Dimerization Constants. Comparison of the hydrolysis and dimerization constants of U(IV)–EDTA and U(IV)–CDTA given in Table I shows that the slightly greater hydrolytic tendency of the U(IV)–EDTA chelate is accompanied by a decrease in its tendency to dimerize. For the corresponding Th(IV) chelates, the difference between the hydrolysis constants is greater, the EDTA chelate again showing the greater tendency to hydrolyze, while the dimerization constants of the CDTA and EDTA chelates are about the same. In attempting to rationalize the influence of constitution on the observed hydrolytic and dimerization tendencies, several factors should be considered: (1) a coulombic effect whereby the greater the coulombic attraction between the hydroxide and metal ion as reflected in the acid dissociation constant, the greater should be the tendency of this same hydroxide ion to form a second ionic bond with another metal chelate to yield a dimer; (2) influence of the nature of the ligand as well as the ionic radius and coordination number of the metal ion upon steric and coulombic repulsions between the negative donor groups of the ligands in the dimer; (3) shielding by the hydrocarbon moieties of the ligand, which would increase the tendency of the chelate to dimerize. Comparing the EDTA *vs.* CDTA dimerization tendencies for the same metal ion, the coulombic effect predicts greater dimerization for the EDTA chelate as indicated by its greater tendency to hydrolyze. The coulombic and steric ligand–ligand repulsions should be somewhat greater for the CDTA dimer, because of the directing influence of the cyclohexane ring on the carboxylate donor groups. Also, the greater hydrophobic nature of the cyclohexane group of CDTA will lead to the formation of a more completely shielded dimer and consequently a higher dimerization constant for the CDTA chelates.

For the U(IV) chelates, the shielding effect which predicts CDTA > EDTA seems to outweight the other factors that predict the opposite trend. However, with Th(IV), the coulombic effect assumes greater importance as indicated by the larger variation in hydrolysis constants between the EDTA and CDTA chelates. In this case the opposing effects seem to balance, resulting in approximately equal dimerization constants.

When the dimerization constants of U(IV) and Th(IV) chelates of the same ligand are compared (Table I), it is found that those of the larger Th(IV) ion always have the greater tendency to dimerize. Although the coulombic effect predicts that the smaller size of the U(IV) ion enhances its tendency to form stronger ionic bonds between the chelated metal ion and the hydroxo groups in the dimer, this effect is overshadowed by the greater opportunity for mutual steric and coulombic repulsions between negative donor groups of the two ligands in the smaller U(IV) dimers.

It is evident from the potentiometric data that no dimerization of the monohydroxo U(IV)–DTPA chelate occurs. This lack of dimerization is to be expected since there would be large coulombic and steric repulsions between ligand donor groups in the ligand, and since the mononuclear species is completely, or almost completely, coordinated by the hydroxide ion and the octadentate DTPA anion. These observations are similar to those described by Bogucki and Martell[18] for the analogous DTPA–Th(IV) chelate compound.

The Structure of Hexa(acetylacetonato)aquotricobalt(II)[1]

F. A. Cotton and Roger Eiss[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received August 11, 1967*

Abstract: Partial hydration of the tetramer of bis(acetylacetonato)cobalt(II), $[Co(AcAc)_2]_4$, leads to $[Co(AcAc)_2]_3 \cdot H_2O$ which can be isolated as pale purple triclinic crystals. The unit cell dimensions are $a = 9.05$, $b = 10.56$, $c = 19.56$ A; $\alpha = 85.80°$, $\beta = 93.71°$, $\gamma = 101.32°$; measured density, 1.44 g/cm^3, calculated density (for $Z = 2$), 1.43 g/cm^3. The structure was solved, including hydrogen atoms, and refined by least squares to a residual of 7.0%, using 3040 nonzero reflections. The molecule consists of three octahedrally coordinated cobalt atoms. Two acetylacetonato chelate rings are closed about each cobalt atom and certain oxygen atoms are shared by two cobalt atoms. Two of the octahedra are fused together on a face while the other two share an edge, and the water molecule is part of the terminal octahedron which shares an edge with the central one. The structure may be derived from that of the tetramer, $[Co(AcAc)_2]_4$, by removing one terminal $Co(AcAc)_2$ moiety and inserting the water molecule in the hole which remains in $[Co(AcAc)_2]_3$. It is therefore structurally as well as stoichiometrically part of the series $[Co(AcAc)_2]_4$, $[Co(AcAc)_2]_3H_2O$, $[Co(AcAc)_2]_2(H_2O)_2$, $Co(AcAc)_2(H_2O)_2$, all members of which have now been characterized by X-ray crystallographic study.

Beginning with the reports[3,4] of the trimeric structure of bis(acetylacetonato)nickel(II), $[Ni(AcAc)_2]_3$, it has become clear that the stereochemical behavior of the bis(β-ketoenolato)metal(II) compounds of the first-row metals (except copper) is dominated by their tendency to have a coordination number greater than four. Provided they have no access to additional donor mole-

---

[1] Research supported in part by the National Science Foundation under Grant No. 7034 X.

[2] Union Carbide Predoctoral Fellow, 1964–1965; National Science Foundation Fellow, 1965–1967.

[3] G. J. Bullen, *Nature*, 177, 537 (1956).

[4] G. J. Bullen, R. Mason, and P. Pauling, *ibid.*, **189**, 291 (1961); *Inorg. Chem.*, **4**, 456 (1965).

cules they try to satisfy this tendency by forming oligomers in which there are bridging oxygen atoms. Thus, in addition to the trimer of Ni(AcAc)$_2$, in which there are three octahedra fused together on faces, there is the Co(AcAc)$_2$ tetramer,[5] in which there are four octahedrally coordinated cobalt atoms with the octahedra sharing either faces or edges, and, quite recently, the trimeric [Zn(AcAc)$_2$]$_3$ has been found to consist[6] of one six-coordinate and two five-coordinate zinc atoms. In addition to these structural studies of crystalline solids, there have been studies of solutions, as yet unconfirmed by X-ray work, indicating that Mn(AcAc)$_2$ is trimeric[7] and that Fe(AcAc)$_2$ is hexameric.[8]

It has, however, been shown that the formation of oligomers can be impeded and even altogether prevented by replacing the CH$_3$ groups or the hydrogen atom of the AcAc$^-$ ligand by bulkier substituents. Evidence for this has been provided both by studies of equilibria in solution[9] and by X-ray structure determinations of the zinc[10] and nickel[11] complexes of dipivaloylmethane, a ligand derived from AcAc$^-$ by replacing the methyl groups with *t*-butyl groups.

When the M(AcAc)$_2$ entities do have access to additional donor molecules, they tend to achieve coordination numbers higher than four by coordinating these donors in preference to or along with the formation of oligomers. In general, when donor molecules, D, are freely available, the limiting species, *trans*-M(AcAc)$_2$D$_2$, are formed. A single-crystal study[12] of *trans*-Co(AcAc)$_2$(H$_2$O)$_2$ in one of its forms[13] was carried out, and comparison of powder patterns indicated that Ni(AcAc)$_2$(H$_2$O)$_2$ and Mn(AcAc)$_2$(H$_2$O)$_2$ are isostructural.[14] For Ni(AcAc)$_2$(H$_2$O)$_2$, this was later confirmed by a single-crystal study.[15] In the case of zinc, the limiting hydrate is apparently[16] the five-coordinate Zn(AcAc)$_2$H$_2$O, though a dihydrate has often been mentioned in the literature without conclusive proof of its composition. Other species of the stoichiometry M(AcAc)$_2$D$_2$, in which D is an amine donor such as pyridine, are known and presumably have a *trans*-octahedral structure,[17] but there have been no single-crystal X-ray studies to prove this.

When donor molecules are in restricted supply, the oligomers, [M(AcAc)$_2$]$_x$, tend to be degraded to species which are more complex than the limiting, mononuclear M(AcAc)$_2$D$_n$ (n = 1, 2) end products. Thus Fackler has reported[18] that upon treatment of [Co(AcAc)$_2$]$_4$ and Ni(AcAc)$_2$]$_3$ with limited quantities of pyridine (py) the substances [M(AcAc)$_2$]$_2$(py)$_2$ (M = Co, Ni) could be isolated, and their existence in solution was indicated by spectrophotometric titrations. Similarly, [Co(AcAc)$_2$]$_2$D$_2$, where D represents cyclohexylamine, was also prepared.[19] With water as the donor molecule, it has been found that two intermediate products may be isolated from [Co(AcAc)$_2$]$_4$. One of these is [Co(AcAc)$_2$]$_2$(H$_2$O)$_2$, the structure of which has been determined.[13] The other is a substance whose formula could not be established definitively by elemental analysis, but which appeared to be either [Co(AcAc)$_2$]$_2$H$_2$O or [Co(AcAc)$_2$]$_3$H$_2$O.

In order to ascertain the correct formula for this intermediate hydration product of [Co(AcAc)$_2$]$_4$ and to establish its structural relationship to the other Co(AcAc)$_2$ species, *viz.*, [Co(AcAc)$_2$]$_4$ and [Co(AcAc)$_2$]$_2$(H$_2$O)$_2$, a single crystal X-ray diffraction investigation was undertaken. The results are reported here.

Experimental Section

The compound was prepared by the previously described procedure[13] and a suitable crystal approximately 0.1 × 0.2 × 0.3 mm was selected and placed in a Lindemann glass capillary which was sealed and mounted on a goniometer head. Precession photographs indicated one of the triclinic space groups, P1 or P$\bar{1}$, and afforded approximate unit cell dimensions. Using a General Electric XRD-5 X-ray diffractometer equipped with a Furnas-Harker single-crystal orienter, the unit cell dimensions were then measured with Co Kα radiation (λ = 1.7902 A), giving $a = 9.05 \pm 0.01$ A, $b = 10.56 \pm 0.01$ A, $c = 19.56 \pm 0.01$ A, $\alpha = 85.80 \pm 0.05°$, $\beta = 93.71 \pm 0.05°$, $\gamma = 101.32 \pm 0.05°$; volume of unit cell: 1826 A^3. These dimensions differ from those previously[13] given. They were calculated from measured values of a^*, b^*, c^*, α, β^*, and γ^*. If α is replaced by its complement and the direct cell parameters calculated from these data, the previously reported (and incorrect) values are obtained. We are dealing here with the same compound as that described before,[13] despite the difference in reported cell constants.

A Delauney reduction[20] indicated no higher symmetry. The observed density (by flotation) was 1.434 ± 0.005 g/cm^3, while those calculated for three [Co(AcAc)$_2$]$_2$H$_2$O and two [Co(AcAc)$_2$]$_3$H$_2$O's per unit cell are respectively 1.456 and 1.440 g/cm^3. Thus the formula which was found to be correct by the subsequent refinement, [Co(AcAc)$_2$]$_3$H$_2$O, is favored by the density measurement.

Approximately 3800 reflections within the sphere bounded by (sin θ)/λ = 0.5 were collected manually on the diffractometer using Co Kα radiation filtered by iron oxide and a θ–2θ scan, with the range of 2θ being 2.66°. Reflections having a background equal to or greater than the peak were assigned an intensity of five counts. Later, 745 reflections were discarded as essentially zero since for them the ratio (peak + background)$^{1/2}$/(peak − background) was $\geq$0.5. The intensities of the remaining reflections were corrected for Lorentz and polarization effects.

The crystal dimensions were carefully measured, and equations for the planes of the faces were derived. Because of the irregular shape of the crystal, there were considerable variations in the intensities of the 100 and 300 reflections (χ = 90°) upon rotation about the ϕ axis. It was considered best to make slight changes (up to 10%) in the coefficients of the equations for the crystal planes which had been derived directly from the measurements of dimensions in order to improve the fit between measured and calculated absorption as a function of ϕ. The modified equations for crystal planes were then used for computing absorption corrections to all reflections.

Solution and Refinement of Structure

A three-dimensional Patterson function was calculated. Attempts to obtain a solution for the space group P$\bar{1}$ were unsuccessful, but a set of cobalt atom positions were determined assuming the space group to be P1. Using the phases given by this set of cobalt atoms, a Fourier map which showed the positions of all

---

[5] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 4, 1145 (1965).

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

[7] D. P. Graddon and G. M. Mockler, *Australian J. Chem.*, 17, 1119 (1964).

[8] D. A. Buckingham, R. C. Gorges, and J. T. Henry, *ibid.*, 20, 281 (1967).

[9] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 83, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, 83, 3775 (1961); F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, 3, 1 (1964).

[10] F. A. Cotton and J. S. Wood, *ibid.*, 3, 245 (1964).

[11] F. A. Cotton and J. J. Wise, *ibid.*, 5, 1200 (1966).

[12] G. J. Bullen, *Acta Cryst.*, 12, 703 (1959).

[13] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 5, 423 (1966).

[14] R. H. Holm and F. A. Cotton, *J. Phys. Chem.*, 65, 321 (1961).

[15] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 17, 1481 (1964).

[16] H. Montgomery and E. C. Lingafelter, *ibid.*, 16, 748 (1963).

[17] J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 87, 2821 (1965).

[18] J. P. Fackler, Jr., *ibid.*, 84, 24 (1962); *Inorg. Chem.*, 2, 266 (1963).

[19] J. A. Bertrand, F. A. Cotton, and W. J. Hart, *ibid.*, 3, 1007 (1964).

[20] "International Tables of Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965.

86 carbon and oxygen atoms was computed. Upon close inspection of this Fourier function, an apparent center of symmetry was found. This was used as the origin for a new coordinate system, and, upon reexamination of the Patterson map, peaks for all Co–Co vectors in the new coordinate system were found. The space group $P\bar{1}$ was therefore assumed to be correct and the successful refinement would appear to confirm this.

Four cycles of full-matrix least-squares refinement of positional parameters, using atomic scattering factors compiled by Ibers,[21] gave a residual, R_1 $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$, of 0.17. Four more cycles in which positional parameters and isotropic temperature parameters, B in the expression $\exp[(-B \sin^2 \theta)/\lambda^2]$, were refined, with the atomic scattering factor for cobalt being corrected for anomalous dispersion, were now carried out. The anomalous dispersion corrections, $\Delta f' = -2.10$ and $\Delta f'' = 0.74$, were interpolated from values reported by Cromer.[22] Then a cycle was run in which the temperature parameters of the cobalt atoms were given the anisotropic form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. Following this, a weighting based on Cruickshank's criterion[23] that $\omega\Delta^2$ should be constant was introduced, and three more cycles of refinement were carried out. Convergence was attained at this point.

A difference Fourier map showed 40 of the 44 hydrogen atoms as peaks varying in intensity from 0.25 to 0.80 electron per cubic angstrom (e/A^3), while the estimated standard deviation in electron density, given by the formula of Cruickshank,[24] $\sigma(\rho) = V^{-1}[\sum_{h,k,l}(\Delta F_{hkl})^2]^{1/2}$, was 0.07 e/A^3. The hydrogen atom positions, which were read directly from the difference Fourier map, gave C–H distances and bond angles of doubtful validity owing to partial overlap of the hydrogen peaks with peaks resulting from anisotropic motion of methyl carbon atoms. Therefore, the hydrogen atoms were assigned to geometrically reasonable positions which gave best agreement with the observed peaks. A difference Fourier map showed that four hydrogen atoms had been assigned incorrect positions. These were corrected, and the next difference Fourier maps confirmed correct placement of all hydrogen atoms while still indicating considerable anisotropic motion of the methyl carbon atoms and the oxygen atoms.

Anisotropic refinement of all atoms was beyond the capacity of the IBM 360–65 computer used. Therefore, only the cobalt atoms and the water oxygen atom were permitted to refine anisotropically. The hydrogen atoms were included in subsequent structure factor calculations, with isotropic temperature factors of 6.5 A^2 for those in methyl groups and 5.5 A^2 for those in the water molecule and on the ring carbon atoms. Hydrogen atom positions were not refined, but after each cycle they were shifted parallel to the shift which had been made in the position of the atom to which they were bonded.

Table I. Computer Programs Used in Analysis and Interpretation of Structure

Author	Title	Description
D. P. Shoemaker	MIXG2	Calculation of diffractometer settings.
R. C. Elder	PDATA2	Corrects MIXG2 output to machine coordinates, introduces scan width, prints diffractometer settings in convenient format
R. C. Elder	RAWRE2	Calculates intensities, makes Lorentz and polarization corrections, punches cards in proper format for GONO9, MIFR2, SFLSQ3
W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende	MIFR-2	Fourier summation for Patterson or Fourier maps
W. C. Hamilton	GONO9	Absorption correction
C. T. Prewitt	SFLSQ3	Least-squares refinement of parameters (Fortran II version)
C. T. Prewitt	SFLS5	Least-squares refinement of parameters (Fortran IV version)
D. L. Weaver	WOFF2	Calculates average Δ^2 *vs.* average F_o for weighting scheme
J. S. Wood	MGEOM	Calculates intramolecular bond lengths and angles, best planes through ligand rings
D. P. Shoemaker	DISTAN	Calculates orthogonal cell coordinates, matrix to convert fractional cell parameters to orthogonal cell coordinates, intramolecular and intermolecular contacts and angles
R. C. Elder	PUBTAB	Prepares structure factors in proper format for publication

Fifteen reflections having $(\sin \theta)/\lambda \leq 0.08$ were rejected because they were believed to suffer from extinction, while five others which also gave very poor agreement between F_o and F_c were rejected on the assumption that the measured intensities were erroneous due to extraneous pulses in the detector circuit. Three more cycles of refinement were now run leading to convergence. The reflections were now arranged in groups of 50, in order of increasing $|F_o|$; $\overline{\Delta^2}$ and $|\bar{F}_o|$ were calculated for each group. From the resulting curve, the following weighting scheme was devised: for $|F_o| \leq 12$, $\sigma = (-0.28|F_o| + 4.4)^{1/2}$; for $12 < |F_o| \leq 45$, $\sigma = 1.0$; for $|F_o| > 45$, $\sigma = (0.063|F_o| - 1.82)^{1/2}$. Four more cycles of refinement using this weighting scheme achieved convergence with $R_1 = 0.070$, $R_2 = \{\Sigma\omega[|F_o| - |F_c|]^2/\Sigma\omega|F_o|^2\}^{1/2} = 0.069$ and no parameter changing by more than 20% of its estimated standard deviation in the final cycle. A final difference Fourier map showed no electron density greater than 0.5 e/A^3, and all significant maxima could be reasonably attributed to anisotropic motion of oxygen atoms or methyl carbon atoms. Structure factors were computed for all of the reflections initially rejected because of poor counting statistics with the satisfying result that no $|F_c|$ was more than 2.5 times the minimum observable $|F_o|$. The observed structure amplitudes, $|F_o|$, and final calculated structure factors, F_c, are on file with the American Documentation Institute.[25] A list of the com-

---

(21) J. A. Ibers in ref 20, Vol. III, 1962, p 202.

(22) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

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

(24) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

(25) This table has been deposited as Document No. 9649 with the

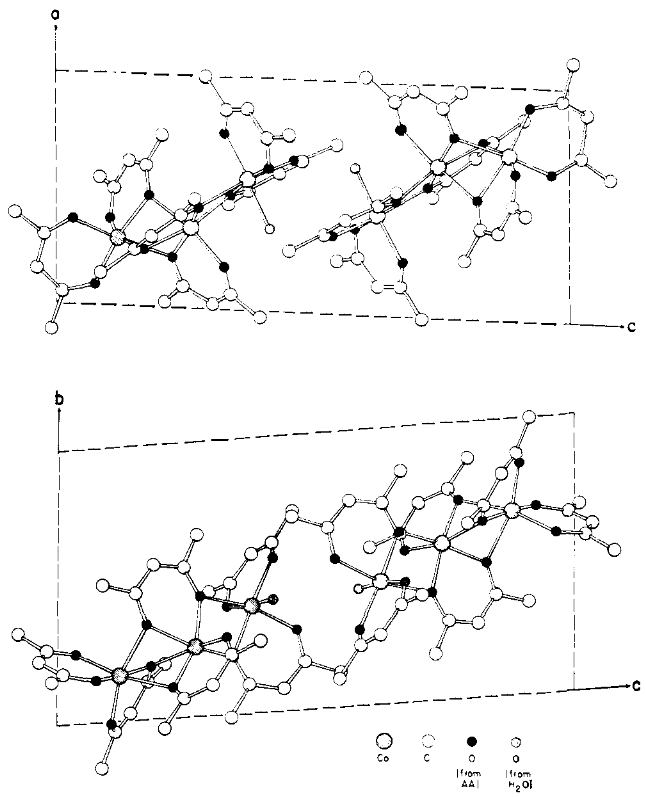

Figure 1. Projections of the contents of one unit cell of [Co-$(AcAc)_2]_3H_2O$ onto (a, top) the *XZ* and (b, bottom) the *YZ* planes of the orthogonal coordinate system. The dashed outlines give the projections of the *ac* and *bc* faces, respectively, of the triclinic cell.

puter programs used in all phases of the structure analysis and its subsequent interpretation is given in Table I.

Results

The final fractional coordinates for all atoms and the isotropic temperature factors for all atoms refined isotropically are given in Table IIa. The elements of the anisotropic temperature factor tensors for the cobalt and water oxygen atoms are recorded in Table IIb. The coordinates, in angstroms, of all atoms in an orthogonal (Cartesian) coordinate system were computed and are listed in Table III. The matrix transforming the triclinic fractional coordinates (Table II) to the orthogonal coordinates is given in Table IV.

The crystal structure is seen along the orthogonal *Y* and *X* axes in Figures 1a and 1b, respectively. Figure 2 employs schematic drawings which define the numbering scheme used in all tables of positional parameters and molecular dimensions.

Bond lengths and angles involving light atoms of the chelate rings are given in Table V, and all Co–O bond lengths and angles are given in Table VI.

The Co–Co separations (A) are: Co(1)–Co(2), 2.966 (2); Co(2)–Co(3), 3.283 (2). The Co(1)–Co(2)–Co(3) angle is 152.8° (1°).

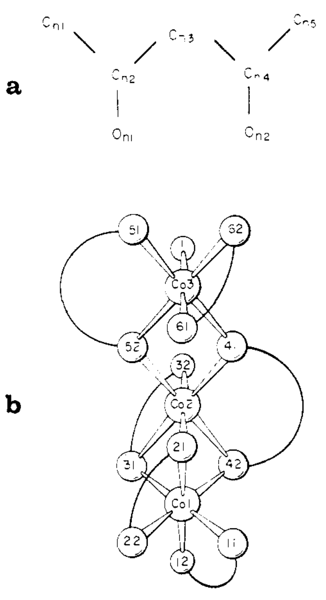

Figure 2. (a) A sketch showing the numbering scheme for atoms in the chelate rings. The subscript *n* (= 1, 2, . . . , 6) is a running index identifying the rings. (b) The numbering scheme for the oxygen atoms. The two oxygen atoms of the *n*th ring are identified as O(*n*1) and O(*n*2).

Discussion

The results of this investigation may be conveniently discussed from two points of view. First, we shall compare the present results with corresponding structural features of other β-ketoenolato structures generally. Second, the place of this structure in the general structural pattern of hydration leading from $[Co(AcAc)_2]_4$ to $Co(AcAc)_2(H_2O)_2$ will be considered.

Comparison with Other Structures Generally. Bond distances within the chelate rings show excellent agreement with the average values for 13 other acetylacetonate structures determined by three-dimensional methods, as surveyed by Lingafelter and Braun.[26] These average values are included in Table V under the heading "literature average." Bond angles in the ligands deviate slightly, up to 1.5°, probably because of intramolecular crowding.

In Table VII the Co–O bond lengths in the four Co-$(AcAc)_2$ compounds for which X-ray structure determinations have been reported[5,12,13] are compared. In general there is little variation, but for two cases notable differences do occur. (1) The Co–Co distances in [Co-$(AcAc)_2]_4$ are significantly longer than corresponding ones in the hydrate molecules. This has been attributed to differences in the Co–O–Co angles.[13] (2) The Co–O bond to water is about 0.15 A shorter in [Co-$(AcAc)_2]_3H_2O$ than in $[Co(AcAc)_2]_2(H_2O)_2$ and Co(Ac-$Ac)_2(H_2O)_2$. In $[Co(AcAc)_2]_3H_2O$, the Co–OH_2 distance is not significantly different from the other Co–O distances, whereas in the same two molecules it is markedly greater than the others. Bullen[12] proposed that in $Co(AcAc)_2(H_2O)_2$ a ligand field effect is responsible, but since $Mg(AcAc)_2(H_2O)_2$ has a similar distortion,[27] this seems doubtful. Similarly, previous explanations involving electronegativity differences[12] or charge differences[5] are rendered questionable by the present struc-

ADI Auxillary Publications Project Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advance remittance ($1.25 for photoprints or $1.25 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

---

[26] E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).

[27] B. Morosin, *Acta Cryst.*, **22**, 315 (1967).

Table II

a. Atom Positions and Isotropic Temperature Factors[a]

Atom	X/a	Y/b	Z/c	$B \times 10^4$
Co(1)	0.28814 (15)	0.21464 (13)	0.12057 (6)	...
Co(2)	0.34692 (15)	0.32468 (12)	0.25710 (6)	...
Co(3)	0.56595 (15)	0.48431 (12)	0.37526 (6)	...
O(1)	0.36001 (64)	0.46844 (59)	0.41780 (28)	...
O(11)	0.36668 (62)	0.31536 (53)	0.03445 (28)	4.32 (12)
O(12)	0.08426 (58)	0.16740 (49)	0.07547 (27)	3.80 (11)
O(21)	0.48098 (58)	0.27664 (49)	0.18029 (26)	3.67 (11)
O(22)	0.36961 (64)	0.05376 (52)	0.10537 (28)	4.35 (12)
O(31)	0.21664 (59)	0.14969 (49)	0.22464 (26)	3.69 (11)
O(32)	0.18692 (61)	0.31530 (51)	0.32724 (27)	4.05 (12)
O(41)	0.43593 (55)	0.51430 (47)	0.27595 (25)	3.34 (11)
O(42)	0.24008 (57)	0.38674 (50)	0.17012 (26)	3.68 (11)
O(51)	0.65917 (60)	0.40472 (52)	0.46353 (27)	4.08 (12)
O(52)	0.50027 (56)	0.29820 (48)	0.34057 (25)	3.37 (11)
O(61)	0.75914 (61)	0.52394 (52)	0.32704 (28)	4.18 (12)
O(62)	0.62279 (62)	0.66090 (52)	0.41622 (27)	4.15 (12)
C(11)	0.37945 (112)	0.40126 (94)	−0.07887 (50)	5.63 (22)
C(12)	0.29384 (90)	0.31898 (75)	−0.02245 (41)	3.66 (17)
C(13)	0.14604 (93)	0.25542 (77)	−0.03591 (42)	3.94 (17)
C(14)	0.05150 (87)	0.18982 (73)	0.01205 (40)	3.41 (16)
C(15)	−0.11328 (101)	0.13662 (85)	−0.01020 (46)	4.84 (20)
C(21)	0.74457 (102)	0.32436 (87)	0.20692 (46)	4.88 (20)
C(22)	0.60791 (90)	0.24099 (75)	0.17476 (40)	3.57 (16)
C(23)	0.62357 (95)	0.13257 (80)	0.14207 (42)	4.16 (18)
C(24)	0.50523 (93)	0.04353 (76)	0.11241 (40)	3.77 (17)
C(25)	0.54439 (104)	−0.07559 (88)	0.08655 (47)	5.00 (20)
C(31)	0.02117 (110)	−0.03241 (94)	0.20810 (50)	5.64 (22)
C(32)	0.09190 (93)	0.08730 (78)	0.24567 (41)	3.82 (17)
C(33)	0.02364 (100)	0.11932 (85)	0.30163 (45)	4.72 (19)
C(34)	0.06895 (96)	0.23007 (80)	0.33720 (42)	4.07 (18)
C(35)	−0.02838 (116)	0.25730 (98)	0.39287 (53)	6.12 (23)
C(41)	0.47432 (107)	0.74152 (92)	0.26844 (48)	5.38 (21)
C(42)	0.39895 (89)	0.61224 (76)	0.24287 (40)	3.63 (16)
C(43)	0.30084 (90)	0.61161 (76)	0.18444 (41)	3.80 (17)
C(44)	0.23050 (89)	0.50183 (78)	0.15041 (40)	3.74 (17)
C(45)	0.13571 (111)	0.51914 (94)	0.08622 (50)	5.67 (22)
C(51)	0.73415 (109)	0.25208 (93)	0.54716 (50)	5.52 (22)
C(52)	0.65607 (91)	0.28678 (79)	0.47849 (41)	3.88 (17)
C(53)	0.59033 (90)	0.18247 (75)	0.43820 (40)	3.71 (17)
C(54)	0.52112 (88)	0.19277 (76)	0.37349 (40)	3.56 (16)
C(55)	0.46195 (110)	0.06958 (94)	0.33770 (50)	5.59 (22)
C(61)	1.00233 (112)	0.61773 (94)	0.29338 (50)	5.76 (22)
C(62)	0.86530 (95)	0.61997 (81)	0.33394 (42)	4.10 (18)
C(63)	0.86630 (102)	0.72315 (86)	0.37455 (46)	4.75 (19)
C(64)	0.74864 (96)	0.73689 (80)	0.41319 (42)	3.96 (17)
C(65)	0.76362 (114)	0.85514 (98)	0.45304 (52)	5.94 (23)
C(11) H(1)	0.501	0.418	−0.064	
H(2)	0.359	0.351	−0.127	
H(3)	0.343	0.495	−0.086	
C(13) H(1)	0.103	0.258	−0.090	
C(15) H(1)	−0.126	0.143	−0.067	
H(2)	−0.146	0.035	0.009	
H(3)	−0.186	0.195	0.010	
C(21) H(1)	0.730	0.426	0.202	
H(2)	0.757	0.294	0.262	
H(3)	0.846	0.315	0.181	
C(23) H(1)	0.738	0.115	0.138	
C(25) H(1)	0.455	−0.159	0.100	
H(2)	0.552	−0.064	0.031	
H(3)	0.653	−0.092	0.110	
C(31) H(1)	0.107	−0.093	0.204	
H(2)	−0.075	−0.091	0.237	
H(3)	−0.021	−0.012	0.157	
C(33) H(1)	−0.077	0.051	0.320	
C(35) H(1)	0.039	0.263	0.442	
H(2)	−0.065	0.350	0.380	
H(3)	−0.128	0.179	0.398	
C(41) H(1)	0.597	0.750	0.270	
H(2)	0.443	0.819	0.232	
H(3)	0.437	0.752	0.319	
C(43) H(1)	0.275	0.705	0.163	
C(45) H(1)	0.208	0.559	0.044	
H(2)	0.069	0.425	0.074	
H(3)	0.060	0.586	0.094	

Table II (*Continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	$B \times 10^4$
C(51) H(1)	0.854	0.256	0.540	
H(2)	0.722	0.321	0.585	
H(3)	0.682	0.154	0.566	
C(53) H(1)	0.592	0.084	0.460	
C(55) H(1)	0.531	0.065	0.294	
H(2)	0.467	−0.014	0.374	
H(3)	0.344	0.068	0.319	
C(61) H(1)	1.088	0.579	0.327	
H(2)	0.968	0.555	0.250	
H(3)	1.051	0.716	0.273	
C(63) H(1)	0.970	0.798	0.375	
C(65) H(1)	0.650	0.859	0.463	
H(2)	0.835	0.850	0.502	
H(3)	0.815	0.944	0.423	
O(1) H(1)	0.385	0.389	0.449	
H(2)	0.266	0.417	0.391	

b. Anisotropic Temperature Factors for the Cobalt Atoms and O(1)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{12}
Co(1)	0.01274 (23)	0.00918 (16)	0.00205 (4)	0.00152 (14)	0.00048 (8)	−0.00111 (6)
Co(2)	0.01231 (21)	0.00691 (14)	0.00193 (4)	0.00099 (13)	0.00020 (7)	−0.00076 (6)
Co(3)	0.01321 (23)	0.00760 (15)	0.00207 (4)	−0.00004 (14)	0.00075 (8)	−0.00119 (6)
O(1)	0.01452 (101)	0.01474 (81)	0.00268 (20)	−0.00036 (70)	0.00076 (35)	−0.00224 (32)

[a] Reported standard deviations, in parentheses, occur in last decimal place listed.

Table III. Atomic Positional Coordinates in an Orthogonal System

Atom	*X* coord	*Y* coord	*Z* coord
Co(1)	2.43573	1.92799	2.34885
Co(2)	2.82006	3.18185	5.00863
Co(3)	4.64493	4.64831	7.31053
O(1)	2.77463	4.90756	8.13926
O(11)	3.21930	2.72851	0.67113
O(12)	0.67184	1.72652	1.47025
O(21)	4.08695	2.32614	3.51227
O(22)	3.17398	0.06268	2.05274
O(31)	1.69659	1.51869	4.37627
O(32)	1.32968	3.46770	6.37504
O(41)	3.59098	5.04384	5.37585
O(42)	1.95942	3.90200	3.31415
O(51)	5.38341	3.76909	9.03014
O(52)	4.09696	2.74980	6.63473
O(61)	6.40779	4.65445	6.37115
O(62)	5.10814	6.47100	8.10848
C(11)	3.44657	3.45015	−1.53649
C(12)	2.63012	2.81435	−0.43735
C(13)	1.33208	2.38630	−0.69957
C(14)	0.44490	1.93035	0.23475
C(15)	−0.99500	1.62923	−0.19871
C(21)	6.39929	2.40020	4.03086
C(22)	5.21889	1.71632	3.40454
C(23)	5.39073	0.49663	2.76770
C(24)	4.37040	−0.27608	2.18989
C(25)	4.74391	−1.64067	1.68610
C(31)	−0.02139	−0.08091	4.05405
C(32)	0.56849	1.11159	4.78596
C(33)	−0.09352	1.65132	5.87613
C(34)	0.27280	2.79148	6.56908
C(35)	−0.64689	3.33184	7.65360
C(41)	3.93921	7.37373	5.22955
C(42)	3.29608	6.10565	4.73141
C(43)	2.48421	6.18929	3.59312
C(44)	1.89422	5.10605	2.93017
C(45)	1.11760	5.36497	1.67967
C(51)	5.96469	2.14419	10.65936
C(52)	5.34085	2.55064	9.32158
C(53)	4.79799	1.50800	8.53668
C(54)	4.24888	1.64672	7.27605
C(55)	3.75979	0.39950	6.57882
C(61)	8.59972	5.16465	5.71541
C(62)	7.34292	5.48991	6.50557
C(63)	7.31096	6.63605	7.29670
C(64)	6.22799	7.04560	8.04946
C(65)	6.32085	8.32497	8.82578

Table IV. Matrix for Conversion from Triclinic to Orthogonal Coordinate System

8.87695	−1.77669	0.00000
0.00000	10.56000	0.00000
−1.00578	1.43254	19.48153

ture. By a process of elimination, one seems to be left with the suggestion of Morosin,[27] that the elongation of the Co–OH_2 distances in other compounds results from crystal packing forces.

For $[Co(AcAc)_2]_3H_2O$, the bond distances and angles involving cobalt and oxygen atoms are quite varied. The range of Co–O distances (0.267 A) is nearly as great as the entire range of M–O distances (0.345 A) spanned by the 13 mononuclear structures previously surveyed.[26] For a consideration of factors which may influence these bond distances, we classify Co–O bonds as follows. *Primary* bonds are those from oxygen to the Co atom about which the chelate ring containing the oxygen atom is closed; they are subdivided into *bridging* and *nonbridging primary* bonds. *Secondary* bonds, always bridging, are between a cobalt atom and one of the oxygen atoms of a ligand which chelates to a neighboring metal atom.

A survey of other structures shows that there is considerable variability from one molecule to another of the lengths of the three types of bonds. In the present case primary bond lengths scarcely depend on whether they are bridging (mean: 2.07 ± 0.03) or nonbridging (mean: 2.03 ± 0.02), but secondary bonds are substantially longer (mean: 2.19 ± 0.05). These are somewhat similar to the results (mean values in the same order: 2.09 ± 0.06, 2.03 ± 0.06, and 2.21 ± 0.06) for $[Co(AcAc)_2]_4$ and for $[Co(AcAc)_2]_2(H_2O)_2$ (mean values: 1.96 ± 0.07, 2.04 ± 0.05, and 2.16 ± 0.04). For $[Ni(AcAc)_2]_3$ the individual values for each type cover such large ranges that it is doubtful if the mean values are useful (2.11 ± 0.05, 2.01 ± 0.05, 2.14 ± 0.13). In the trinuclear $Co_3(CH_3COCHP(O)(OC_2H_5)_2)_6$ structure,[28]

---

(28) F. A. Cotton, R. Hugel, and R. Eiss, *Inorg. Chem.*, in press.

Table V. Bond Distances (A) and Angles (deg) within Acetylacetonato Ligands[a]

	a. Bond Distances		
Ring	C(n1)–C(n2), C(n4)–C(n5)	C(n2)–C(n3), C(n3)–C(n4)	C(n2)–O(n1), C(n4)–O(n2)
1	1.510 (13), 1.534 (12)	1.392 (11), 1.367 (11)	1.258 (10), 1.273 (9)
2	1.501 (12), 1.502 (12)	1.387 (11), 1.404 (12)	1.290 (9), 1.251 (10)
3	1.518 (13), 1.521 (13)	1.385 (12), 1.384 (12)	1.267 (10), 1.270 (10)
4	1.507 (12), 1.495 (13)	1.401 (11), 1.400 (11)	1.277 (9), 1.265 (10)
5	1.531 (13), 1.510 (12)	1.413 (11), 1.382 (11)	1.254 (10), 1.285 (9)
6	1.520 (13), 1.499 (13)	1.393 (12), 1.381 (12)	1.261 (10), 1.260 (10)
Average	1.512 (4)	1.391 (3)	1.268 (3)
Literature average	1.524 (3)	1.390 (3)	1.274 (3)

	b. Bond Angles			
Ring	C(n1)–C(n2)–C(n3), C(n3)–C(n4)–C(n5)	C(n1)–C(n2)–O(n1), O(n2)–C(n4)–C(n5)	C(n2)–C(n3)–C(n4)	O(n1)–C(n2)–C(n3), C(n3)–C(n4)–O(n2)
1	119.8 (7), 118.8 (7)	114.5 (7), 114.2 (7)	125.4 (8)	125.6 (7), 127.0 (7)
2	119.7 (7), 117.2 (7)	116.1 (7), 116.6 (7)	125.7 (8)	124.2 (7), 126.2 (8)
3	120.0 (8), 119.3 (8)	116.2 (7), 115.0 (7)	126.1 (8)	123.7 (8), 125.6 (8)
4	117.8 (7), 118.7 (7)	115.8 (7), 116.5 (7)	125.6 (7)	126.4 (7), 124.8 (7)
5	116.5 (7), 117.8 (7)	116.6 (7), 116.1 (7)	125.8 (7)	126.9 (7), 126.0 (7)
6	119.4 (8), 119.1 (8)	114.6 (7), 114.8 (7)	124.9 (8)	126.1 (8), 126.0 (8)
Average	118.7 (2)	115.6 (2)	125.6 (3)	125.7 (2)
Literature average	119.8 (3)	114.9 (2)	124.0 (3)	125.3 (3)

[a] Reported standard deviations, in parentheses, occur in the last decimal place listed.

Table VI. Co–O Bond Distances (A) and Angles (deg)[a]

		a. Bond Distances			
Co(1)–O(11)	2.017 (6)	Co(2)–O(31)	2.104 (5)	Co(3)–O(51)	2.068 (5)
Co(1)–O(12)	1.981 (5)	Co(2)–O(32)	2.042 (5)	Co(3)–O(52)	2.088 (5)
Co(1)–O(21)	2.059 (5)	Co(2)–O(41)	2.048 (5)	Co(3)–O(61)	1.998 (6)
Co(1)–O(22)	2.028 (6)	Co(2)–O(42)	2.032 (5)	Co(3)–O(62)	2.043 (5)
Co(1)–O(31)	2.196 (5)	Co(2)–O(21)	2.139 (5)	Co(3)–O(1)	2.062 (6)
Co(1)–O(42)	2.248 (5)	Co(2)–O(52)	2.112 (5)	Co(3)–O(41)	2.238 (5)
		b. Bond Angles			
Co(1)–O(21)–Co(2)	89.9 (2)	Co(2)–O(41)–Co(3)	99.9 (2)		
Co(1)–O(31)–Co(2)	87.2 (2)	Co(2)–O(52)–Co(3)	102.8 (2)		
Co(1)–O(42)–Co(2)	87.5 (2)				
O(11)–Co(1)–O(12)	91.0 (2)	O(31)–Co(2)–O(32)	85.5 (2)	O(51)–Co(3)–O(52)	88.6 (2)
O(21)–Co(1)–O(22)	88.2 (2)	O(41)–Co(2)–O(42)	89.2 (2)	O(61)–Co(3)–O(62)	88.9 (2)
O(11)–Co(1)–O(21)	94.7 (2)	O(32)–Co(2)–O(41)	91.6 (2)	O(1)–Co(3)–O(41)	84.2 (2)
O(11)–Co(1)–O(22)	95.9 (2)	O(32)–Co(2)–O(42)	101.5 (2)	O(1)–Co(3)–O(51)	92.5 (2)
O(11)–Co(1)–O(42)	95.2 (2)	O(32)–Co(2)–O(52)	87.4 (2)	O(1)–Co(3)–O(52)	90.4 (2)
O(12)–Co(1)–O(22)	99.5 (2)	O(21)–Co(2)–O(52)	95.7 (2)	O(1)–Co(3)–O(62)	86.4 (2)
O(12)–Co(1)–O(31)	95.2 (2)	O(21)–Co(2)–O(41)	105.4 (2)	O(41)–Co(3)–O(61)	90.5 (2)
O(12)–Co(1)–O(42)	95.2 (2)	O(31)–Co(2)–O(52)	113.1 (2)	O(41)–Co(3)–O(62)	106.7 (2)
O(22)–Co(1)–O(31)	94.9 (2)			O(51)–Co(3)–O(61)	94.4 (2)
				O(51)–Co(3)–O(62)	88.5 (2)
				O(52)–Co(3)–O(61)	94.7 (2)
O(21)–Co(1)–O(31)	77.5 (2)	O(21)–Co(2)–O(31)	77.9 (2)		
O(21)–Co(1)–O(42)	76.0 (2)	O(21)–Co(2)–O(42)	79.0 (2)		
O(31)–Co(1)–O(42)	72.3 (2)	O(31)–Co(2)–O(42)	78.7 (2)		
		O(41)–Co(2)–O(52)	79.7 (2)	O(41)–Co(3)–O(52)	76.0 (2)
O(11)–Co(1)–O(31)	166.5 (2)	O(21)–Co(2)–O(32)	163.0 (2)	O(1)–Co(3)–O(61)	171.5 (2)
O(12)–Co(1)–O(21)	169.9 (2)	O(31)–Co(2)–O(41)	166.7 (2)	O(41)–Co(3)–O(51)	164.2 (2)
O(22)–Co(1)–O(42)	161.3 (2)	O(42)–Co(2)–O(52)	166.0 (2)	O(52)–Co(3)–O(62)	175.5 (2)

[a] Reported standard deviations, in parentheses, occur in last decimal place listed.

bridging primary bonds and secondary bonds are of equal lengths. Finally in the trinuclear $[Zn(AcAc)_2]_3$ structure the secondary bonds (2.10 ± 0.04) are again no longer than the primary bridging bonds (2.10 ± 0.01), while the primary nonbridging bonds are shorter (2.00 ± 0.02). There is clearly no reigning regularity valid for all polynuclear molecules of this type. Presumably both inter- and intramolecular packing effects are significant in all cases.

The occurrence of hydrogen bonds in this structure, and in other hydrated $Co(AcAc)_2$ derivatives, is noteworthy. Bullen[12] reports intermolecular hydrogen bonding in $Co(AcAc)_2(H_2O)_2$ with O···O distances of ~2.90 for the hydrogen bonds. $[Co(AcAc)_2]_3H_2O$, however, contains only one intramolecular hydrogen bond and no intermolecular hydrogen bonds.

A computation of all O···O distances in the asymmetric unit shows that five are shorter than 2.80 A.

Table VII. Comparison of Bond Lengths (A)[a] in the Four $Co(AcAc)_2$ Structures

Bond in $[Co(AcAc)_2]_3H_2O$ Number	Length	Comparable bond in $[Co(AcAc)_2]_4$	$[Co(AcAc)_2]_2(H_2O)_2$	$Co(AcAc)_2(H_2O)_2$
Co(1)–O(11)	2.017 (6)	2.00 (2)		
Co(1)–O(12)	1.981 (5)	2.09 (3)		
Co(1)–O(22)	2.028 (6)	1.93 (3)		
Co(1)–O(21)	2.059 (5)	2.14 (3)		
Co(2)–O(31)	2.104 (5)	2.08 (3)		
Co(2)–O(32)	2.042 (5)	2.07 (3)		
Co(2)–O(42)	2.032 (5)	1.99 (3)		
Co(2)–O(41)	2.048 (5)	2.13 (2)		
Co(1)–O(31)	2.196 (5)	2.17 (3)		
Co(1)–O(42)	2.248 (5)	2.28 (3)		
Co(2)–O(21)	2.139 (5)	2.26 (3)		
Co(2)–O(52)	2.112 (5)	2.13 (3)		
Co(3)–O(62)	2.043 (5)		2.04 (3), 1.94 (3)	2.05 (1), 2.06 (1)
Co(3)–O(61)	1.998 (6)		2.14 (3), 2.08 (3)	
Co(3)–O(51)	2.068 (5)		1.98 (3), 2.06 (3)	
Co(3)–O(52)	2.088 (5)		2.03 (3), 1.89 (3)	
Co(3)–O(41)	2.238 (5)		2.20 (3), 2.12 (3)	
Co(3)–O(1)	2.062 (6)		2.19 (3), 2.20 (3)	2.23 (1)
Co(1)–Co(2)	2.966 (2)	3.19 (1)		
Co(2)–Co(3)	3.283 (2)	3.57 (1)	3.33 (1), 3.22 (1)	

[a] Reported standard deviations, in parentheses, occur in last decimal place listed.

Four of these, *viz.*, O(21)–O(42), O(31)–O(42), O(21)–O(31) and O(41)–O(52), ranging from 2.65 to 2.67 A, are between members of the two sets of bridging oxygen atoms. The fifth close contact is between O(1) (the water oxygen) and O(32), its nearest oxygen neighbor on Co(2), and has a distance of 2.67 A. Moreover, the difference Fourier map used to locate hydrogen atoms clearly showed a hydrogen atom lying approximately along the line between O(1) and O(32), about 0.9 A from O(1). It seems clear that there is an intramolecular hydrogen bond of fair strength between O(1) and O(32).

All intermolecular contacts between O(1) and other oxygen atoms were also examined. Of these only one, that to O(51) of the molecule related by a center of symmetry, was short enough, namely 2.795 A, to suggest the possibility of a hydrogen bond. However, the hydrogen atom, located from the difference Fourier map, lies very far off the O···O line; the O–H···O angle is about 90°. Consequently, no significant hydrogen bonding is to be assumed. Instead, the interaction here is best regarded as primarily a normal van der Waals contact, for which a distance of ~2.8 A would be expected.

In the course of examining the $[Co(AcAc)_2]_3H_2O$ structure for hydrogen bonds, the previously reported[13] absence of any hydrogen bonds in crystalline $[Co(AcAc)_2]_2(H_2O)_2$ was reconsidered. The intermolecular and nonbonded intramolecular contacts for this structure were recalculated and the previous ones found to be in error, for unknown reasons. It is now found that there are close intermolecular contacts between O_2 and R_2O_1 (2.80 A) and between O_1 and R_3O_1 (2.71 A). There are also close intramolecular contacts involving the water oxygen atoms between O_1 and R_2O_{2c} (2.72 A) and between O_2 and R_3O_{2c} (2.73 A). Presumably some of these contacts represent hydrogen bonds, but in the absence of any direct knowledge of hydrogen atom locations in this structure, neither further discussion nor more positive statements would be warranted.

All other intermolecular contacts (C···C and C···O) under 4.0 A were calculated, and none were abnormal.

The isotropic temperature factors for ligand atoms, listed in Table II, all seem reasonable and show consistency for corresponding atoms of different rings. As expected, the methyl carbon atoms have the greatest thermal amplitudes, and the carbonyl carbon atoms have the smallest.

Position of This Molecule in the Hydration Sequence. Now that the structures of all known molecules in the series from anhydrous cobalt(II) acetylacetonate, $[Co(AcAc)_2]_4$, through $[Co(AcAc)_2]_3H_2O$ and $[Co(AcAc)_2]_2(H_2O)_2$ to the most hydrated species, *trans*-$Co(AcAc)_2(H_2O)_2$, are known, it is worthwhile to comment on some of the systematic structural features which characterize this set of compounds. Before doing so, however, it is important to register clearly two *caveats*. First, there *may* be other intermediate hydrates, not as yet recognized, which might either complicate or further clarify the picture. Second, and perhaps more important, it must be clearly recognized that the structures found for the solid compounds, and indeed the compounds themselves, need not necessarily play a role in the reactions and equilibria which constitute the hydration sequence in solution. Thus, only the structural relations between the solid compounds are being *explicitly* discussed. Whatever information concerning the solution equilibria *may* be *implicit* in this set of structures is still a subject for investigation.

Bearing in mind that no actual reaction mechanisms are being postulated, we ask what is the simplest set of formal structural transformations which leads through the series of established structures. This question can be answered with the help of Figure 3. The first step, from $[Co(AcAc)_2]_4$ to $[Co(AcAc)_2]_3H_2O$, is most simply accomplished by removal of a terminal cobalt atom and its AcAc rings. The fragments must then (or in a manner concerted with the fragmentation of the $[Co(AcAc)_2]_4$ molecule) acquire a total of three H_2O ligands. There must be a rearrangement of the $Co(AcAc)_2$ fragment, either before or after its initial acquisition of H_2O ligands, in order to produce *trans*-$Co(AcAc)_2(H_2O)_2$, since the two AcAc rings are initially

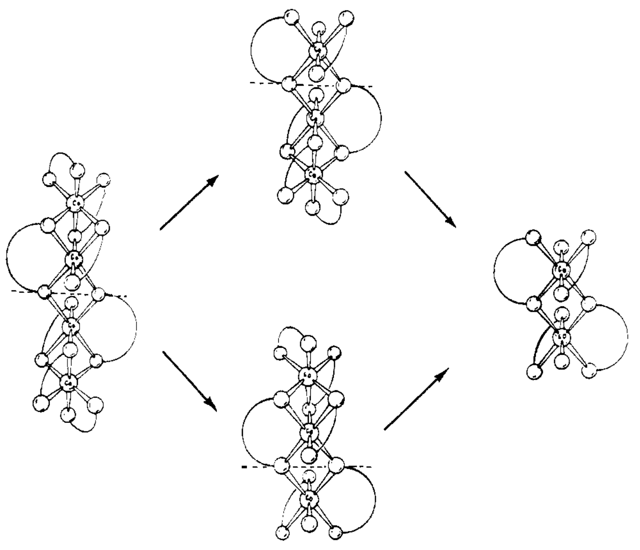

Figure 3. Schematic drawings showing what appears to be the simplest sequence of rearrangements in order to pass from the tetramer, $[Co(AcAc)_2]_4$ (left), through the enantiomorphic $[Co(AcAc)_2]_3H_2O$ structures (center) to the *meso*-$[Co(AcAc)_2]_2(H_2O)_2$ structure (right). Large open circles represent oxygen atoms and curved lines represent the chelate rings.

oriented so as to leave two *cis* positions open in the coordination octahedron.

Upon removal of a terminal $Co(AcAc)_2$ moiety from $[Co(AcAc)_2]_4$, there remains a fragment with chelate rings arranged exactly as are those in the $[Co(AcAc)_2]_3H_2O$ molecule. It is only necessary that one water molecule enter the position left vacant by the departure of the $Co(AcAc)_2$ moiety to achieve the $[Co(AcAc)_2]_3H_2O$ structure. It should be noted that the $[Co(AcAc)_2]_4$ molecule is a *meso* form and that a terminal $Co(AcAc)_2$ can be stripped so as to form either of two enantiomorphic $[Co(AcAc)_2]_3H_2O$ molecules with equal probability. The crystal of $[Co(AcAc)_2]_3H_2O$ does, in fact, contain an equimolar mixture of the two enantimorphs, related in pairs by the crystallographic center of symmetry in the space group $P\bar{1}$.

In passing from $[Co(AcAc)_2]_3H_2O$ to $[Co(AcAc)_2]_2(H_2O)_2$, we return to a *meso* structure. As shown on the right side of Figure 3, this structure is equally accessible from either enantiomorph of $[Co(AcAc)_2]_3(H_2O)$ by removal of that terminal $Co(AcAc)_2$ moiety which shares an octahedron face with the octahedron about the center cobalt atom. As before, this leaves one vacancy in the coordination octahedron of the central cobalt atom. When this vacancy is filled by a water molecule, the $[Co(AcAc)_2]_2(H_2O)_2$ structure is obtained. It may be noted that there is no simple way to pass from the $[Co(AcAc)_2]_3H_2O$ structure to the $[Co(AcAc)_2]_2(H_2O)_2$ structure by severing the $Co(AcAc)_2H_2O$ group from the other end. The dinuclear fragment which then remains must undergo extensive rearrangement, equivalent at least to inversion of the configuration at one cobalt atom, in order to achieve the *meso* structure of $[Co(AcAc)_2]_2(H_2O)_2$.

Finally, the conversion of $[Co(AcAc)_2]_2(H_2O)_2$ into *trans*-$Co(AcAc)_2(H_2O)_2$ must involve at some stage a *cis* → *trans* isomerization. There is no basis at present for speculation on mechanistic details.

Acknowledgments. We thank Mr. B. M. Foxman for helpful advice concerning the least-squares program for the IBM 360 system.