The Molecular Structure of a Trinuclear Cobalt(II)
Complex of the Diethoxyphosphonylacetylmethane Anion[1a]

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The crystal and molecular structure of the compound $Co_3[(C_2H_5O)_2P(O)CHC(O)CH_3]_6$ has been determined by standard single-crystal X-ray diffraction procedures. The unit cell, belonging to space group P2$_1$/c, has the dimensions $a = 11.20$, $b = 12.83$, $c = 23.95$ A, $\beta = 114.5°$, and contains two trinuclear formula units, each lying at a center of symmetry. The calculated and measured densities are, respectively, 1.42 and 1.40 ± 0.02 g cm^{-3}. Using 2026 reflections above background, collected with a manually operated counter diffractometer, the structure has been refined by full-matrix least squares to a conventional R factor of 9.2%. In the trinuclear structure each cobalt atom is surrounded by six oxygen atoms in a slightly distorted octahedral array, and the three octahedra are fused together so that the center one shares one of two opposite triangular faces with each of the terminal octahedra. Three chelate rings are closed about each of the terminal cobalt atoms and *none* about the center cobalt atom. Thus, considerable rearrangement must occur in the association and dissociation reactions in which the bis-chelate monomers and the trimers are interconverted. All Co–O distances lie within a small range (2.09 ± 0.05 A); this and other structural features are consistent with the idea, previously proposed on magnetic and spectroscopic evidence, that all three cobalt atoms are to be regarded as octahedrally coordinated Co(II). The question of whether there is significant π delocalization through the O–P–C–C–O chain of the chelate ring is not resolved by the available data.

Introduction

Several years ago[2] as part of a general study of the ability of the bis(dialkoxyphosphonyl)methane[2,3] and dialkoxyphosphonylacetylmethane[2] molecules to form bidentate anionic ligands, and transition metal complexes thereof, a cobalt(II) complex of the diethoxyphosphonylacetylmethanido ion (I) was prepared. Sodium, zinc, and chromium(III) complexes of this ligand were also prepared. For brevity, we shall henceforth use the abbreviation DEPAM for the ligand (as an anion) in the complexes.

I
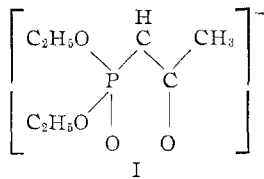
The cobalt complex was of particular interest, however, because magnetic and spectroscopic evidence strongly implied that all cobalt atoms in this compound are in octahedral environments in the crystalline state. Moreover, molecular weight measurements indicated that in freezing benzene at concentrations around 0.05 M the compound is trimeric. In other solvents, such as chloroform or 1,1,2,2-tetrachloroethane,[4] the spectra were found to depend strongly on temperature and concentration in a way which suggests that an endothermic dissociation of the trimer, Co$_3$-

(DEPAM)$_6$, to an apparently tetrahedral monomer, Co-(DEPAM)$_2$, takes place.

In view of the fact that an interesting variety of structures has been found[5-8] for polymers of bis(β-ketoenolato)metal(II) compounds, it was considered worthwhile to investigate the crystal structure of Co-(DEPAM)$_2$ in order to see if it were really trinuclear in the crystalline state and to obtain structural details.

Experimental Section

Collection and Reduction of Data.—Co(DEPAM)$_2$ was prepared by the reported method.[2] Well-formed light purple crystals, obtained by slowly cooling a saturated solution in ether to $-5°$, were monoclinic with well-developed faces including $\{100\}$, $\{001\}$, $\{011\}$, and $\{01\bar{1}\}$. The systematic absences $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$ uniquely indicated the space group P2$_1$/c. The unit cell dimensions,[9] measured at *ca.* 25° on the General Electric XRD-5 manual diffractometer using Co Kα radiation (λ 1.7902 A), were $a = 11.203 \pm 0.005$, $b = 12.825 \pm 0.010$, $c = 23.945 \pm 0.010$ A, and $\beta = 114.48 \pm 0.05°$. A density of 1.40 g/cm^3, measured by flotation, is consistent with that of 1.42 g/cm^3 calculated for six Co(DEPAM)$_2$ units per unit cell.

A crystal approximately $0.3 \times 0.3 \times 0.2$ mm was mounted along the a^* axis and sealed in a thin-walled Lindemann glass capillary. The 2515 independent reflections within the Co Kα sphere, $2\theta < 115°$, were collected at 25° using an iron oxide filter and a modified form of the moving-crystal–moving-counter technique,[10] with a 2θ scan of 2.66°. Each peak was scanned for 40 sec. Two background counts, measured for 20 sec at each end of the scan, were added to give total background. Of these, 2026 were accepted as statistically above background ($\sigma < 0.5$, where $\sigma =$ (peak + bgd)$^{1/2}$/(peak − bgd)) and were used in refinement. The data accepted as nonzero were corrected for Lorentz and

(1) (a) Research supported by the National Science Foundation under Grant No. GP-4329 and the Atomic Energy Commission under contract No. AT(30-1)-1965; (b) On leave from the Institute de Chimie, Strasbourg, as a NATO Postdoctoral Fellow, 1966–1967; (c) National Science Foundation Predoctoral Fellow, 1966–1967.

(2) F. A. Cotton and R. A. Schunn, *J. Am. Chem. Soc.*, **85**, 2394 (1963).

(3) J. D. Baldeschwieler, F. A. Cotton, B. D. N. Rao, and R. A. Schunn, *ibid.*, **84**, 4454 (1962).

(4) J. J. Bishop, unpublished studies at Massachusetts Institute of Technology.

(5) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

(6) F. A. Cotton and R. C. Elder, *ibid.*, **4**, 1145 (1965).

(7) F. A. Cotton and R. C. Elder, *ibid.*, **5**, 423 (1966).

(8) M. J. Bennett, F. A. Cotton, R. Eiss, and R. C. Elder, *Nature*, **213**, 174 (1967).

(9) The uncertainty intervals given represent the precision of the diffractometer data points used to calculate the cell constants.

(10) T. G. Furnas, Jr., "Single Crystal Orienter Instruction Manual," X-Ray Department, General Electric Co., 1957.

polarization factors and were used as input for computing the Patterson function.

Solution and Refinement of the Structure.—Cobalt atom positions were determined from the three-dimensional map of the Patterson function.[11] A three-dimensional Fourier synthesis using the signs calculated from the cobalt atoms alone (11% of the total electron density) indicated the coordinates of the phosphorus, bridging oxygen, and four other oxygen atoms. A second Fourier synthesis phased on all these atoms was used to locate the remaining oxygen atoms. At this point the atoms were assigned reasonable temperature factors and a set of structure factors, F_o's, were calculated[12a] using the atomic scattering factors of Ibers;[12b] the residual R_1 (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.54.

After two cycles of full-matrix least-squares refinement[13] of all positional parameters for the atoms which had been located, a new Fourier map showed all carbon positions. Five cycles of refinement of coordinates and isotropic temperature parameters for all atoms reduced R_1 to 0.115, with reasonable temperature factors for all atoms except C26, which had an isotropic temperature parameter, B, greater than 24 $Å^2$ (*vide infra*).

After corrections for absorption[14] made using $\mu = 45.0$ cm^{-1} (transmission coefficients ranged from 0.26 to 0.46) and anomalous dispersion, using anomalous dispersion constants ($\Delta f' = -2.19$, $\Delta f'' = 0.74$) estimated by interpolation from values for Cr in Cr radiation and Zn in Zn radiation reported by Cromer,[15] five cycles of isotropic refinement again gave convergence. Three cycles were then executed using anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ for cobalt and phosphorus atoms and isotropic ones for all other atoms. In the next cycle of refinement, the weighted R factor, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, dropped from 0.121 to 0.102. A weighting scheme, chosen in accordance with Cruickshank's criterion[16] that $w\Delta^2$ should be a constant, was assigned as follows: for $F_o \leq 20$, $\sigma = \sqrt{-2.15F_o + 55}$; for $F_o > 20$, $\sigma = \sqrt{0.29F_o + 4.2}$. One cycle of refinement caused no significant shift in the parameters and a moderate decrease in the estimated standard deviations.

The isotropic temperature parameter, B, for C26 was still unreasonably high (23 $Å^2$), so a difference Fourier map was calculated from structure factors derived after eliminating this atom from the structure. A diffuse area of moderate electron density was seen about 1.5 Å from C25, indicating considerable positional disorder for C26. Consequently four fractional positions were assigned to the disordered atom as shown below.

Fractional atom	X/a	Y/b	Z/c	Assigned B	Rel wt
C26A	0.467	0.200	0.294	12.0	0.2
C26B	0.467	0.236	0.300	12.0	0.4
C26C	0.427	0.260	0.317	12.0	0.3
C26D	0.393	0.266	0.327	12.0	0.1

A final cycle of refinement, using the weighted data and varying all parameters except those for C26, gave $R_1 = 0.092$, $R_2 = 0.098$, and no parameter shifts greater than half the estimated standard deviations. A final difference Fourier map showed no electron density greater than 0.7 e/$Å^3$. The observed and final calculated structure amplitudes are given in Table I.

(11) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090," ERFR-2 1962.

(12) (a) C. T. Prewitt, "A Full-Matrix Crystallographic Least Squares Program for the IBM 709/7090," SFLSQ3, 1962; "A Full-Matrix Crystallographic Least Squares Program for the IBM 360," SFLS5, 1966; (b) J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(13) The least-squares refinement program[12a] minimizes the function $\Sigma w(|F_o| - |F_c|)^2$.

(14) W. C. Hamilton, "Extinction and Absorption Correction for Goniostat Data on Polyhedral Crystals," GONO9.

(15) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1967).

(16) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 113.

Results

The numbering scheme for the atoms is shown in Figure 1.

Positional coordinates for all atoms except C26 and the isotropic temperature factors for oxygen and carbon atoms are listed in Table II. The components of the anisotropic thermal vibration tensors for the cobalt and phosphorus atoms are given in Table III. Bond distances and angles within chelate rings are listed in Table IV. Other bond distances and angles are given in Tables V and VI. Figure 2 is a projection of the structure on the *ac* plane.

Discussion

It has been found that the crystalline compound has a trinuclear structure, as had been anticipated from the molecular weight measurements on benzene solutions. Moreover, the structure provides each cobalt atom with a nearly regular octahedral environment so that the electronic spectrum and magnetic properties previously reported can also be accounted for in terms of structure. However, the way in which the chelate rings are disposed about the metal atoms, namely, three rings closed around each terminal atom and none around the central metal atom, is a remarkable and entirely unanticipated feature of the structure.

The structure consists of three octahedra sharing faces as in the case of the trimeric form of bis(acetylacetonato)nickel(II)[5] but differs in the arrangement of the rings. Like the $[Ni(AcAc)_2]_3$ structure, this one obeys the numerical requirement[17] that, in order to utilize each oxygen atom at a coordination site and simultaneously satisfy a coordination number of 6 for each metal ion in a polymeric structure consisting of n octahedra fused together on faces, the number n must be 3.

Crystallographically, the structure has as its only symmetry element a center of inversion. Hence the molecule, consisting of two tris-chelated metal atoms of virtual local symmetry C_3, is an optically inactive *meso* form. Neglecting the conformations of the ethoxy groups, the molecule has very nearly a threefold symmetry axis passing through the chain of metal atoms. When this C_3 axis is combined with the inversion center, the point group representing the virtual symmetry of the skeleton of the molecule is $S_6(\bar{3})$.

The coordination polyhedron about the central cobalt atom, Co1, is an octahedron whose only appreciable distortion consists in being stretched out along that threefold axis which corresponds to the molecular axis, thus reducing the virtual local symmetry to D_{3d}. The largest difference between two Co1–O bond lengths is only twice the sum of the standard deviations and presumably without chemical significance even if real.

This work has led to the most accurate[18] structural parameters yet determined for a polynuclear β-keto-enolato complex with bridging keto oxygen atoms at shared octahedral faces. It thus provides the best

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

(18) See, however, a forthcoming report from this laboratory on [Co(AcAc)$_2$]$_3$H$_2$O.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10), IN ELECTRONS, FOR Co8(DEPAM)6

[Large multi-column table of observed and calculated structure factors; individual numeric entries not legibly resolvable.]

evidence yet available as to the tendency of these bridge systems to be symmetrical. Actually, the very large standard deviations (~0.07 A) in the individual Ni–O distances in [Ni(AcAc)₂]₃ render the apparent differences between them meaningless, with perhaps one exception among the six pairs. In the [Co(AcAc)₂]₄ case[6] there appear to be consistent, real differences in the range 0.1–0.3 A between the shorter Co–O bond

which is within a chelate ring and the other longer one which completes the bridge to the next Co atom. The estimated standard deviations of the Co–O bonds in this case were about 0.03 A, so that the observed differences should be real. In the present case, there is no significant asymmetry in any of the three crystallographically distinct Co1–O–Co2 sets. The Co2–O distances (bonds within chelate rings) lie in the narrow
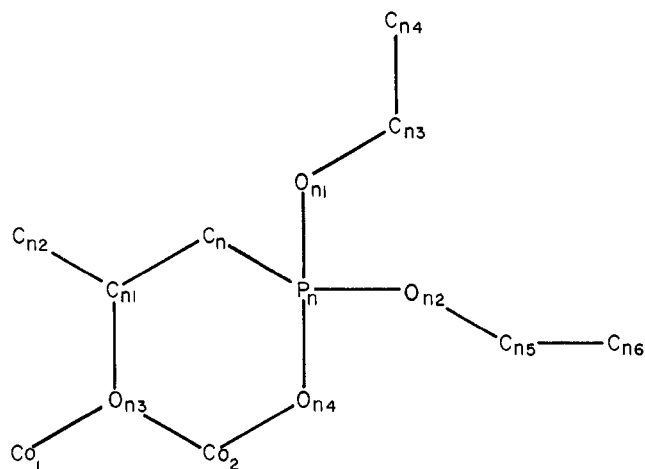
Figure 1.—The numbering scheme for the atoms. The index subscript n ($=1$, 2, or 3) identifies the particular crystallographically distinct chelate ring.

TABLE II

FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE
FACTORS FOR THE ATOMS OF $Co_3(DEPAM)_6{}^a$

Atom	x	y	z	B
Co1	0.0	0.0	0.0	
Co2	0.0034 (2)	0.1265 (2)	0.1019 (1)	
P1	0.0851 (4)	0.3590 (3)	0.0865 (2)	
P2	0.2057 (4)	0.0320 (3)	0.2288 (2)	
P3	−0.2888 (3)	0.1312 (3)	0.0932 (2)	
O13	−0.0439 (7)	0.1570 (6)	0.0085 (3)	3.41 (18)
O23	0.1481 (7)	0.0428 (6)	0.0868 (3)	3.12 (17)
O33	−0.0962 (8)	−0.0105 (6)	0.0583 (3)	3.45 (17)
O14	0.0984 (8)	0.2691 (7)	0.1259 (4)	3.98 (19)
O24	0.0758 (8)	0.0758 (7)	0.1916 (4)	4.22 (19)
O34	−0.1632 (8)	0.1829 (7)	0.1063 (4)	4.22 (20)
O11	0.0290 (9)	0.4587 (7)	0.1055 (4)	5.47 (23)
O12	0.2235 (11)	0.4105 (9)	0.1001 (5)	7.36 (28)
O21	0.2016 (11)	−0.0580 (9)	0.2716 (5)	7.51 (28)
O22	0.2924 (10)	0.1036 (9)	0.2848 (5)	6.95 (26)
O31	−0.3273 (9)	0.1297 (7)	0.1495 (4)	5.20 (21)
O32	−0.4085 (9)	0.1994 (7)	0.0502 (4)	5.56 (23)
C1	−0.0009 (13)	0.3392 (10)	0.0092 (6)	3.89 (28)
C11	−0.0494 (12)	0.2459 (10)	−0.0193 (6)	3.53 (27)
C12	−0.1211 (14)	0.2404 (11)	−0.0899 (7)	5.17 (33)
C13	−0.1060 (20)	0.4551 (16)	0.0974 (9)	9.01 (52)
C14	−0.1462 (21)	0.5591 (18)	0.1109 (10)	9.88 (56)
C15	0.3303 (24)	0.3429 (19)	0.1042 (11)	10.79 (63)
C16	0.4525 (28)	0.3861 (24)	0.1421 (13)	13.67 (80)
C2	0.2955 (14)	−0.0011 (12)	0.1880 (7)	5.28 (33)
C21	0.2593 (12)	0.0071 (10)	0.1263 (6)	3.96 (29)
C22	0.3520 (15)	−0.0267 (12)	0.0983 (7)	6.11 (37)
C23	0.1522 (23)	−0.1548 (19)	0.2496 (10)	10.34 (60)
C24	0.0093 (23)	−0.1665 (18)	0.2292 (10)	10.64 (62)
C25	0.3211 (23)	0.2097 (19)	0.2717 (10)	10.79 (62)
C26		(See text)		
C3	−0.3044 (13)	0.0044 (11)	0.0646 (6)	4.80 (32)
C31	−0.2116 (13)	−0.0432 (10)	0.0519 (6)	4.14 (30)
C32	−0.2411 (15)	−0.1562 (12)	0.0243 (7)	6.03 (37)
C33	−0.2441 (18)	0.0619 (15)	0.0226 (9)	8.06 (47)
C34	−0.2995 (22)	0.0762 (18)	0.2499 (11)	10.83 (63)
C35	−0.4009 (19)	0.2478 (16)	−0.0022 (9)	8.20 (47)
C36	−0.4660 (23)	0.3533 (20)	−0.0119 (11)	11.75 (69)

^{a} Figures in parentheses are the estimated standard deviations, occurring in the last recorded decimal place of each parameter.

range 2.096–2.111 A, each with an esd of 0.008 A, while the three Co1–O distances, each with an esd of 0.007 or 0.008 A, lie in the range 2.092–2.125 A. The aver-

TABLE III

A. Anisotropic Temperature Parameters^a for the
Cobalt and Phosphorus Atoms ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	86 (3)	33 (2)	17 (1)	1 (2)	9 (1)	0 (1)
Co2	92 (3)	36 (2)	18 (1)	−1 (2)	11 (1)	0 (1)
P1	120 (5)	37 (3)	27 (1)	−14 (3)	21 (2)	−3 (1)
P2	136 (5)	68 (3)	20 (1)	2 (3)	13 (2)	10 (1)
P3	92 (4)	56 (3)	27 (1)	−7 (3)	21 (2)	2 (1)

B. Rms Amplitudes of Thermal Vibration

Atom	Minor axis	Median axis	Major axis
Co1	0.1657	0.1931	0.2378
Co2	0.1731	0.2017	0.2401
P1	0.1683	0.2527	0.2638
P2	0.1937	0.2530	0.2914
P3	0.2025	0.2285	0.2580

^{a} Figures in parentheses are estimated standard deviations occurring in the last significant figure.

TABLE IV

DISTANCES AND ANGLES IN THE CHELATE RINGS^a

A. Bond Lengths, A

Ring, n	$Cn2-Cn1$	$Cn1-Cn$	$Cn1-On3$	$Cn-Pn$	$Pn-On4$
1	1.54 (2)	1.37 (2)	1.309 (15)	1.714 (13)	1.458 (9)
2	1.52 (2)	1.37 (2)	1.296 (15)	1.721 (15)	1.467 (9)
3	1.57 (2)	1.35 (2)	1.306 (15)	1.746 (15)	1.467 (9)
Mean	1.543 (12)	1.363 (11)	1.304 (9)	1.727 (9)	1.464 (5)

Ring, n	$Pn-On1$, $Pn-On2$	$On1-Cn3$, $On2-Cn5$	$Cn3-Cn4$, $Cn5-Cn6$
1	1.574 (10), 1.589 (12)	1.44 (2), 1.45 (3)	1.49 (3), 1.41 (4)
2	1.556 (12), 1.582 (11)	1.37 (3), 1.46 (3)	1.48 (3), ...^{b}
3	1.576 (10), 1.574 (10)	1.50 (2), 1.44 (2)	1.51 (3), 1.51 (3)
Mean	1.575 (5)	1.44 (1)	1.48 (2)

B. Bond Angles, Deg

Ring, n	$Cn2-Cn1-Cn$	$Cn2-Cn1-On3$	$On3-Cn1-Cn$	$Cn1-Cn-Pn$
1	120 (1)	114 (1)	125 (1)	127 (1)
2	120 (1)	114 (1)	126 (1)	128 (1)
3	118 (1)	112 (1)	130 (1)	123 (1)
Mean	119.3 (7)	113.3 (7)	127 (1)	126 (1)

Ring, n	$Cn-Pn-On4$	$On1-Pn-On2$	$Cn-Pn-On1$, $Cn-Pn-On2$
1	116.3 (6)	94.3 (6)	108.6 (6), 110.4 (6)
2	114.6 (6)	92.8 (6)	112.0 (7), 109.0 (7)
3	115.9 (6)	96.1 (5)	107.8 (6), 110.0 (6)
Mean	115.6 (4)	94.4 (3)	109.6 (4)

Ring, n	$On4-Pn-On1$, $On4-Pn-On2$	$Pn-On1-Cn3$, $Pn-On2-Cn5$	$On1-Cn3-Cn4$, $On2-Cn5-Cn6$
1	113.6 (5), 111.5 (6)	117 (1), 118 (1)	110 (1.5), 111 (2)
2	113.0 (6), 113.5 (6)	122 (1), 118 (1)	115 (2), ...^{b}
3	113.6 (5), 111.7 (5)	116 (1), 118 (1)	105 (1.5), 109 (1.6)
Mean	112.6 (2)	118.3 (5)	110 (1)

^{a} Figures in parentheses are standard deviations occurring in the last figure listed for each parameter. ^{b} Dimensions involving C26 are omitted for reasons explained in the text.

age values for each set, 2.105 ± 0.005 and 2.107 ± 0.005 A, are effectively identical.

The Co1–Co2 distance, 2.916 ± 0.002 A, may be compared with the metal–metal separations across shared octahedral faces in related compounds. In [Ni(AcAc)₂]₃ the distances[5] are 2.88 and 2.90 A, each with an esd of 0.02 A, while in [Co(AcAc)₂]₄ this type of Co–Co distance is 3.19 ± 0.01 A.

Perhaps the most interesting dimensions in the structure are those within the chelate rings. This is because one might hope that these bond lengths would provide some basis for assessing the electronic structure and,

Table V
Bond Distances to Cobalt Atoms (A)[a]

Co1–O13	2.103 (8)	
Co1–O23	2.125 (7)	Av 2.107 (5)
Co1–O33	2.092 (8)	
Co2–O13	2.109 (8)	
Co2–O23	2.096 (8)	Av 2.105 (5)
Co2–O33	2.111 (8)	
Co2–O14	2.074 (9)	
Co2–O24	2.062 (9)	Av 2.061 (5)
Co2–O34	2.046 (9)	
Co1–Co2	2.916 (2)	

[a] Numbers in parentheses following each bond length are standard deviations occurring in the least significant figure. For the average values, the numbers in parentheses are standard deviations of the mean occurring in the least significant figure.

Table VI
Bond Angles Involving Cobalt and Oxygen Atoms (deg)[a]

A. O–Co2–O Angles within the Chelate Rings

O12–Co2–O14	90.3
O23–Co2–O24	91.1
O33–Co2–O34	90.7
Mean	90.7

B. O–Co2–O Angles Involving Bridging Oxygen Atoms Only

O13–Co2–O23	77.6
O13–Co2–O33	77.4
O23–Co2–O33	77.1
Mean	77.4

C. O–Co2–O Angles Involving Terminal Oxygen Atoms Only

O14–Co2–O24	93.1
O14–Co2–O34	92.8
O24–Co2–O34	91.7
Mean	92.5

D. Remaining O–Co2–O Angles

O13–Co2–O34	98.9
O14–Co2–O23	98.9
O24–Co2–O33	98.7
Mean	98.8

E. O–Co1–O Angles

O13–Co1–O23	77.1
O13–Co1–O33	77.9
O23–Co1–O33	76.9
Mean	77.3

F. Co1–O–Co2 Angles

Co1–O13–Co2	87.6
Co1–O23–Co2	87.4
Co1–O33–Co2	87.9
Mean	87.6

[a] The standard deviation in each angle is 0.3°.

particularly, the extent of π-electron delocalization in the chelate rings. It has previously been proposed,[2] on the basis of several types of spectroscopic data, that there is considerable delocalization, as represented by the assignment of an appreciable coefficient to canonical form III in a resonance description of the chelated ligand
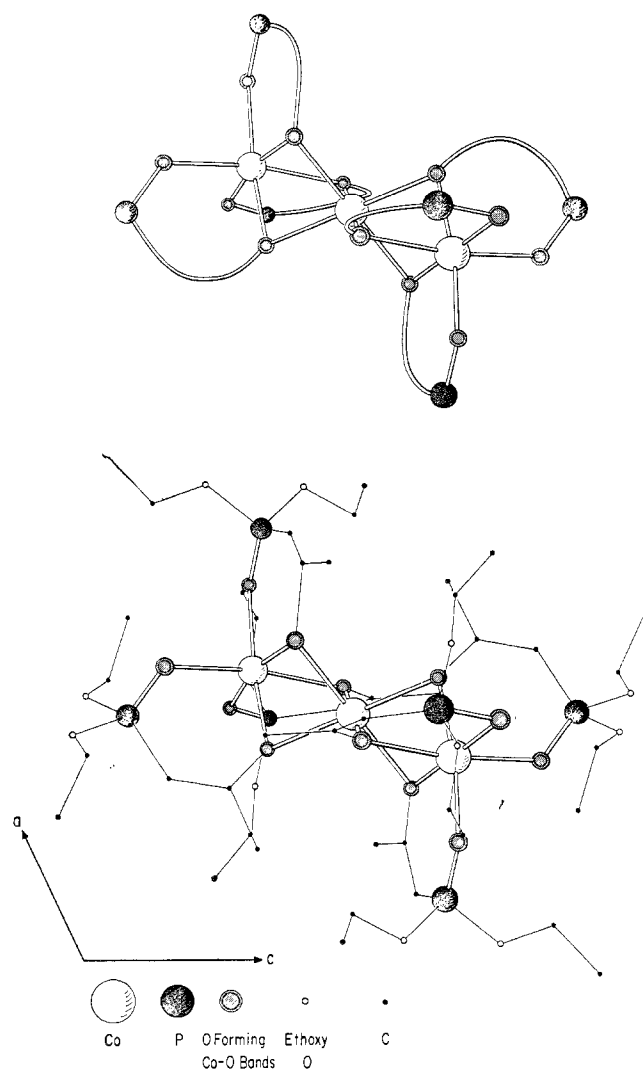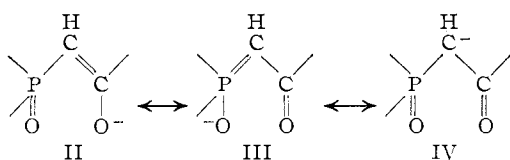

Figure 2.—Upper: A schematic representation of the trinuclear molecule of $Co_3(DEPAM)_6$ as seen in the (010) projection. For clarity the ethoxy groups have not been included and portions of the ligand rings are represented by heavy lines. Lower: A more detailed view of the same projection in which all atoms and bonds are shown. The origin of the unit cell is at the middle cobalt atom.

It is to be noted, however, that the previous arguments in favor of considerable delocalization were based solely on data for compounds believed to be mononuclear; that is, the data and deductions therefrom applied only to the situation where the oxygen atoms were nonbridging. It is reasonable to suppose that in the compound studied here, where the carbonyl oxygen atoms are coordinated to two cobalt ions, the contribution of II will be increased relative to III and IV. This means that less delocalization would be expected in this polynuclear compound than in the typical mononuclear ones to which the previous discussion[2] referred.

In comparing the observed bond lengths in the chelate rings with values which might be expected for localized (II) and delocalized (II ↔ III ↔ IV) systems, we may begin by noting that there are no significant differences between the dimensions of the three crystallographically

distinct rings. Hence, the mean values given in Table IV may be used. These are listed in the third column of Table VII. Column 2 of Table VII lists bond lengths which might be expected for a completely localized structure, essentially the canonical form II. Column 4 has values for a delocalized structure, which we take for simplicity to be an equal mixture of the canonical forms II and III, so that each of the four bonds should have an order of 1.5. The bond lengths selected for each of the reference structures were obtained from the sources indicated in footnotes to the table.

TABLE VII

COMPARISON OF OBSERVED CHELATE RING DIMENSIONS
WITH THOSE FOR LIMITING STRUCTURES

Bond	Localized	Bond lengths, A Observed	Delocalized
OP	$1.40–1.52^a$	1.464 ± 0.005	$1.55–1.65^a$
PC	$\sim1.81^a$	1.73 ± 0.01	$1.72–1.75^a$
CC	$\sim1.34^b$	1.36 ± 0.01	$\sim1.40^b$
CO	$\sim1.31^b$	1.30 ± 0.01	$\sim1.29^b$

[a] Estimated from the compilation of D. E. C. Corbridge in "Topics in Phosphorus Chemistry," Vol. 3, E. J. Griffith and M. Grayson, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, pp 57–394. [b] From "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement, Special Publication No. 18, The Chemical Society, London, 1965.

It is evident that the present data do not resolve the problem. Comparison of the observed C–C and C–O bond lengths with those of the reference structures leads to no decision because of the inherently small differences between the values expected for the two reference structures. The observed P–C distance by itself appears to favor the delocalized structure; however, the observed P–O distance appears, equally strongly, to favor the localized structure. We believe that this impasse arises from the fact that the relation of P–O and P–C distances to bond orders depends on the nature of the other bonds to the phosphorus atom. Unfortunately, none of the compounds appearing in the tabulations from which the bond lengths for the reference structures were selected is a really close analog. For example, as a standard of reference for the localized structure, a coordination compound formed by a diethylphosphonic acid would be appropriate, but no

such compound, or even a very near relative thereof, has yet been studied structurally.

Undoubtedly, the most important stimulating aspect of this structure is the fact that it is built up of a non-chelated Co(II) atom sandwiched between two tris-chelated Co(II) atoms. This is particularly surprising since there appears[2,4] to be a readily reversible equilibrium between $Co_3(DEPAM)_6$ and the monomers, $Co(DEPAM)_2$, in solution. This equilibrium, and the rate laws, are being studied. One might reasonably expect that with the extent of opening and closing of chelate rings required in order to interconvert the trinuclear molecule and the monomers, the association and dissociation processes would differ in rate from corresponding processes (as, for example, in the Co-(AcAc)$_2$ and Ni(AcAc)$_2$ systems) in which no opening and closing of rings is required.

A very obvious question concerning the structure of $Co_3(DEPAM)_6$ is why the molecule has the unexpected arrangement of rings. The DEPAM ion is quite unsymmetrical, sterically and perhaps also electronically. Models indicate that steric factors alone *might* provide sufficient reasons for the observed arrangement. In a structure like that of $[Ni(AcAc)_2]_3$, in which two chelate rings remain closed around each metal atom, several close contacts (~4.6 A) between P atoms of $(C_2H_5O)_2P$ groups would have to occur, whereas in the structure actually found, the six close P–P distances are about 7.1 A. With β-ketoenolato complexes of nickel(II) it has been shown[17] that by increasing the bulk of the substituents on *both* carbonyl carbon atoms equally, association can be inhibited and, finally, prevented altogether. However, the consequence of increasing the bulk of only one substituent remains to be determined. Such a study should help to show how satisfactory a purely steric explanation of the structure may be in the present case.

Finally, it may be observed that the structure of $Co_3(DEPAM)_6$ has some interesting chemical implications. There must be an electronically excited state corresponding to the description of the molecule as two tris-chelated Co(III) atoms sandwiching a Co(0) atom. The extent to which the molecule may actually react as such a description might suggest is presently under investigation.