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Crystal Structure of Tetrameric Cobalt(II) Acetylacetonate[1a]

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As indicated previously,[2] a structural analysis of $Co^{II}(AA)_2$ has been performed by X-ray crystal techniques. The triclinic unit cell contains one centrosymmetric tetramer. Octahedral coordination is achieved by sharing of oxygen atoms between cobalt atoms. The terminal cobalt atom is joined to the center pair by sharing a common octahedral face with three bridging oxygen atoms. The central two cobalt atoms are joined by sharing an edge with only two bridging oxygen atoms. The bond lengths and angles found are those expected for such a structure.

Introduction

Since the original suggestion that bis(acetylacetonato)cobalt(II) was not tetrahedral but rather square-planar,[3] several problems have remained to the present. The finding that $Ni(AA)_2$ is trimeric[4a,b] and that the nickel atoms are octahedrally coordinated led to the suggestion that perhaps $Co(AA)_2$ was also an octahedrally complexed polymer. The spectral measurements as well as magnetic data all led to this conclusion[5]; however, it was not possible to postulate the actual structure of the solid compound. In order to determine the structure, a single crystal X-ray analysis was undertaken. We report here the results of that determination.

Experimental

Preparation of Crystals.—Crystals of bis(acetylacetonato)-cobalt(II) are quite difficult to produce in the laboratory. The compound is extremely soluble in nonpolar, noncoordinating solvents such as benzene and toluene; the hydrated forms are rather insoluble in these same solvents. This makes the crystallization of the anhydrous substance from solution a difficult task. In general, material deposited from solution is of several types: two crystalline modifications of $Co(AA)_2\cdot 2H_2O$, $[Co(AA)_2\cdot H_2O]_2$, the structure of which has been determined by single crystal X-ray methods,[6] $[Co(AA)_2]_{2-3}\cdot H_2O$, which is currently under study, and $[Co(AA)_2]_4$. The anhydrous compound can be obtained in crystalline form by extended heating *in vacuo* of the dihydrate according to Cotton and Holm.[3] However, the crystalline material thus obtained is unsuitable for single crystal X-ray work. Soderberg[7] suggests that the material may be sublimed at 120° under vacuum. Attempts were made in the course of a year to grow single crystals by sublimation. The substance sublimes readily to give a material which, in general, appears crystalline. Appreciable decomposition accompanies the sublimation process, and a light violet residue remains. The extent of decomposition seems to increase with increasing temperature, and therefore sublimations were run at approximately 100°.

The crystals obtained by sublimation are exceedingly fragile and many were fractured as they were removed from the cold probe. Several of the crystals which appeared single when viewed through a microscope were mounted in capillaries and studied with the precession camera. After more than 50 crystals had been so examined, no single crystal was obtained; however, one crystal which was twinned, but not seriously cracked, was reserved. All of the next 15 crystals examined were fractured and twinned. Since in the course of the investigation all of the crystals had appeared twinned, we decided to collect intensity data on the previously reserved crystal.

Preliminary Investigation: Unit Cell and Space Group.—All cell constants and intensity data were obtained from this crystal. The similarity of the photographs of the numerous cracked crystals to the photographs used guarantees that the twinned crystal was of the form generally present.

The unit cell is triclinic, which makes it difficult to align and more difficult to index the twinned lattices. The reduced primitive cell dimensions[8] are $a = 8.516 \pm 0.012$, $b = 10.243 \pm 0.017$, $c = 13.781 \pm 0.020$ Å., $\alpha = 93.5 \pm 0.3°$, $\beta = 90.4 \pm 0.3°$, $\gamma = 98.7 \pm 0.3°$, where the standard deviations are determined from the variation within the measurements. The volume of the cell is 1186 Å.^{3}. This, together with the measured density of 1.45 g. cm.$^{-3}$, gives a calculated value of 4.1 $Co(AA)_2$ units per cell. Although this calculation is somewhat inexact, there can be no doubt that the final structure accounts for all the atoms in the cell.

Data Measurement: Consideration of Twinning.—The measurement of intensities proved a large problem since the triclinic cell and the twinned lattices gave an extremely complex set of spots on the film. The twinning, which was through the (1,0,0) plane with a twinning angle of 17° 10′, was such that the series $h,0,l$; $h,1,l$; $h,2,l$; $h,3,l$ could be recorded for each lattice separately with these exceptions: The set in the principal zone of twinning $(0,k,l)$ was the superposed image of the two lattices, and thus the lines $0,0,l$; $0,1,l$; $0,2,l$; $0,3,l$ were placed on a separate scale. Also, the layer screen, which is used to remove other levels and was here used to blank out the second lattice, passed

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the reflections $\pm3',1',l'$ onto the $h,0,l$ photograph, and in general $\pm3',n+1',\ l'$ appeared on any h,n,l level and made it difficult to read the $3,n,l$ spots. In some cases, the overlapping spot was so intense that no estimate of the first spot could be made.

The set $h,k,0$; $h,k,1$; $h,k,2$; $h,k,3$; $h,k,4$ was also recorded. In this case, the h',k',n', level fell onto the same record as the h,k,n level with the two lattices separated by the twinning angle $m',k',n';\ \begin{Bmatrix}0,k',n'\\0,k,n\end{Bmatrix};\ m,k,n$, which was equal to 17° 10′. There was no difficulty in reading the spots with the following two exceptions: The $0,k,n$, and $0,k',n'$ spots superposed and were given a separate scale factor; the $\pm3,k,n$ and $\pm3',k+1',n'$ spots overlapped and were sometimes impossible to read.

Normally, intensity data for a cobalt compound would be recorded with Mo Kα radiation to ensure low absorption. Unfortunately, in this instance, it was no longer possible to separate the two lattices with the screens available using the shorter wave length X-rays. Copper Kα radiation was used, although absorption became a problem, as no other more suitable target material was available at the time. An "intensity wedge" was prepared from the crystal in the usual manner by exposing the 1,1,0 reflection on a masked film for measured periods of time. The intensities of 880 independent reflections were estimated visually from the precession photographs listed above. At least four timed exposures (45 min., 3 hr., 12 hr., 48 hr.) were taken of each level to allow the detection of a wide range of intensities. Most of the reflections were read on two or more films, and an average was taken to obtain one set of data per level.

Since there is a considerable amount of data which is common to two different sets of films, *i.e.*, 2,2,2 occurs on $h,k,2$ and also on $h,2,l$, this provides a method of scaling the sets of films. The program XCIT[9] is designed to perform this task. Each measured intensity is multiplied by the reciprocal Lorentz and polarization corrections, or if absorption corrections are needed by $1/LpA$. The corrections are those of Burbank and Knox.[10] A least-squares procedure is used to find film-to-film scale factors for the corrected data. An over-all temperature factor is calculated by the method of Wilson,[11] and the final scaled set of data is punched onto cards for structure calculations.

The absorption corrections are made on the basis of the cylindrical approximation. The crystal was of dimensions $0.5 \times 0.2 \times 0.07$ mm. A mean radius, R, for the cylinder was estimated as 0.11 mm.; this together with the value of $\mu = 112$ cm.$^{-1}$ yields μR for the cylinder of 1.3. The data were first run with the original XCIT without absorption corrections to produce input for a Patterson synthesis.

Structure Determination.—Since there were only four cobalt atoms per cell, the Patterson function[12] was fairly featureless. The seven most intense peaks were in the range 315–218 on an arbitrary scale. With this small number of peaks it was feasible to try all possible vector combinations. None of these gave completely satisfactory results with either the two positions of $P\bar{1}$ or the four positions of P1. However, the two $P\bar{1}$ positions 0.125, 0.775, 0.742 and 0.037, 0.039, 0.100 gave by far the most promising fit to the vector map. The four vector peaks arising from these positions were second, third, fifth, and eighth in order of magnitude on the map. The last was only one-half the height of the most prominent peak. This sort of difficulty in the solution of the Patterson was not considered alarming since the cobalt atoms represent only 20.3% of the electrons.

Signs of the structure factors[13] were estimated from the contributions of the cobalt atoms, and a Fourier synthesis was then computed. The Fourier map showed reasonable positions for oxygen atoms, octahedrally surrounding the cobalt atoms. It was impossible to determine the location of the carbon atoms.

A second Fourier synthesis was computed using signs assigned on the basis of the cobalt and oxygen positions. All of the atoms, with the exception of hydrogen atoms, were found on the second electron density map. Some of the assignments were rather tentative, but all made good sense chemically and gave approximately the expected bond lengths.[14] A structure factor calculation gave a residual of 0.35 once the scale factor was adjusted, where the residual, R, is the usual discrepancy factor $R = \Sigma|F_o - F_c/\Sigma|F_o|$ and the weighted residual $= \sqrt{\Sigma w(F_o - F_c)^2}/\sqrt{\Sigma w F_o{}^2}$. At this stage in the structure determination, the set of data which had been corrected for absorption was introduced. Two cycles of refinement on the cobalt atoms, followed by one cycle in which all positional parameters were varied, yielded a residual of 0.30. Four cycles of refinement of scale factors and all positional parameters reduced the residual to 0.25. At this stage the movements of the atoms were about equal to the standard deviations, which were large. An attempt to refine the temperature factors met with disaster as the cobalt factors reached 5 Å.^{2}, and those for six of the light atoms became negative.

It seemed that the unit weighting which had been used until this point might be responsible for the peculiar values of the temperature factors. A weighting scheme suggested by Cruickshank[15] was used and several cycles of positional adjustment were run. There was little change in the parameters, so adjustment of the temperature factors was tried. Again, nonsensical results ensued. At this point, it was decided to make some correction for anomalous dispersion. The corrections for the Co with Cu Kα radiation[16] are -2.2 electrons for the real part of the scattering curve and 3.9 electrons for the imaginary part. The real part of the correction was subtracted from the cobalt scattering curve; the imaginary part was neglected. The scattering curve used for cobalt was that for the dipositive valence state as calculated by Watson and Freeman.[17] Those for neutral carbon and oxygen were by Hoerni and Ibers.[18] Again the positions were adjusted and the residual was lowered to 0.20. A cycle of adjustment of the temperature parameters followed by one of positional and scale factor adjustment led to an R value of 0.17 and a weighted residual of 0.14. One cycle of adjustment of all parameters gave 0.125 as the weighted discrepancy factor. A second cycle lowered the value to 0.120 and gave 0.154 for the unweighted value. As this point, all changes in parameters were less than one standard deviation. A Fourier difference synthesis was computed. No peaks with densities greater than 1 electron/Å.^{3} were observed, indicating that no unaccounted atoms other than hydrogen atoms were present. It was possible to ascribe several of the peaks to hydrogen atoms with reasonable hydrogen–carbon bond lengths resulting. However, there was considerable noise of the same magnitude as the peaks and some of the hydrogen atoms could not be found. It seemed that almost all the useful information had been obtained, and although further refinement with anisotropic temperature parameters might yield a lower residual, the parameters would in all probability be meaningless and would only serve to account for the uncorrected part of the absorption and other systematic errors known to be present.

The positional and temperature parameters from the last cycle are listed in Table I, as are the standard deviations estimated in the last cycle by the Prewitt program. The orthogonal coordinates of all atoms are listed in Table II. The values of $|F_o|$ and F_c for each reflection in the last cycle have been listed in Table III.

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TABLE I
POSITIONAL AND TEMPERATURE PARAMETERS[a]

Atom	x	s.d. x	y	s.d. y	z	s.d. z	B
Co_1	0.626	1	0.773	1	0.236	1	3.8 ± 0.1
Co_2	0.469	1	0.607	1	0.407	1	4.0 ± 0.1
R_1O_1	0.842	3	0.872	2	0.226	2	5.3 ± 0.8
R_1O_2	0.524	3	0.928	2	0.186	1	3.5 ± 0.7
R_1C_1	0.069	7	0.044	5	0.177	4	9.5 ± 1.7
R_1C_2	0.884	6	0.980	5	0.186	3	7.1 ± 1.5
R_1C_3	0.769	5	0.069	4	0.139	2	4.2 ± 1.1
R_1C_4	0.604	5	0.022	3	0.143	2	2.6 ± 1.0
R_1C_5	0.513	4	0.130	3	0.096	2	4.0 ± 1.1
R_2O_1	0.653	3	0.709	3	0.102	2	5.8 ± 0.8
R_2O_2	0.672	3	0.603	2	0.304	2	4.8 ± 0.8
R_2C_1	0.745	5	0.599	4	0.970	3	7.0 ± 1.3
R_2C_2	0.710	6	0.610	5	0.066	4	8.3 ± 1.6
R_2C_3	0.762	5	0.512	4	0.144	3	5.8 ± 1.3
R_2C_4	0.734	4	0.526	4	0.256	2	2.5 ± 1.0
R_2C_5	0.783	5	0.396	4	0.304	3	4.9 ± 1.2
R_3O_1	0.399	3	0.667	2	0.274	1	3.2 ± 0.6
R_3O_2	0.255	2	0.646	2	0.460	1	2.9 ± 0.6
R_3C_1	0.238	5	0.719	3	0.136	3	4.4 ± 1.2
R_3C_2	0.252	6	0.681	4	0.247	3	4.2 ± 1.2
R_3C_3	0.134	7	0.695	5	0.300	4	8.1 ± 1.6
R_3C_4	0.128	5	0.666	4	0.390	4	6.1 ± 1.4
R_3C_5	0.996	4	0.692	3	0.470	2	4.4 ± 1.2
R_4O_1	0.591	4	0.784	3	0.400	2	7.0 ± 0.9
R_4O_2	0.571	3	0.591	2	0.546	1	3.9 ± 0.7
R_4C_1	0.710	5	0.011	4	0.434	3	7.4 ± 1.4
R_4C_2	0.648	5	0.867	4	0.451	3	4.0 ± 1.2
R_4C_3	0.653	4	0.807	4	0.549	3	3.9 ± 1.6
R_4C_4	0.624	4	0.688	4	0.598	3	2.5 ± 1.0
R_4C_5	0.686	5	0.651	4	0.694	3	4.9 ± 1.2

[a] s.d. represents standard deviation × 10^3.

TABLE II
ORTHOGONAL COORDINATES OF ALL ATOMS[a] $[Co(AA)_2]_4$

Atom	x coord.	y coord.	z coord.
Co_1	5.272	7.002	3.235
Co_2	3.899	5.322	5.574
R_1O_1	7.116	7.758	3.098
R_1O_2	4.417	8.785	2.554
R_1C_1	9.046	9.303	2.423
R_1C_2	7.478	8.857	2.563
R_1C_3	6.515	9.980	1.906
R_1C_4	5.118	9.701	1.979
R_1C_5	4.341	10.982	1.328
R_2O_1	5.529	6.431	1.407
R_2O_2	5.654	5.113	4.169
R_2C_1	6.360	5.282	−0.404
R_2C_2	6.029	5.361	0.909
R_2C_3	6.451	4.206	1.975
R_2C_4	6.186	4.283	3.513
R_2C_5	6.592	2.824	4.157
R_3O_1	3.339	6.162	3.757
R_3O_2	2.065	5.955	6.302
R_3C_1	1.997	7.036	1.882
R_3C_2	2.103	6.511	3.386
R_3C_3	1.079	6.770	4.105
R_3C_4	0.996	6.386	5.337
R_3C_5	−0.143	6.753	6.434
R_4O_1	4.939	7.022	5.493
R_4O_2	4.740	4.906	7.488
R_4C_1	5.941	9.185	5.934
R_4C_2	5.424	7.771	6.188
R_4C_3	5.429	7.033	7.515
R_4C_4	5.174	5.802	8.192
R_4C_5	5.665	5.230	9.494
R_4O_2C	3.531	3.264	6.194
Co_2C	4.372	2.847	8.108

[a] The orthogonal Y axis is taken coincident to the cell y axis, and the orthogonal Z axis is chosen normal to the xy plane of the cell.

Discussion of Structure

From the parameters in Table II, the intermolecular distances and bond angles were calculated using MGEOM, molecular geometry program for the IBM 709/7090/7094 computer by Dr. J. S. Wood[19] of this group. The bond lengths and angles are listed in Tables IV and V, respectively; they refer to the labels used in Figure 1.

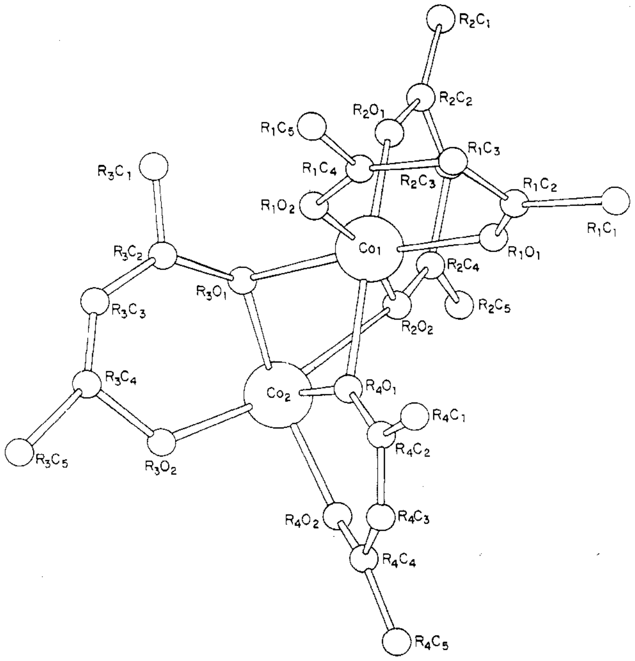

Figure 1.—A projection of the asymmetric unit of tetrameric cobalt acetylacetonate onto the (0,1,0) plane.

Temperature Factors.—Several comments are in order concerning the final values for the isotropic temperature factors. Most important, since the absorption corrections were rather approximate (although better than no corrections or those of a spherical approximation),[20] the temperature factors undoubtedly were partially adjusted to account for uncorrected absorption.

The program, XCIT, utilizes a Wilson[11] plot of the observed intensities to put the data approximately on an absolute scale and to derive the average temperature factor for the structure. The value of 4.34 Å.^{2} was obtained for the average temperature factor, which is in good agreement with the average value of 3.96 ± 0.19 Å.^{2} obtained in the least-squares procedure for the cobalt atoms. Also the ready sublimation of the compound is in agreement with the rather high values of B obtained.

The large standard deviations estimated for the light atom temperature factors indicate that they are of

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Table III

Observed and Calculated Structure Factors

H	K	L	FOBS	FCAL
1	0	0	147.93	138.40
2	0	0	34.09	-26.95
3	0	0	18.56	17.58
4	0	0	12.64	-6.35
5	0	0	7.52	5.29
0	1	0	51.28	-52.82
0	1	0	51.28	-52.82
1	1	0	9.72	-13.07
2	1	0	109.48	110.12
3	1	0	33.55	-39.30
4	1	0	57.11	-61.56
5	1	0	58.59	53.35
-1	1	0	87.30	79.63
-2	1	0	71.93	-66.17
-3	1	0	50.73	42.94
-4	1	0	9.76	-5.35
-5	1	0	42.25	-44.67
0	2	0	34.78	-33.60
1	2	0	5.86	-3.94
2	2	0	8.90	-9.92
3	2	0	73.09	-76.56
4	2	0	71.71	78.20
5	2	0	34.75	-35.46
-1	2	0	67.05	56.59
-2	2	0	15.22	19.07
-3	2	0	12.34	-12.97
-4	2	0	17.08	15.29
-5	2	0	25.24	-18.76
0	3	0	73.91	75.80
1	3	0	14.86	6.67
2	3	0	46.81	-46.11
3	3	0	18.20	27.15
4	3	0	8.92	-2.01
-1	3	0	7.22	-8.02
-2	3	0	49.15	50.24
-3	3	0	32.87	-33.50
-4	3	0	36.45	34.33
-5	3	0	8.72	-5.11
0	4	0	28.33	-32.14
1	4	0	62.91	72.39
2	4	0	32.25	-38.52
3	4	0	31.37	33.62
-1	4	0	25.32	-30.27
-2	4	0	7.30	5.98
-3	4	0	50.07	50.79
-4	4	0	39.55	-37.09
0	5	0	37.42	35.94
1	5	0	60.51	-67.39
2	5	0	36.33	37.55
3	5	0	17.56	-16.08
-1	5	0	32.63	-27.36
-2	5	0	8.22	0.33
-3	5	0	23.70	25.23
-4	5	0	14.84	-16.00
0	6	0	14.11	-13.69
1	6	0	37.93	24.51
-1	6	0	33.31	33.51
-2	6	0	30.77	-32.52
-3	6	0	19.02	22.95
0	0	1	63.62	-67.27
1	0	1	106.42	102.30
2	0	1	78.93	-77.71
3	0	1	7.86	1.07
4	0	1	7.58	5.21
5	0	1	23.28	-26.66
-1	0	1	17.58	-12.88
-2	0	1	5.24	0.56
-3	0	1	6.86	-3.89
-4	0	1	8.96	-6.78
-5	0	1	34.71	30.36
1	1	1	55.61	-60.18
1	1	-1	17.74	-17.24
1	-1	1	52.31	49.39
2	1	1	20.46	16.84
2	1	-1	55.77	45.20
2	-1	1	63.33	64.65
3	1	1	16.74	20.64
3	1	-1	77.71	-73.49
3	-1	1	18.18	-20.39
4	1	1	42.39	-40.99
4	1	-1	76.45	71.54
4	-1	1	7.54	11.41
5	1	1	8.06	0.55
5	1	-1	28.49	-28.83
5	-1	1	9.48	-1.61
-1	1	1	97.54	-95.18
-2	1	1	99.70	92.72
-3	1	1	76.89	-75.36
-4	1	1	12.60	6.57
-5	1	1	17.90	17.65
0	2	1	10.08	-4.76
0	-2	1	63.62	62.75
1	2	1	85.84	97.09
1	2	-1	23.32	15.87
1	-2	1	15.20	-17.61
2	2	1	18.38	18.27
2	2	-1	41.57	-39.84
2	-2	1	71.45	61.04
3	2	1	42.37	-35.20
3	2	-1	35.27	31.93
3	-2	1	28.73	-29.26
4	2	1	35.53	-33.21
4	2	-1	9.16	8.99
4	-2	1	27.10	19.60
5	2	1	38.49	51.10
5	2	-1	10.02	-8.91
5	-2	1	7.92	1.15
-1	2	1	60.75	-47.84
-2	2	1	25.14	-24.78
-3	2	1	60.07	51.50
-4	2	1	16.80	-15.24
-5	2	1	7.86	-14.46
0	3	1	51.68	-49.66
0	-3	1	3.04	-5.17
1	3	1	62.19	-60.52
1	3	-1	35.57	34.73
1	-3	1	31.09	-34.31
2	3	1	20.66	22.05
2	3	-1	41.97	-44.70
2	-3	1	17.54	-12.79
3	3	1	26.50	-21.31
3	3	-1	48.61	57.53
3	-3	1	36.01	35.92
4	3	1	28.07	25.51
4	3	-1	40.33	-44.64
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0	1	6	39.49	40.97
0	-1	6	23.71	16.70
1	1	6	19.40	-15.32
1	1	-6	20.72	19.61
1	-1	6	29.09	-24.48
2	1	6	17.02	24.19
2	1	-6	24.46	-22.68
2	-1	6	43.53	46.59
3	1	6	12.88	-18.30
3	1	-6	10.76	4.77
3	-1	6	19.70	-14.12
4	1	6	15.70	6.74
4	1	-6	31.21	27.66
4	-1	6	13.22	11.88
-1	1	6	70.25	-68.32
-2	1	6	49.21	53.93
-3	1	6	40.63	-39.43
-4	1	6	11.12	-3.18
0	2	6	68.86	68.18
0	-2	6	15.05	17.28
1	2	6	27.44	-33.21
1	2	-6	23.96	23.74
1	-2	6	80.93	-74.53
2	2	6	12.12	-10.55
2	2	-6	13.88	-16.56
2	-2	6	48.55	50.91
3	2	6	38.07	39.70
3	2	-6	12.78	19.75
3	-2	6	8.80	-3.70
4	2	6	40.73	-38.24
4	2	-6	41.81	-38.72
4	-2	6	9.26	-15.16
5	-2	6	6.96	7.20
-1	2	6	10.80	-9.59
-2	2	6	21.56	-16.66
-3	2	6	13.66	10.96
-4	2	6	18.78	-20.96
-5	2	6	10.62	18.00
0	3	6	11.49	21.44
0	-3	6	9.46	-8.52
1	3	6	12.94	-16.92
1	3	-6	8.34	-10.17
1	-3	6	32.69	31.66
2	3	6	52.13	46.66
2	3	-6	9.56	11.10
2	-3	6	51.51	-47.27
3	3	6	55.13	-52.93
3	3	-6	10.97	14.86
3	-3	6	20.64	54.51
4	3	6	11.90	13.27
4	3	-6	11.96	-16.14
4	-3	6	42.57	-32.68
5	-3	6	24.82	17.31
-1	3	6	32.55	24.63
-2	3	6	26.82	-29.27
-3	3	6	16.00	23.00
-4	3	6	11.42	-1.35
-5	3	6	11.86	-8.44
0	0	7	37.94	39.09
1	0	7	30.11	-43.96
2	0	7	9.14	13.14
3	0	7	5.62	-3.76
-1	0	7	6.04	-1.18
-2	0	7	15.74	-23.23
-3	0	7	6.06	-6.12
0	1	7	72.86	-71.26
0	-1	7	17.97	19.07
1	1	7	59.53	64.61
1	1	-7	9.96	1.47
1	-1	7	39.91	-37.94
2	1	7	14.96	-15.84
2	1	-7	19.26	-16.66
2	-1	7	10.38	0.11
3	1	7	10.90	7.32
3	1	-7	43.29	40.42
3	-1	7	10.86	-1.02
4	1	7	10.30	6.38
4	1	-7	37.05	-40.33
4	-1	7	10.78	-5.70
-1	1	7	22.34	25.69
-2	1	7	12.30	-8.05
-3	1	7	10.82	13.75
-4	1	7	16.68	16.85
0	2	7	43.28	44.22
0	-2	7	11.85	-6.56
1	2	7	23.46	-20.23
1	2	-7	8.28	4.56
1	-2	7	37.37	33.04
2	2	7	8.86	-0.90
2	2	-7	8.74	4.53
2	-2	7	54.03	-56.84
3	2	7	8.74	-5.05
3	2	-7	9.02	11.06
3	-2	7	68.35	59.61
4	2	-7	7.46	-12.93
4	-2	7	20.96	-27.67
-1	2	7	47.41	-59.97
-2	2	7	32.75	37.77
-3	2	7	24.58	-30.95
-4	2	7	8.26	9.49
0	3	7	33.24	33.21
0	-3	7	20.91	18.37
1	3	7	9.68	-13.33
1	3	-7	23.38	-24.27
1	-3	7	15.42	13.84
2	3	7	12.80	-8.62
2	3	-7	31.51	37.26
2	-3	7	9.84	-5.77
3	3	7	33.57	30.50
3	3	-7	29.97	-40.70
3	-3	7	15.24	-9.46
4	3	7	36.27	-38.42
-1	3	7	27.34	-36.35
-2	3	7	9.76	-8.18
-3	3	7	10.94	8.42
-4	3	7	11.62	-7.50
0	0	8	5.34	3.59
1	0	8	14.84	-18.17
2	0	8	10.62	8.53
-1	0	8	9.36	12.29
-2	0	8	20.04	-23.67
0	1	8	6.16	-4.00
0	-1	8	12.76	3.75
1	1	8	14.38	-19.47
1	1	-8	10.42	8.30
1	-1	8	16.14	10.36
2	1	8	13.64	15.47
2	1	-8	10.36	-8.94
2	-1	8	42.31	-43.79
3	1	8	22.52	-18.60
3	1	-8	11.62	6.63
3	-1	8	47.01	50.22
4	-1	8	28.41	-27.51
-1	1	8	14.44	-16.14
-2	1	8	22.32	22.81
-3	1	8	17.08	-23.64
-4	1	8	9.90	11.29
0	2	8	40.56	-48.70
0	-2	8	5.87	-2.44
1	2	8	46.33	47.43
1	2	-8	32.33	-32.38
1	-2	8	25.34	19.97
2	2	8	23.64	-31.54
2	2	-8	33.45	37.88
2	-2	8	8.74	-10.14
3	2	8	5.56	13.15
3	2	-8	38.73	-35.40
3	-2	8	22.66	-13.41
-1	2	8	21.92	18.19
-2	2	8	17.54	-15.69
-3	2	8	8.28	6.35
0	3	8	7.59	9.89
0	-3	8	37.72	-37.74
1	3	8	18.26	-15.33
1	3	-8	43.29	48.23
1	-3	8	15.50	13.95
2	3	8	11.20	10.55
2	3	-8	42.43	-47.69
3	3	8	10.84	7.34
3	3	-8	13.62	26.72
-1	3	8	35.41	-38.48
-2	3	8	38.21	44.28
-3	3	8	11.22	-12.43
-4	3	8	10.72	-6.06
0	3	9	48.49	-47.30
1	3	9	24.72	25.46
-1	3	9	44.69	39.38

TABLE IV

$[Co(AA)_2]_4$ BOND LENGTHS (Å.)

Primary cobalt keto-oxygen $Co{-}O_K(1)$

Co_1	R_1O_1	2.00 ± 0.02
Co_1	R_1O_2	2.09 ± 0.03
Co_1	R_2O_1	1.93 ± 0.03
Co_1	R_2O_2[a]	2.14 ± 0.03
Co_2	R_3O_1	2.08 ± 0.03
Co_2	R_3O_2	2.07 ± 0.03
Co_2	R_4O_1[a]	1.99 ± 0.03
Co_2	R_4O_2[a]	2.13 ± 0.02
		av. 2.055

Secondary or bridging cobalt keto-oxygen bonds $Co{-}O_K(2)$

Co_1	R_3O_1	2.17 ± 0.03
Co_1	R_4O_1	2.28 ± 0.03
Co_2	R_2O_2	2.26 ± 0.03
		av. 2.237

Double bridging cobalt keto-oxygen bond $Co{-}O_K(2)_P$

Co_2	R_4O_2C[b]	2.13 ± 0.03

Oxygen–carbon bonds

R_1O_1	R_1C_2	1.27 ± 0.06	R_1O_2	R_1C_4	1.29 ± 0.05
R_2O_1	R_2C_2	1.28 ± 0.06	R_2O_2	R_2C_4	1.18 ± 0.05
R_3O_1	R_3C_2	1.34 ± 0.06	R_3O_2	R_3C_4	1.50 ± 0.06
R_4O_1	R_4C_2	1.13 ± 0.06	R_4O_2	R_4C_4	1.22 ± 0.05
		av. 1.277			

Ring carbon–carbon bonds

R_1C_2	R_1C_3	1.62 ± 0.07	R_1C_3	R_1C_4	1.43 ± 0.07
R_2C_2	R_2C_3	1.63 ± 0.07	R_2C_3	R_2C_4	1.56 ± 0.06
R_3C_2	R_3C_3	1.28 ± 0.08	R_3C_3	R_3C_4	1.29 ± 0.08
R_4C_2	R_4C_3	1.52 ± 0.07	R_4C_3	R_4C_4	1.43 ± 0.06
		av. 1.469			

Terminal carbon–β-carbon bonds

R_1C_1	R_1C_2	1.64 ± 0.08	R_1C_4	R_1C_5	1.63 ± 0.06
R_2C_1	R_2C_2	1.36 ± 0.07	R_2C_4	R_2C_5	1.65 ± 0.06
R_3C_1	R_3C_2	1.60 ± 0.06	R_3C_4	R_3C_5	1.62 ± 0.07
R_4C_1	R_4C_2	1.52 ± 0.07	R_4C_4	R_4C_5	1.50 ± 0.06
		av. 1.565			

Cobalt–cobalt distances

Co_1	Co_2	3.19 ± 0.01
Co_2	Co_2C	3.57 ± 0.01

[a] These oxygens form secondary bonds also. [b] All atoms labeled with a terminal C are generated by a center from the atom without the C.

TABLE V

BOND ANGLES (DEG.)

Atom A	Atom B	Atom C	Angle ABC	Std. dev. ABC
R_1O_1	Co_1	R_1O_2	91.8	1.1
R_1O_1	Co_1	R_4O_1	101.5	1.2
R_1O_1	Co_1	R_2O_2	101.5	1.1
R_1O_1	Co_1	R_2O_1	85.6	1.2
R_1O_2	Co_1	R_4O_1	104.7	1.1
R_1O_2	Co_1	R_3O_1	92.5	1.0
R_1O_2	Co_1	R_2O_1	89.8	1.2
R_2O_2	Co_1	R_3O_1	73.3	1.0
R_2O_2	Co_1	R_4O_1	66.5	1.1
R_2O_2	Co_1	R_2O_1	97.3	1.2
R_2O_1	Co_1	R_3O_1	103.3	1.1
R_3O_1	Co_1	R_4O_1	68.6	1.0
R_4O_1	Co_2	R_3O_1	76.1	1.1
R_4O_1	Co_2	R_2O_2	69.4	1.2
R_4O_1	Co_2	R_4O_2	89.8	1.2
R_4O_1	Co_2	R_3O_2	102.4	1.1
R_4O_2	Co_2	R_3O_2	95.3	1.0
R_4O_2	Co_2	R_2O_2	103.5	1.0
R_3O_1	Co_2	R_3O_2	86.8	1.0
R_3O_1	Co_2	R_2O_2	72.7	1.0
R_4O_2	Co_2	R_4O_2C[a]	68.0	1.4
R_3O_1	Co_2	R_4O_2C	125.7	1.1
R_2O_2	Co_2	R_4O_2C	102.7	1.0
R_3O_2	Co_2	R_4O_2C	92.2	1.0
R_1C_1	R_1C_2	R_1O_1	122.8	4.3
R_1O_1	R_1C_2	R_1C_3	126.8	4.3
R_1C_2	R_1C_3	R_1C_4	115.3	3.7
R_1C_3	R_1C_4	R_1O_2	133.7	3.6
R_1O_2	R_1C_4	R_1C_5	118.4	3.5
R_2C_1	R_2C_2	R_2O_1	121.3	4.7
R_2O_1	R_2C_2	R_2C_3	116.0	4.3
R_2C_2	R_2C_3	R_2C_4	124.4	3.8
R_2C_3	R_2C_4	R_2O_2	131.0	3.8
R_2O_2	R_2C_4	R_2C_5	120.9	3.6
R_3C_1	R_3C_2	R_3O_1	114.1	3.4
R_3O_1	R_3C_2	R_3C_3	129.6	4.2
R_3C_2	R_3C_3	R_3C_4	121.8	4.8
R_3C_3	R_3C_4	R_3O_2	130.6	4.2
R_3O_2	R_3C_4	R_3C_5	97.4	3.2
R_4C_1	R_4C_2	R_4O_1	130.9	4.5
R_4O_1	R_4C_2	R_4C_3	102.5	4.0
R_4C_2	R_4C_3	R_4C_4	146.4	4.2
R_4C_3	R_4C_4	R_4O_2	115.0	3.6
R_4O_2	R_4C_4	R_4C_5	109.6	3.7

[a] All atoms labeled with a terminal C are generated by a center from the atom without the C.

limited significance. However, several general trends can be noted and may be physically meaningful. Thus, the oxygen atom factors are higher than those for the cobalt atoms, and those of the carbon atoms are higher still. In general, there is a correspondence of the temperature factor for a β carbon atom to that of the oxygen atom to which it is bound. The terminal methyl group seems to have a higher value in almost all cases than the more tightly held β carbon atom. The progression of the temperature factors in ring number two is entirely consistent with the additional restrictions on the vibration of the bridging oxygen atom; however, the difference in the values for the two oxygen atoms is probably not significant. The carbon atoms of ring three show this same trend with higher factors in the terminal (C_5) end of the ring. However, the large differences in ring four are not subject to this interpretation, as both oxygens are bridging and should both have relatively low *B* values in contrast to the actual case.

Intermolecular Contacts.—The intermolecular distances were calculated using DISTAN, a FORTRAN program of Shoemaker.[21] Two rather short methyl–methyl contacts were found. One distance (R_1C_5–R_1C_5 centered $^1/_2$,0,0) was 3.65 Å., and a second (R_3C_1–R_2C_1) was 3.75 Å. Aside from these rather close approaches, the distances are those predicted on the basis of van der Waals radii,[22] and so all further discussion will be about the tetramer itself.

Discussion of the Molecular Structure.—As reported earlier[2] the structure of tetrameric anhydrous cobalt

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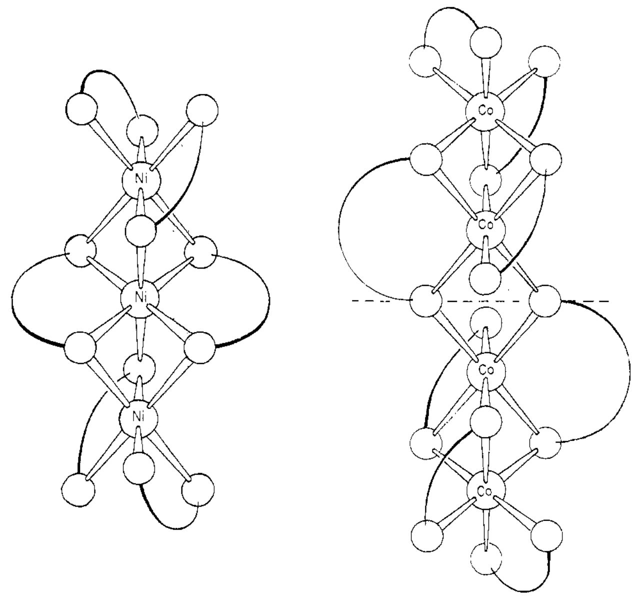
(21) D. P. Shoemaker, "DISTAN-Crystallographic Bond Distance, Bond Angle, and Dihedral Angle Computer Program" (1963).

(22) L. A. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.



Nickel Acetylacetonate Trimer Cobalt Acetylacetonate Tetramer

Figure 2.—A schematic drawing illustrating the ring arrangements in $[Co(AA)_2]_4$ and $[Ni(AA)_2]_3$.

acetylacetonate is similar in some respects to that of trimeric nickel acetylacetonate. The compounds both achieve six coordination through sharing of oxygen atoms between adjacent metal atoms. Both structures are illustrated schematically in Figure 2. In $[Ni(AA)_2]_3$ trimerization occurs by sharing of triangular faces of octahedra. It has been shown that a trimer is the only polymer which can result if all of the units are bridged by the method of sharing a common triangular face[4b] and if all the metal atoms are to be six-coordinate. However, the structure of $[Ni(AA)_2]_3$ is only one of the nine possible trimeric structures.

There are three possible ways to position two chelate rings to fill four of six coordination positions. First, the ligands can be placed so that the oxygen atoms are all coplanar and the two vacancies are *trans* to each other, *t;* second, the two vacancies may be *cis* to each other and the rings adopt a *d* configuration, *d;* third, the vacancies may be *cis* again but the rings arranged in the mirror image of the second case, *l.* With these distinctions the structure of $[Ni(AA)_2]_3$ may be represented *dtl.* The nine different structures possible and their highest symmetries are listed in Table VI.

The tetramer may be considered to be composed of two diastereoisomeric fragments which are joined along an edge common to two octahedra. Each of the fragments is formed by sharing a common octahedral face between two cobalt atoms. The overall structure may be represented as *ddll.* Thus the two major differences between the nickel trimer and the cobalt tetramer are first, no cobalt atom adopts the *t* configuration; second, one cobalt–cobalt bridge is effected by sharing a common octahedral edge.

Table VI

Possible[a] Structures for Trimers with Two Chelate Rings about Each Metal Atom

Structure	Sym. elem.	Structure	Sym. elem.
ddd	2-fold axis	*ddl*	Asymmetric
lll	2-fold axis	*lld*	Asymmetric
dtd	2-fold axis	*dld*	Asymmetric
ltl	2-fold axis	*ldl*	Asymmetric
	dtl	Center of symmetry	

[a] All of the structures except the centric one exist in right- and left-handed forms making 17 types possible if the enantiomorphs are to be considered.

Cobalt–Oxygen Bonds.—Although we report a large variation in bond lengths which seem to be chemically equivalent, a large number of independent determinations have been made, and, therefore, the average values obtained are undoubtedly of considerable value. In the structure of $[Co(AA)_2]_4$ there are three significantly different types of cobalt atom to oxygen atom bond. The first type is that between a nonbridging oxygen atom and a cobalt atom. This is the same type as the bond which occurs in $Co(AA)_2(H_2O)_2$. Also included in this class of bond, $Co–O_K(1)$, is the primary bond between a bridging oxygen atom and the cobalt atom which the particular ligand chelates. However, these bond lengths have been differentiated by a superscript *b* in Table IV. The second type is then the bridging or secondary bond, $Co–O_K(2)$, which is formed between an oxygen atom of the chelate and a cobalt atom not chelated by the ligand. It should be noted that the direction of the $Co–O_K(2)$ bond is nearly at right angles to the plane of the ligand in all cases except one. The bridge bonds in the center of the tetramer are approximately coplanar with the chelate ring. They are labeled $Co–O_K(2)_P$. The length of these bonds and their average standard deviations[23] are listed in Table VII along with the relevant data from the structures of $Co(AA)_2 \cdot 2H_2O$, $[Co(AA)_2H_2O]_2$, and $[Ni(AA)_2]_3$.

Table VII

Metal–Oxygen Bond Lengths (Å.)

Bond	Type	Distance	Std. dev.
$Co–O_{H_2O}$	in $[Co(AA)_2H_2O]_2$	2.197	0.018
$Co–O_{H_2O}$	in $Co(AA)_2(H_2O)_2$	2.23	0.01
$Co–O_K(1)$	in $[Co(AA)_2]_4$	2.055	0.026
$Co–O_K(1)$	in $[Co(AA)_2H_2O]_2$	2.021	0.017
$Co–O_K(1)$	in $Co(AA)_2(H_2O)_2$	2.055	0.01
$Ni–O_K(1)$	in $[Ni(AA)_2]_3$	2.056	0.05
$Co–O_K(2)$	in $[Co(AA)_2]_4$	2.237	0.026
$Ni–O_K(2)$	in $[Ni(AA)_2]_3$	2.123	0.05
$Co–O_K(2)_P$	in $[Co(AA)_2]_4$	2.13	0.03
$Co–O_K(2)_P$	in $[Co(AA)_2H_2O]_2$	2.162	0.016

The agreement between lengths for $Co–O_K(1)$ bonds is rather close. The most interesting comparison, however, is between the cobalt–water oxygen atom bond, $Co–O_w$ and $Co–O_K(2)$. Bullen reasoned that the tetragonal distortion of $Co(AA)_2 \cdot 2H_2O$ was due to the asymmetry of the $3d_\gamma$ and/or the $3d_\epsilon$ subshell which resulted in extremely long $Co–O_{H_2O}$ lengths. In this

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(23) The average standard deviation is listed as a measure of the degree to which the structure was refined. In general there are not sufficient independent crystallographic determinations to allow a meaningful standard deviation of the average to be computed. The latter will usually have a greater value.

case, however, there is no tetragonal distortion. The longer bonds Co–$O_K(2)$ are *cis* to each other and thus an alternate explanation must be sought.

The chelate is a charged species and thus might be expected to form a somewhat stronger bond than water. The difference in length between Co–$O_K(1)$ and the bridge bond Co–$O_K(2)$ may be explained on the basis of π-bonding. The cobalt atom may well form a dπ–pπ bond to the planar ring system and thus shorten the Co–$O_K(1)$ length. The Co–$O_K(2)$ bond is almost at right angles to the planar ring system which should allow no effective overlap and thus no shortening. The bridge bond, Co–$O_K(2)_P$, which is coplanar with the ligand is indeed shorter than the other bridge bonds (2.13 *vs.* 2.24 Å.). This shortening of Co–$O_K(2)_P$ is also observed in the structure of $[Co(AA)_2H_2O]_2$.[6]

All of the oxygen atoms are located approximately at the vertices of octahedra; however, the requirements of forming the tetramer by sharing of oxygen atoms seems to result in considerable angular distortion.

The bond distances found in the chelate rings agree with previously reported values[4a,24–31] and are of no great interest. The carbon–carbon ring distances (1.47 Å.) again are seen to be considerably shorter than a single bond distance.

Chelate Ring Distortion.—The distortion of the structure such that the metal atom does not lie in the plane of the chelate ring has been noted[31] in studies of several β-diketone complexes. The "best planes" for the ligands were calculated using MGEOM. The direction cosines for the planes and the distance of the five ligand atoms, O_1, C_2, C_3, C_4, O_2, from the plane as well as those for other atoms of interest are shown in Table VIII. The cobalt atoms range from 0.25 to 0.47 Å. out of the plane.

TABLE VIII

DISTANCES OF ATOMS FROM IDEAL LIGAND PLANE (Å.,)

Cosines of best plane[a]			
$L = 0.005$	$M = 0.482$	$N = 0.876$	$D = 6.43$
Distances of atoms from plane			
R_1O_1	−0.016		
R_1O_2	0.015		
R_1C_2	0.043	Co_1	−0.251
R_1C_3	0.013	R_1C_1	0.126
R_1C_4	−0.054	R_1C_5	0.000
$L = 0.899$	$M = 0.412$	$N = 0.147$	$D = 7.81$
R_2O_1	0.016		
R_2O_2	−0.010		
R_2C_2	−0.048	Co_1	0.288
R_2C_3	−0.011	R_2C_1	0.023
R_2C_4	0.029	R_2C_5	−0.112
$L = 0.249$	$M = 0.947$	$N = 0.201$	$D = 7.42$
R_3O_1	0.004		
R_3O_2	0.004		
R_3C_2	−0.048	Co_2	−0.285
R_3C_3	0.086	R_3C_1	0.119
R_3C_4	−0.049	R_3C_5	0.235
$L = 0.925$	$M = 0.308$	$N = 0.220$	$D = -1.21$
R_4O_1	0.018		
R_4O_2	−0.009		
R_4C_2	−0.046	Co_2	0.474
R_4C_3	0.021	R_4C_1	−0.146
R_4C_4	0.021	R_4C_5	−0.323

[a] Cosines of best planes are relative to the orthogonal coordinate system of Table II.

Conclusion

That $Co(AA)_2$ is composed of octahedrally coordinated cobalt atoms in the solid state has been established. The original suggestion of square-planar coordination in these compounds has been shown to be in error. The suggestion of Soderberg and Cotton of polymerization to achieve octahedral coordination has been borne out, although the detailed structure is not the one which was suggested.

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