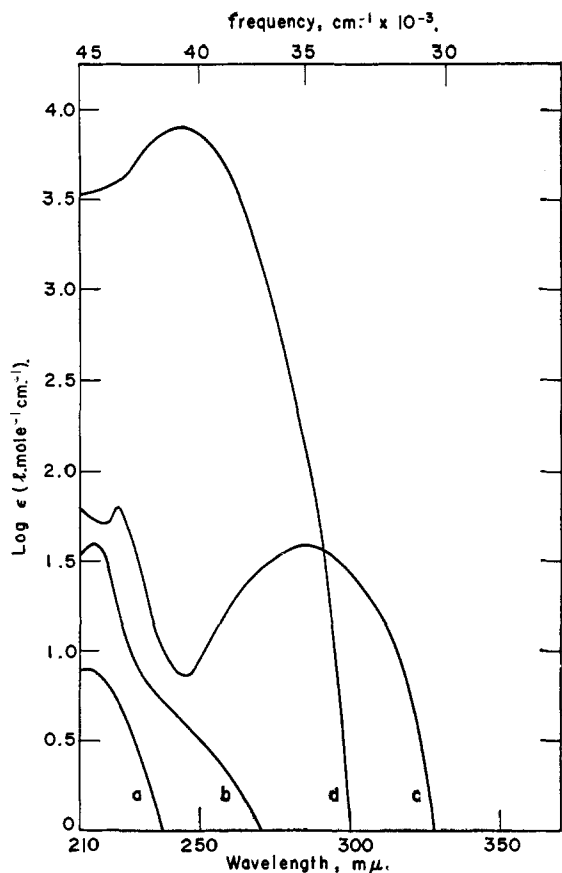


Fig. 3.—Ultraviolet spectra of diethoxyphosphonylacetyl-methane, its sodium salt, and some phosphorus analogs: a, $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{Cl}$; b, $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CH}=\text{CH}_2$; c, $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{COCH}_3$; d, $[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHCOCH}_3]\text{Na}$. All spectra are of THF solutions.

plexes¹⁷ with the largest decrease being 70 cm^{-1}). The larger decrease in the $\text{P}=\text{O}$ stretching frequency in the phosphonylacetyl-methano complexes suggests a further lowering of the $\text{P}=\text{O}$ bond order over that expected for simple coordination of the $\text{P}=\text{O}$ oxygen atom to the metal atom.

The two strong bands at 1530 and 1415 cm^{-1} are remarkably similar to those found in metal acetylacetonate complexes where several (usually two) rather intense bands are found in the region 1600 – 1400 cm^{-1} . In the acetylacetonates, these bands have been assigned to vibrations which are mixtures of CO stretching and CC stretching in the planar six-membered chelate rings.¹⁸ A similar assignment is plausible here. It must be noted, however, that this assignment requires the participation of only a and c in the resonance, although it is entirely consistent with the substantial inclusion of b. When the marked lowering of the $\text{P}=\text{O}$ stretching frequency is also considered, however, the natural conclusion seems to be that a, b, and c contribute in about the same proportions to IV as they do to V.

3. Ultraviolet Spectra.—If all of the canonical structures, a, b, and c, make important contributions to the electronic structure of IV, then the entire OPCCO chain must constitute a chromophore which would be expected to absorb more strongly and at longer wave lengths than the localized chromophores represented by a, b, or c separately. Conversely, observation of much greater near-ultraviolet absorption by the metal salts and complexes of $\{[(\text{EtO})_2\text{P}(\text{O})]_2\text{CH}\}^-$ than by com-

(17) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(18) K. Nakamoto, *et al.*, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

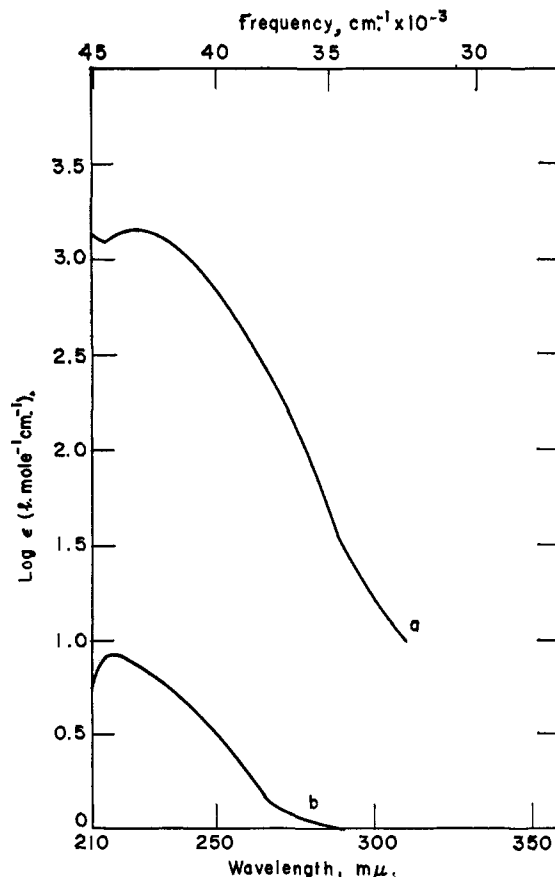


Fig. 4.—Ultraviolet spectra of bis-(diethoxyphosphonyl)-methane and its potassium salt: a, $\{[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})]_2\text{CH}\}\text{K}$ in THF; b, $[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})]_2\text{CH}_2$ in THF.

pounds containing single chromophores analogous to those in the separate canonical forms should constitute good evidence for the existence of strong resonance interaction of all of the forms a, b, and c. This sort of observation has been made. The data are summarized in Table VI and displayed in part in Fig. 3.

It will be noted that $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{X}$ and $(\text{RO})_2\text{P}(\text{O})\text{CH}=\text{CH}_2$ systems have scarcely any ultraviolet absorption at wave lengths greater than $210\text{ m}\mu$ nor does the $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{COCH}_3$ system, except for the $n \rightarrow \pi^*$ absorption characteristic of the keto group.¹⁹ The sodium salt of diethoxyphosphonylacetyl-methane, however, has an absorption band at $\sim 245\text{ m}\mu$ with a decadic molar extinction coefficient (ϵ) of at least 8000 and perhaps twice this great because of rapid hydrolysis occurring in the dilute solution. Furthermore, all of the complexes have very strong absorption with maxima at about the same wave length. The only weak point in the argument being used is that we cannot say for certain that a simple enol anion system, $\text{C}=\text{C}=\text{O} \leftrightarrow \text{C}=\text{C}-\text{O}^-$, might not have a similar ultraviolet spectrum. There do not appear to be any data for such a system in the literature and the preparation and handling of suitable compounds would probably be excessively difficult. We believe, however, that the simple enol anion would not be likely to absorb in the region of the ultraviolet being considered.

Similarly, as shown in Fig. 4, the diphosphonyl-methane has practically no near-ultraviolet absorption while the anion has strong absorption with a peak at $225\text{ m}\mu$ ($\epsilon \approx 2000$).

(19) In all cases there is also some weak absorption in the far-ultraviolet. The apparent maxima at $\sim 220\text{ m}\mu$ may be only experimental artifacts. This absorption is perhaps associated with isolated $\text{P}=\text{O}$ groups.

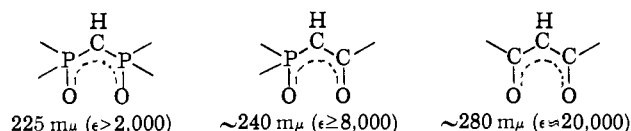
Comparison of spectra c and d of Fig. 3 shows that not more than ~ 0.1 mole % of diethoxyphosphonylacetylmethane exists as the enol tautomer at equilibrium in THF at $\sim 25^\circ$. Similarly, in the diphosphonylmethane in THF solution, the ultraviolet spectrum shows that an upper limit on the concentration of the enol form is $\sim 0.5\%$.

TABLE VI
ULTRAVIOLET SPECTRA OF PHOSPHONYLACETYL METHANE
DERIVATIVES^a

Compound	Absorption maxima		ϵ , l. mole ⁻¹ cm. ⁻¹
	$m\mu$	cm. ⁻¹	
$(C_2H_5O)_2P(O)CH_2COCH_3$	285	35,100	38
	222	45,100	68
$(ClCH_2CH_2)_2P(O)CH=CH_2$	215	46,500	19
$(C_2H_5O)_2P(O)CH_2Cl$	210 ^b
$[(C_2H_5O)_2P(O)CHCOCH_3]Na$	245	40,800	8,000 ^c
$[(C_2H_5O)_2P(O)CHCOCH_3]_2Zn$	236	42,300	7,000 ^d
$[(C_2H_5O)_2P(O)CHCOCH_3]_2Co$	215	46,500	1,400
$[(CH_3O)_2P(O)CHCOCH_3]_2Cr$	225	44,500	26,000
	258	39,800	22,000

^a All spectra were taken in THF solution. ^b The absorption is still rising at 210 $m\mu$, which is the limit of the observations. ^c This band decreased slowly with time and ϵ represents a lower limit. ^d This band decreased rather rapidly with time and ϵ represents a lower limit.

4. Summary.—The P^{31} chemical shifts indicate that the environment of phosphorus is about the same in both the mono- and diphosphonylmethanide ions. Infrared spectra indicate a considerable similarity of the diethoxyphosphonylacetylmethanide and acetylacetonate anions. Finally the ultraviolet spectra suggest that the phosphonylacetylmethanide and diphosphonylmethanide ions possess extended π -orbital systems which undergo $\pi-\pi^*$ transitions similar to the one characteristic of the acetylacetonate ion.¹⁵ In fact there is a regular progression of band energies and intensities in the three types of anions, *viz.*



Experimental

General.—All manipulations were performed in an atmosphere of prepurified nitrogen unless otherwise noted. Wherever possible, compounds were retained within an all-glass vacuum system, although for mechanical reasons it was necessary to perform some transfers and other operations in open vessels which were continuously flushed with a rapid stream of prepurified nitrogen. Prior to distillation and storage under nitrogen, solvents were treated as follows: Ether and tetrahydrofuran (THF) were refluxed over $LiAlH_4$ for 4 hr. Benzene, toluene, and cyclohexane were refluxed over Na-Pb alloy (Fisher "Dri-Na") for 4 hr. Acetone was refluxed 0.5 hr. with $KMnO_4$ and distilled from K_2CO_3 . Chloroform and carbon tetrachloride were refluxed over P_2O_5 for 2 hr.

Preparation of Compounds. Bis-(diethoxyphosphonyl)-methanopotassium, $\{[(C_2H_5O)_2PO]_2CH\}K$.—A solution of 15.66 g. (52.5 mmoles) of bis-(diethoxyphosphonyl)-methane in 30 ml. of THF was added dropwise to a magnetically stirred solution of 2.90 g. (73.2 mg.-atoms) of potassium metal in 80 ml. of THF. After gas evolution had ceased, the solution was refluxed for 0.5 hr., filtered free of excess potassium, and the solvent removed under vacuum at 50° . The pale yellow solid residue was dissolved in 50 ml. of hot *n*-hexane, filtered, and evaporated to 35 ml. in a nitrogen stream. After cooling to -80° for 4 hr., the white crystalline solid which was deposited was filtered onto a medium frit cooled to -80° , washed with hexane, and dried at 40° (0.1 mm.) for 3 hr; yield 6.0 g., 35%, m.p. $122-125^\circ$ (uncor.). *Anal.* Calcd. for $C_8H_{15}KO_6P_2$: C, 33.12; H, 6.49; P, 18.99. Found: C, 32.2; H, 6.7; P, 18.8.

Bis-(diethoxyphosphonyl)-methanopotassium is an extremely hygroscopic white crystalline solid. It is soluble in THF, benzene, hexane, acetone, and ether and reacts rapidly with chloroform, carbon tetrachloride, and carbon disulfide. Cry-

scopic molecular weight measurements in benzene show the compound to be highly associated (at least a hexamer) but consistent values could not be obtained owing to the extreme hygroscopic nature of the compound.

The infrared spectrum of $[(EtO)_2P(O)]_2CHK$, recorded on a 10% w./v. solution in benzene, contains the following main bands which match very closely those already reported⁶ for the sodium analog. Band maxima are in cm^{-1} , figures in parentheses are % transmission at the maxima: 2950(45), 2920(56), 2880(59), 1485(sh), 1445(71), 1390(60), 1365(83), 1290(sh), 1207(18), 1165(65), 1100(31), 1045(18), 965(sh), 940(18), 840(66), 785(31), 737(40).

The proton magnetic resonance spectrum recorded in benzene solution consisted of a 1-2-1 triplet centered at $\tau = 9.00$ with splittings of 6.5 cycles, another 1-2-1 triplet at $\tau = 8.70$ with splittings of 7.0 cycles, and a symmetrical group of nine lines centered at $\tau = 4.93$ with its components separated by ~ 3.5 cycles. The integrated intensities of these three groups of peaks were in the ratio 1.0 to 12.0 to 7.7. The spectrum is generally similar to that previously reported⁶ for the sodium compound and can presumably be assigned in the same way.

Reaction of Bis-(diethoxyphosphonyl)-methanopotassium with Methyl Iodide.—A solution of 8.11 g. (28.2 mmoles) of bis-(diethoxyphosphonyl)-methane in 10 ml. of ether was added dropwise to a magnetically stirred solution of 0.91 g. (39.6 mg.-atoms) of sodium sand in 40 ml. of ether. When gas evolution had ceased, the solution was filtered and added dropwise to a magnetically stirred solution of 4.61 g. (32.4 mmoles) of methyl iodide in 30 ml. of ether. A white solid separated and the mixture was gently refluxed for 1 hr. Filtration, followed by solvent removal and vacuum distillation of the residue, gave 0.96 g. (11%) of 1,1-bis-(diethoxyphosphonyl)-ethane, $[(C_2H_5O)_2PO]_2CHCH_3$, b.p. $97-100^\circ$ (0.2 mm.). *Anal.* Calcd. for $C_{10}H_{24}O_6P_2$: C, 39.74; H, 8.00. Found: C, 40.1; H, 7.9.

Reaction of Bis-(diethoxyphosphonyl)-methane with Calcium Amalgam and Calcium Hydride.—Two attempts were made to prepare the calcium salt of bis-(diethoxyphosphonyl)-methane. To calcium amalgam (prepared by shaking 0.22 g. (5.5 mg.-atoms) of calcium metal in 51.0 g. of mercury for 24 hr.) in 30 ml. of ether was added 1.61 g. (5.6 mmoles) of bis-(diethoxyphosphonyl)-methane in 10 ml. of ether. After stirring for 6 hr., no gas had been evolved. The solution was then filtered and the solvent removed under vacuum to give a colorless liquid whose infrared spectrum showed it to be bis-(diethoxyphosphonyl)-methane.

In the second attempt, a solution of 3.06 g. (10.6 mmoles) of bis-(diethoxyphosphonyl)-methane in 10 ml. of THF was added slowly to a magnetically stirred solution of 0.45 g. (10.7 mmoles) of calcium hydride in 30 ml. of THF. The mixture was refluxed for 24 hr. and no gas was evolved. Filtration, followed by solvent removal, gave back the free ligand (identified by its infrared spectrum).

Apparently bis-(diethoxyphosphonyl)-methane is too weak an acid to react with calcium amalgam or calcium hydride although qualitative tests show that it will react with sodium amalgam or sodium hydride.

Diethoxyphosphonylacetylmethane, $(C_2H_5O)_2P(O)CH_2COCH_3$.—Diethoxyphosphonylacetylmethane was prepared according to methods described in the literature.²⁰ It is a mobile, colorless liquid, b.p. $81-83^\circ$ (0.6 mm.), which slowly becomes yellow on standing in the light. The yellow color is probably due to isomerization to the vinyl phosphate, $(C_2H_5O)_2P(O)OCC=CH_2$. *Anal.* Calcd. for $C_7H_{15}O_4P$: C, 43.30; H, 7.79. Found: C, 43.1; H, 7.6.

Dimethoxyphosphonylacetylmethane, $(CH_3O)_2P(O)CH_2COCH_3$.—An improved yield²¹ of dimethoxyphosphonylacetylmethane was obtained by the following method. In a 300-ml. 3-neck flask equipped with an addition funnel, nitrogen inlet tube, 30-cm. Vigreux column, vacuum distillation head, and magnetic stirrer, 72.1 g. (0.581 mole) of trimethyl phosphite was added dropwise to 109.6 g. (0.568 mole) of iodoacetone in 75 ml. of benzene. The reaction mixture was maintained at 65° in an oil-bath and methyl iodide continuously distilled during the addition. The mixture was refluxed for 0.5 hr. after addition was complete. The mixture was then vacuum distilled, discarding all fractions except that boiling at $119-123^\circ$ (11 mm.). Redistillation gave the desired product, b.p. $121-123^\circ$ (11 mm.), 62.0 g. (66%), as a colorless mobile liquid which became yellow on standing in the light. *Anal.* Calcd. for $C_5H_{11}O_4P$: C, 36.15; H, 6.68. Found: C, 35.5; H, 6.6.

Diethoxyphosphonylbenzoylmethane, $(C_2H_5O)_2P(O)CH_2COC_6H_5$, was prepared according to Pudovik²² in 33% yield as a viscous,

(20) H. I. Jacobson, M. J. Griffith, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2608 (1957).

(21) A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **106**, 745 (1955); *Chem. Abstr.*, **50**, 11230g (1956).

(22) A. N. Pudovik, *Zh. Obshchei. Khim.*, **25**, 2173 (1953); *Chem. Abstr.*, **50**, 8486 (1956).

colorless liquid, b.p. 127–129° (0.08 mm.). No analysis was obtained.

Diethoxyphosphonylacetylmethanosodium, $[(C_2H_5O)_2P(O)CHCOCH_3]Na$.—A solution of 17.3 g. (0.089 mole) of diethoxyphosphonylacetyl methane in 20 ml. of benzene was added dropwise to a magnetically stirred solution of 3.13 g. (0.136 g.-atom) of sodium sand in 160 ml. of benzene at 25° so as to maintain a steady evolution of gas. When gas evolution was complete, the precipitated solid was dissolved by warming to the reflux temperature and the solution filtered through a coarse glass frit. Solvent was removed under vacuum at 35°, leaving a sirupy residue. On addition of 100 ml. of diethyl ether, the product separated as a white solid, which was filtered onto a coarse glass frit, washed well with ether, and dried at 60° (0.05 mm.) for 14 hr.; yield 14.4 g., 75%. *Anal.* Calcd. for $C_7H_{11}NaO_4P$: C, 38.99; H, 6.53; P, 14.33. Found: C, 38.9; H, 6.5; P, 14.4.

Diethoxyphosphonylacetylmethanosodium is an extremely hygroscopic solid, m.p. 158–160° (uncor.), soluble in benzene, THF, and acetone. It is insoluble in carbon tetrachloride and ether and decomposed by chloroform and carbon disulfide. Both the solid and solutions appear to be stable toward oxygen.

Bis-(diethoxyphosphonylacetylmethano)-zinc(II), $[(C_2H_5O)_2P(O)CHCOCH_3]_2Zn$.—A solution of 3.70 g. (17.1 mmoles) of diethoxyphosphonylacetylmethanosodium in 80 ml. of THF was added dropwise to a stirred solution of 1.22 g. (8.95 mmoles) of anhydrous zinc chloride in 70 ml. of THF at 25°. The solution soon became cloudy and after stirring for 2 hr. was filtered free of sodium chloride through a medium glass frit. Solvent removal under vacuum at 35° left a viscous colorless oil which solidified on standing. This solid was dissolved in 30 ml. of toluene, the solution filtered, evaporated to 15 ml. in a nitrogen stream, and cooled over a 4-hr. period to –80°. After 16 hr. the solution was filtered through a medium frit cooled to –80° and the white solid dried at 40° (0.1 mm.) for 4 hr.; yield 1.5 g., 38%. *Anal.* Calcd. for $C_{14}H_{28}O_8P_2Zn$: C, 37.22; H, 6.25; P, 13.72. Found: C, 37.1; H, 6.3; P, 13.7.

Bis-(diethoxyphosphonylacetylmethano)-zinc(II) is an extremely hygroscopic, white, crystalline solid which melts at 76–78° (uncor.) to a colorless liquid. It is soluble in THF, benzene, toluene, ether, and acetone but insoluble in *n*-hexane.

Bis-(diethoxyphosphonylacetylmethano)-cobalt(II), $[(C_2H_5O)_2P(O)CHCOCH_3]_2Co$.—A solution of 3.51 g. (16.2 mmoles) of diethoxyphosphonylacetylmethanosodium in 60 ml. of THF was added dropwise to a magnetically stirred solution of 1.88 g. (8.6 mmoles) of anhydrous cobaltous bromide in 60 ml. of THF at 25°. The solution soon became turbid and after stirring for 2 hr. was filtered free of sodium bromide. Solvent removal under vacuum at 30° left a purple solid. Treatment of this with 100 ml. of ether gave a blue solution and a pink residue. This residue was dissolved in 20 ml. of toluene, the solution filtered through a medium frit, and 40 ml. of ether was added. Slow cooling to –80° gave a pink crystalline product which was collected at –80° on a medium frit, washed with ether, and dried at 40° (0.05 mm.) for 4 hr. Recrystallization by the same procedure and drying at 60° (0.05 mm.) for 12 hr. gave 1.6 g. (44%) of bis-(diethoxyphosphonylacetylmethano)-cobalt(II), m.p. 165–166° (uncor.). *Anal.* Calcd. for $C_{14}H_{28}CoO_8P_2$: C, 37.76; H, 6.34; P, 13.91. Found: C, 38.1; H, 6.3; P, 14.0.

This compound is a slightly hygroscopic, pink, crystalline solid, soluble in benzene, THF, toluene, chloroform, carbon tetrachloride, and acetone, slightly soluble in ether, and insoluble in *n*-hexane. At room temperature, fresh solutions in benzene are pink at all concentrations (10^{-1} to 10^{-4} M) as are concentrated (10^{-1} to 10^{-2} M) solutions in chloroform. However, more dilute solutions (10^{-3} M) in chloroform are rather more purple in color. On heating, the benzene solution becomes purple at the boiling point (80°) and in higher boiling solvents (e.g., xylene, b.p. 140°) the color at the boiling point is dark blue. The color changes are reversible in the absence of air. All solutions slowly become red on exposure to air at room temperature, more rapidly when heated in air.

Cryoscopic molecular weight determinations in benzene gave a molecular weight of 1280 ± 65 . The calculated molecular weight for a monomer is 445. The apparent molecular weight in benzene is within experimental error of that calculated for a trimer, 1335, and appears to be independent of concentration over the range 0.032 to 0.059 M.

If the preparation is performed at the reflux temperature of THF (65°) and the solvent removed under vacuum at 60°, the only products obtained are dark blue crystalline solids which give variable analyses (*viz.*, C, 25.4, 26.0; H, 5.6, 5.6; P, 14.8, 16.1 on different batches) that are very low in carbon and hydrogen and high in phosphorus compared to that calculated for the 2:1 complex. Also, the carbonyl absorption is completely absent from the infrared spectra, suggesting that some degradation of the ligand has occurred. These products have not been further investigated.

Tris-(diethoxyphosphonylacetylmethano)-chromium(III), $[(C_2H_5O)_2P(O)CHCOCH_3]_3Cr$ may be prepared either by reaction of the sodium salt with chromium chloride tetrahydrofuranate (method a) or by reaction of the free ligand with chromium carbonyl analogous to the reactions of chromium and molybdenum carbonyls with β -diketones as described by Dunne and Cotton.²³

a.—A solution of 0.82 g. (3.8 mmoles) of diethoxyphosphonylacetylmethanosodium in 20 ml. of THF was added dropwise to a magnetically stirred solution of 0.53 g. (1.42 mmoles) of $CrCl_3 \cdot 3THF$ ²⁴ in 50 ml. of THF at 25°. After stirring for 2 hr., the solution was filtered free of sodium chloride and evaporated under vacuum at 50° to a dark green oil (0.7 g., 86%). This oil was dissolved in 3 ml. of hexane and 1.4 ml. of the solution placed on an alumina column (30 cm. \times 1 cm.) packed under nitrogen as a slurry in hexane. Elution with a hexane-acetone mixture (80% v./v. hexane) developed a dark green band which was collected and the solvent removed to give 0.16 g. (43%) of a dark green oil. Attempts to crystallize this oil (and samples obtained in other preparations) were unsuccessful and the oily product was used in subsequent physical studies. *Anal.* Calcd. for $C_{21}H_{42}CrO_{12}P_3$: C, 29.94; H, 6.71; P, 14.72. Found: C, 29.1; H, 6.7; P, 15.0.

b.—A similar product was obtained by refluxing 1.71 g. (8.8 mmoles) of diethoxyphosphonylacetylmethane and 0.70 g. (3.16 mmoles) of chromium hexacarbonyl in 40 ml. of cyclohexane. Gas was evolved, the solution gradually became dark green, and a pale green solid was deposited. After 10 days, when gas evolution had ceased, the solution was filtered and the solvent evaporated to give a dark green oil. The pale green solid was apparently a decomposition product of chromium carbonyl, perhaps Cr_2O_3 , and was discarded. The dark green oil obtained by this process was similar to that previously described except that it was contaminated by high boiling phosphorus compounds which resulted from decomposition of the ligand under the reaction conditions. A typical elemental analysis gave: C, 38.5; H, 6.6; P, 13.3. Chromatography on alumina was ineffective in separating the product and the impurities. Thus the chromium complex is best prepared according to method a where decomposition is kept to a minimum.

Tris-(diethoxyphosphonylacetylmethano)-chromium(III) is a dark green, slightly hygroscopic oil, soluble in all common organic solvents. It freezes to a glass at about –10°.

Attempted Preparation of Dimethoxyphosphonylacetylmethanosodium.—Since tris-(diethoxyphosphonylacetylmethano)-chromium(III) could not be crystallized, it was hoped that the methyl ester would have more favorable properties permitting the complex to solidify. However, reaction of dimethoxyphosphonylacetylmethane with sodium or potassium in THF produced an immediate precipitate which was insoluble in all common organic solvents. Extraction with THF in a Soxhlet extractor or attempted crystallization from bis-(2-ethoxyethyl) ether at 150° gave only gummy products. Analyses of the initial precipitate were variable (*viz.*, C, 29.46, 21.72; H, 5.45, 4.84; P, 16.11, 19.20 on different batches; calcd. for $C_8H_{10}NaO_4P$: C, 31.92; H, 5.35; P, 16.47) depending on length of reaction time and temperature. It seems likely that the initial precipitate is the desired product which reacts further with itself in a manner analogous to that described for the dialkyl phosphonates and their sodium salts.^{25,26}

Tris-(dimethoxyphosphonylacetylmethano)-chromium(III), $[(CH_3O)_2P(O)CHCOCH_3]_3Cr$.—Since the sodium salt could not be obtained, this complex was necessarily prepared *via* reaction of the ligand with chromium carbonyl. A solution of 2.53 g. (15.2 mmoles) of dimethoxyphosphonylacetylmethane and 1.26 g. (5.73 mmoles) of chromium hexacarbonyl in 50 ml. of cyclohexane was refluxed until gas was no longer evolved (about 2 weeks). The green solution was filtered free of some pale green insoluble matter and evaporated under vacuum at 40° to a dark green oil. On standing for 3 days, the oil solidified. The resulting solid was dissolved in 15 ml. of ether, filtered, and cooled over an 8-hr. period to –80°. After 12 hr. at –80°, the dark green crystals were collected on a medium frit cooled to –80°, washed with ether, and dried at 50° (0.1 mm.) for 3 hr.; yield 0.58 g., 21%, m.p. 100–102° (uncor.). *Anal.* Calcd. for $C_{15}H_{30}CrO_{12}P_3$: C, 32.95; H, 5.53; P, 16.89. Found: C, 32.4; H, 5.6; P, 17.2.

Tris-(dimethoxyphosphonylacetylmethano)-chromium(III) is a slightly hygroscopic, dark green crystalline solid soluble in ether, THF, benzene, carbon tetrachloride, and carbon disulfide and insoluble in *n*-hexane and cyclohexane.

Reaction of Diethoxyphosphonylbzenzoylmethane with Sodium.—This reaction, also in THF, does not produce the desired sodium salt, but the solution dissolves the sodium metal without

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evolution of gas and becomes dark red in color. It is possible that some type of ketyl is formed, but the reaction was not investigated further. No other attempts were made to prepare complexes with this ligand.

Magnetic susceptibilities of the cobalt and chromium complexes were measured in benzene solution by observing the shift in the proton resonance frequency of benzene due to the presence of the paramagnetic species.²⁷ A concentric double-walled sample tube was used in which the sample solution was in the inner tube and the pure solvent in the outer annular ring. Proton shifts were measured at 60 Mc. on a Varian Associates A-60 spectrometer and are accurate to ± 1 c.p.s.

The magnetic moment of solid bis-(diethoxyphosphonylacetyl-methano)-cobalt(II) was also measured by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a calibrant. In all cases, diamagnetic corrections were made using Pascal's constants.²⁸

Visible and near-infrared spectra were recorded on a Cary model 14 recording spectrophotometer. Wave lengths are accurate to ± 3 m μ and molar extinction coefficients, ϵ , are accurate to about $\pm 5\%$. Quartz cells of 1 mm., 1 cm., and 10 cm. path length were used for solutions of appropriate concentrations.

Ultraviolet spectra were recorded from 350 to 210 m μ on a Cary model 11 recording spectrophotometer using 1-cm. quartz

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cells. Band maxima are believed accurate to ± 2 m μ . All solutions were prepared in a nitrogen atmosphere and the cells were filled through serum caps as rapidly as possible with a hypodermic syringe.

Infrared spectra were recorded on a Perkin-Elmer model 21 double beam spectrophotometer equipped with NaCl optics. Calibration of the frequencies was made with polystyrene film. The recorded locations of band maxima are believed accurate to ± 2 cm.⁻¹. Solutions were prepared in a nitrogen atmosphere and the cells filled immediately using a hypodermic syringe.

Nuclear Resonance Spectra.—Proton resonance spectra were recorded at 60 Mc. on a Varian Associates A-60 high resolution spectrometer equipped with an integrator. Tetramethylsilane was used as an internal standard. Resonance frequencies are believed accurate to ± 0.02 p.p.m. and the resolution is about 1 c.p.s. Solutions were prepared in a nitrogen atmosphere and used immediately.

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The Crystal and Molecular Structure of Bis-(trimethylphosphine oxide)-cobalt(II) Dinitrate

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The crystal structure of bis-(trimethylphosphine oxide)-cobalt(II) dinitrate has been determined using three-dimensional X-ray diffraction data. Although magnetic and spectroscopic data had suggested tetrahedrally coordinated cobalt, it is found that the cobalt is 6-coordinate with a very irregular arrangement of ligand atoms, possessing no strict symmetry elements whatever and only one quasi or approximate one, a 2-fold axis. Among the interesting results are (1) the P—O—Co groups are bent ($\sim 133^\circ$, $\sim 140^\circ$), (2) the P—O bond is longer than in the free $(\text{CH}_3)_3\text{PO}$ molecule, (3) the nitrate ions are bidentate but little distorted from their inherent D_{3h} symmetry.

Introduction

Recent studies² have led to the preparation and characterization by magnetic and spectroscopic studies of compounds of the general type $\text{Co}(\text{R}_3\text{MO})_2(\text{NO}_3)_2$, where R may be CH_3 or C_6H_5 and M may be P or As.

A complete X-ray diffraction investigation of the crystal and molecular structures of one of these, namely $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$, was undertaken because it was felt that the results would be of interest for three different reasons. (1) There have not previously been any precise data concerning the structures of nitrate complexes. (2) Very little has been reported about the structures of phosphine oxide complexes and more detailed structural data would be desirable. (3) The coordination geometry about the Co(II) ion was of interest in connection with the interpretation of the magnetic and spectroscopic data.

Structure Determination

Unit Cell and Space Group.—Suitable crystals for X-ray work were prepared by slow evaporation of a solution of the complex in a 1:1 mixture of benzene and methylene chloride. The crystals grow as purple parallelepipeds, elongated on one axis. The compound is quite hygroscopic and it was therefore necessary to enclose crystals in thin-walled, soft glass capillary tubes.

From zero layer and several upper layer precession photographs, taken using $\text{Cu K}\alpha$ and $\text{Mo K}\alpha$ radiations, the crystals were found to be monoclinic and by superposition of NaCl powder lines on Weissenberg photographs taken later with $\text{Mo K}\alpha$ radiation the following unit cell dimensions (in Å.) were measured: $a = 11.70 \pm 0.02$, $b = 12.11 \pm 0.02$, $c = 11.37 \pm 0.02$, $\beta = 93^\circ \pm$

$10'$. The density measured by flotation was 1.53 g./ml. which indicates 4 molecules (4.02 calcd.) per unit cell. Systematic absences observed on the precession photographs were: $h0l$, $l \neq 2n$; $0k0$, $l \neq 2n$. These unambiguously indicate that the space group is $\text{P}2_1/c$ (C_{2h}^2). With four molecules in the unit cell it follows that all atoms are in general fourfold positions.

Intensity Measurements.—A crystal of dimensions $0.1 \times 0.1 \times 0.15$ mm. was mounted in a capillary tube with its c -axis parallel to the capillary axis. Equi-inclination Weissenberg photographs were taken for $0 \leq l \leq 6$ using $\text{Mo K}\alpha$ radiation. Using another crystal of similar dimensions mounted for rotation about the b -axis a set of $h1l$ photographs were taken to tie together intensities on the various hkl ($l = 0-6$) photographs.

The multiple film technique was used and intensities were measured visually using sets of standard spots prepared from the crystals studied. Approximate corrections were made for spot expansion and contraction on upper layer photographs, as well as the usual Lorentz and polarization corrections. Absorption corrections were neglected in view of the small size of the crystals and the short wave length of the radiation used. In all, 973 data of measurable intensity were collected.

The F^2 -values were placed approximately on an absolute scale and a mean temperature factor obtained using Wilson's method.³

Treatment of Data.—A three-dimensional Patterson synthesis was calculated using the measured F^2 -values. This synthesis and the several Fourier summations subsequently calculated were done on an IBM 7090 digital computer using Sly, Shoemaker, and Van den Hende's program.⁴ A trial and error analysis of the Patterson synthesis indicated positions for the phosphorus atoms (almost in the glide plane) and only two possible sets of positions for the cobalt atoms. One of these alternatives was adopted and structure factors, F_{calc} 's, computed from the Co and P positions only, giving for the usual discrepancy index a value of 45%. Signs for the F 's of 423 of the 530 strongest reflections were then taken to be those just computed. An electron density map was then calculated which showed the NO_3 groups and the oxygen

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