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Crystal and Molecular Structure of Dimeric Bis(2,4-Pentanedionato)Cyclohexylaminecobalt(II)

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The structure of bis(2,4-pentanedionato)cyclohexylaminecobalt(II) has been determined by a single-crystal x-ray diffraction study. The compound crystallizes as monoclinic crystals ($a=8.886(2)$ Å, $b=9.347(2)$ Å, $a=23.020(4)$ Å, *and* $\beta=109.92(4)°$) *of space group* $P2_1/c$ *with two dimers per unit cell* ($\rho_{obs}=1.31(2)$ g/cm^3 *and* $\rho_{calc}=1.32$ g/cm^3). *The structure was solved from Patterson and electron density maps and refined by full matrix least-squares methods to a conventional R value of 0.057 for 1413 independent, nonzero reflections. The centrosymmetric dimer consists of two octahedra sharing an edge, the two chelate rings coordinated to one cobalt are not coplanar, and the second oxygen of each bridging 2,4-pentanedionato group is in the plane of the four-membered cobalt-oxygen ring.*

Introduction

As part of a general study of polynuclear complexes with oxygen bridges, the preparation and properties of bis(2,4-pentanedionato)cyclohexylaminecobalt(II), Co(AA)$_2$(Cha), were reported.[1] From studies of spectra and molecular weights in various solvents, it was concluded that the compound exists primarily as a dimer in carbon tetrachloride, primarily as a monomer in chloroform, and as an equilibrium mixture of monomer and dimer in benzene. Since the spectrum of the solid corresponded to that of the dimer in solution, it was concluded that the dimer was present in the solid; although a structure based on octahedra sharing an edge was proposed, no attempt was made to identify the particular isomeric form. Later, a dimeric structure was reported[2] for bis(2,4-pentanedionato)aquocobalt(II), [Co(AA)$_2$(H$_2$O)]$_2$; the structure consists of centrosymmetric dimers in which octahedra share an edge, the two chelate rings cordinated to one cobalt are not coplanar, and the second oxygen of each bridging 2,4-pentanedionato group is in the plane of the four-membered cobalt-oxygen ring.

Although there was a possibility that the structure of [Co(AA)$_2$(Cha)]$_2$ would be similar to that of [Co(AA)$_2$(H$_2$O)]$_2$, it was also possible that the structure could correspond to a different isomeric form of the dimer. Different isomeric forms of bis-adducts have been reported for bis(2,4-pentanedionato)nickel(II), Ni(AA)$_2$; the adducts with water[3] and pyridine[4] crystallize as the trans-isomers and the adduct with pyridine-N-oxide[5] crystallizes as the *cis*-isomer. Since a similar structural difference could occur in the monoadducts, a structure study of [Co(AA)$_2$(Cha)]$_2$ was carried out and in this paper we report the results of that study.

Experimental Section

Collection and Reduction of the X-ray Data. Crystals were prepared by both methods of reference 1; crystals prepared by the two methods were identical. The crystal chosen for the space group determination was prepared by method 1 and was a prism of approximate dimensions 0.325×0.225×0.45 mm; it was mounted along the long dimension (*a*-axis). Precession photographs, using Zr-filtered Mo Kα radiation ($\lambda=0.7107$ Å), indicated a monoclinic unit cell; the absence of $h0\ell$ reflections for odd values of ℓ and the absence of $0k0$ reflctions for odd values of k defined the space group as $P2_1/c$, No. 14.[6]

The crystal was transferred to an automated Picker four-circle diffractometer; 14 reflections were used to refine cell parameters by a least-squares procedure; the cell parameters obtained[7] are $a=8.886(2)$ Å, $b=9.347(2)$ Å, $c=23.020(4)$ Å, $\beta=109.92(4)°$, and $V=1797.5$ Å^3 (25°C, Mo radiation). The calculated density of 1.317 g/cm^3 for 4 formula units (two dimers) per unit cell agrees well with the observed density of 1.31(2) g/cm^3 measured by the flotation method using a mixture of benzene and chloroform.

The x-ray intensity measurements were made on the same crystal as used for the unit cell determination and Mo radiation was again used. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ-2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° per minute. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary background counts of 20

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[1] J.A. Bertrand, F.A. Cotton, and W.J. Hart, *Inorg. Chem.*, 3, 1007 (1964)).

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

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

[4] R.C. Elder, *Inorg. Chem.*, 7, 2316 (1968).

[5] W.D. Horrocks, Jr., D.H. Templeton, and A. Zalkin, *Inorg. Chem.*, 7, 1552 (1968).

[6] «International Tables for X-ray Crystallography», Vol. 1, The Kynoch Press, Birmingham, England, 1965.

[7] Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the least significant digits

Table I. Positional and Thermal[a] Parameters for Non-hydrogen Atoms of $[Co(AA)_2(Cha)]_2$.

Atom	x	y	z	B,Å^2 or β_{11} x 10^4	β_{22} x 10^4	β_{33} x 10^4	β_{12} x 10^4	β_{13} x 10^4	β_{23} x 10^4
Co	—0.0167(1)	0.0725(1)	0.0636(1)	104(1)	98(1)	13.2(1)	4(2)	14.0(3)	5.1(1)
01	—0.0872(5)	0.1147(5)	—0.0321(2)	116(8)	72(8)	15(1)	15(6)	13(2)	7(2)
02	0.0427(6)	0.0454(6)	0.1570(2)	144(8)	114(9)	18(1)	13(7)	22(3)	10(3)
03	—0.2175(6)	—0.0480(6)	0.0500(2)	152(8)	126(9)	20(1)	—33(7)	24(3)	—7(3)
04	—0.1222(6)	0.2647(6)	0.0739(2)	158(9)	140(9)	18(1)	42(8)	28(3)	2(3)
N	0.2053(7)	0.1753(8)	0.0700(3)	143(9)	132(9)	16(2)	—28(9)	15(3)	—9(3)
C11	—0.172(1)	0.244(1)	—0.1260(5)	5.8(3)					
C12	—0.169(1)	0.360(1)	0.0353(4)	3.3(2)					
C13	—0.142(1)	0.231(1)	—0.0576(3)	3.3(2)					
C14	—0.180(1)	0.349(1)	—0.0275(4)	4.2(2)					
C15	—0.225(1)	0.497(1)	0.0557(5)	5.3(3)					
C21	—0.274(1)	—0.084(1)	0.0917(3)	3.4(2)					
C22	—0.202(1)	—0.059(1)	0.1537(4)	4.7(2)					
C23	—0.053(1)	0.004(1)	0.1836(3)	3.1(2)					
C24	—0.437(1)	—0.155(1)	0.0686(5)	5.6(3)					
C25	0.002(1)	0.032(1)	0.2528(4)	5.0(2)					
CB1	0.336(1)	0.208(1)	0.1289(3)	3.1(2)					
CB2	0.489(1)	0.252(1)	0.1170(4)	4.1(2)					
CB3	0.623(1)	0.290(1)	0.1775(4)	4.7(2)					
CB4	0.571(1)	0.409(1)	0.2101(4)	4.5(2)					
CB5	0.419(1)	0.367(1)	0.2237(4)	5.1(2)					
CB6	0.285(1)	0.323(1)	0.1639(4)	4.1(2)					

[a] Anisotropic temperature factors expressed as exp $(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$.

sec each were taken at the beginning (bgd 1) and at the end (bgd 2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/second. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak. A recorder monitored the scan of each peak and the scans were examined for erratic background and for the inclusion of Kβ peaks. A standard reflection (402) was intermittently scanned to check for instrument or crystal variations; no significant variation in the number of counts for the reflection was observed during the entire data collection period. Corrected intensities (I) were obtained by subtracting three times the total measured background from the total integrated peak count (CT),

$$I = CT - 0.5(t_c/t_b)(bgd1 + bgd2)$$

where t_c is the scan time and t_b is the counting time of each background (either bgd 1 or bgd 2). The corrected intensities were assigned standard deviations according to the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(bgd1 + bgd)]^{1/2}.$$

A total of 1413 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30. The intensities were corrected for Lorentz and polarization effects; since the linear absorption coefficient, μ, was 10 cm^{-1}, it was not necessary to correct for absorption.

Solution of the Structure. Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer; programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy OR FLS and ORFFE least-squares and function and error programs, Johnson's ORTEP thermal ellipsoid plotting program, and various locally written programs.

In structure factor calculations, the scattering factors tabulated by Ibers[8] were employed for all atoms.

Coordinates for the cobalt atoms were obtained from a three-dimensional Patterson synthesis; an electron density calculation, using calculated phases based on the cobalt contribution, revealed the positions of all but

Table II. Coordinates for Hydrogen Atoms of $[Co(AA)_2(Cha)]_2$

Atom[a]	x	y	z
H111	—0.080	0.260	—0.130
H112	—0.240	0.190	—0.130
H113	—0.250	0.340	—0.130
H141	—0.200	0.440	—0.050
H151	—0.200	0.560	0.030
H152	—0.320	0.490	0.050
H153	—0.140	0.520	0.090
HN1	0.240	0.120	0.040
HN2	0.180	0.240	0.060
H241	—0.507	—0.080	0.050
H242	—0.467	—0.195	0.102
H243	—0.441	—0.223	0.033
H221	—0.230	—0.100	0.190
H251	0.075	0.100	0.260
H252	—0.110	0.090	0.250
H253	0.000	0.000	0.265
HB11	0.357	0.120	0.155
HB21	0.464	0.340	0.090
HB22	0.524	0.174	0.095
HB31	0.720	0.320	0.168
HB32	0.650	0.200	0.205
HB41	0.547	0.500	0.185
HB42	0.660	0.430	0.250
HB51	0.385	0.450	0.245
HB52	0.445	0.280	0.253
HB61	0.254	0.410	0.137
HB62	0.190	0.290	0.173

[a] H111, H112, H113 are the hydrogen attached to C11.

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(8) J.A. Ibers in «International Tables for X-Ray Crystallography», Vol. 3. The Kynoch Press, Birmingham, England, 1962.

six of the non-hydrogen atoms; a subsequent electron density calculation, phased on the known part of the structure, revealed positions for the remaining non-hydrogen atoms. Full-matrix least-squares refinement, using a weighting scheme based on counting statistics ($w=4I/\sigma(I)^2$) and minimizing $w(|F_o|-|F_c|)^2$, was used to refine an overall scale factor, atomic coordinates, and isotropic temperature factors; the refinement converged to an R_2 value ($R_2=[\Sigma W(|F_o|)-|F_c|)^2/\Sigma W(F_o)^2]^{1/2}$) of 0.093. At this point, a difference Fourier was calculated and all but one of the hydrogen atoms of the molecule were located; coordinates for one hydrogen of methyl carbon C24 were obtained by calculating its position. Hydrogen atoms were introduced into the structure factor calculations (each hydrogen was assigned the isotropic temperature factor of the atom to which it was bonded) but their coordinates and temperature factors were not refined; further least-squares refinement dropped the value of R_2 to 0.068. A further difference Fourier calculation indicated anisotropic motion around the cobalt atom; least-squares refinement varying anisotropic temperature factors on the cobalt and the atoms bonded to it (oxygen and nitrogen atoms) converged to an R_2 value of 0.053. The value of R_1 ($R_1=(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$) at this point was 0.057. Final atomic parameters are listed in Table I for all non-hydrogen atoms; coordinates of the hydrogen atoms are listed in Table

Table III. Observed and Calculated Structure Factors (in Electrons) for $[Co(AA)_2(Cha)]_2$.

L= 0

H	K	FO	FC
1	0	178	160
2	0	49	52
3	0	13	8
4	0	80	73
5	0	76	74
6	0	35	35
7	0	21	23
8	0	12	8
9	0	13	10
1	1	11	11
2	1	100	101
3	1	64	60
5	1	29	28
8	1	16	14
9	1	12	9
0	2	93	90
1	2	122	124
2	2	66	67
3	2	94	93
4	2	90	91
5	2	51	52
1	3	50	49
2	3	18	19
3	3	35	34
4	3	32	32
5	3	25	24
6	3	19	14
7	3	26	25
5	4	13	11
5	5	20	20
8	5	13	14
0	6	52	52
1	6	43	43
2	6	47	46
3	6	25	22
4	6	10	10
6	6	17	19
7	6	15	17
8	6	18	16
1	7	20	20
2	7	21	21
0	8	16	18
1	8	16	18
3	8	32	33
4	8	25	27
5	8	19	23
6	8	14	12
1	9	14	10
5	9	14	14

L= 1

H	K	FO	FC
-5	1	21	21
-4	1	68	65
-3	1	31	39
-2	1	60	65
-1	1	92	82
0	1	178	161
1	1	136	129
2	1	91	93
3	1	55	56
4	1	67	63
5	1	49	48
6	1	21	22
7	1	17	16
8	1	18	19
9	1	17	14
-9	2	15	17
-8	2	19	18
-6	2	32	30
-5	2	32	31
-4	2	85	85
-3	2	87	85
-2	2	51	50
-1	2	18	19
0	2	37	40
1	2	151	153
2	2	31	31
4	2	34	36
6	2	19	19
-5	3	24	22
-1	3	28	27
0	3	14	15
1	3	48	45
2	3	25	27
3	3	16	13
4	3	15	15
6	3	24	23
-8	4	18	18
-7	4	51	52
-6	4	29	28
-5	4	16	13
-4	4	50	51
-3	4	76	73
-2	4	66	65
0	4	35	36
2	4	44	44
-5	5	13	14
-4	5	26	25
-3	5	36	38
-2	5	31	30
-1	5	27	27
0	5	48	46
1	5	54	50
2	5	27	26
3	5	25	25
4	5	23	24
-7	6	16	14
-3	6	18	17
-2	6	23	26
0	6	14	17
1	6	23	26
2	6	23	26
3	6	20	21
4	6	12	14
-6	7	21	22
-5	7	23	22
-4	7	26	28
-3	7	31	34
-1	7	41	42
0	7	52	54
1	7	35	35
2	7	18	21
4	7	26	26
5	7	27	30
6	7	25	27
-2	8	15	14
2	8	13	18
-5	9	15	18
-4	9	13	17
0	9	14	12
1	9	15	16

L= 2

H	K	FO	FC
-4	0	42	38
-3	0	74	75
-2	0	29	27
-1	0	116	113
0	0	153	132
1	0	88	127
2	0	29	33
3	0	30	27
4	0	26	27
5	0	48	50
6	0	42	43
7	0	14	10
8	0	24	26
9	0	21	20
10	0	19	19
-8	1	22	22
-7	1	10	8
-6	1	18	16
-4	1	38	39
-3	1	85	79
-2	1	109	113
-1	1	23	20
0	1	94	89
1	1	44	43
2	1	32	30
3	1	14	13
6	1	23	20
-7	2	19	20
-6	2	10	12
-4	2	52	47
-3	2	89	78
-2	2	48	48
-1	2	98	102
1	2	70	71
4	2	25	23
5	2	30	30
6	2	19	17
7	2	20	19
8	2	12	12
-8	3	18	16
-7	3	47	44
-6	3	49	51
-5	3	62	62
-4	3	84	80
-3	3	93	83
-2	3	101	94
-1	3	84	79
1	3	80	79
2	3	67	62
3	3	26	22
5	3	24	22
-7	4	17	17
-6	4	12	13
-4	4	16	17
-3	4	17	20
-2	4	38	37
-1	4	51	49
0	4	31	29
1	4	33	36
2	4	18	18
3	4	18	20
-8	5	18	17
-7	5	15	15
-6	5	20	17
-5	5	19	19
-4	5	36	34
-3	5	57	55
-2	5	85	82
-1	5	18	13
0	5	31	29
1	5	40	39
2	5	64	62
3	5	23	23
-3	6	43	42
-2	6	34	36
-1	6	33	30
0	6	32	32
1	6	53	54
2	6	36	36
3	6	25	26
4	6	25	25
5	6	12	12
6	6	17	17
7	6	18	16
8	6	17	18
-2	7	21	20
0	7	13	8
1	7	22	22
3	7	14	14
-4	8	17	21
-3	8	15	15
-2	8	13	15
2	8	20	21
3	8	24	22
4	8	16	15
5	8	20	19
-6	9	14	11
-5	9	17	18
-4	9	16	14
0	9	14	13
1	9	19	18

L= 3

H	K	FO	FC
-6	1	20	20
-5	1	31	30
-3	1	20	21
-2	1	47	50
-1	1	55	57
1	1	17	22
2	1	17	15
3	1	14	18
4	1	16	17
5	1	32	31
7	1	29	29
8	1	24	27
9	1	19	21
10	1	19	19
-7	2	18	17
-6	2	46	42
-5	2	71	71
-4	2	79	76
-3	2	117	103
-2	2	63	60
-1	2	24	20
0	2	39	43
1	2	43	40
2	2	36	50
3	2	12	14
5	2	32	30
6	2	15	16
-6	3	12	12
-5	3	16	14
-3	3	18	18
-2	3	42	39
-1	3	38	37
0	3	43	47
1	3	16	19
3	3	20	18
6	3	24	24
-8	4	24	24
-7	4	42	43
-6	4	29	30
-5	4	52	48
-4	4	26	27
-3	4	61	56
-2	4	126	117
-1	4	79	71
0	4	98	94
1	4	29	27
2	4	60	57
3	4	38	32
4	4	16	17
6	4	16	14
-7	5	16	14
-6	5	15	11
-3	5	20	18
-2	5	21	21
0	5	28	27
1	5	57	55
2	5	39	38
3	5	12	14
4	5	12	12
5	5	12	10
-7	6	12	11
-6	6	20	19
-5	6	28	28
-2	6	17	12
-1	6	22	22
2	6	22	21
0	7	20	20
1	7	25	26
2	7	15	15
4	7	16	14
5	7	31	32
6	7	20	22
7	7	15	13
8	7	14	12
-3	8	20	21
-2	8	16	16
-1	8	18	21
2	8	15	18
3	8	14	14
-1	9	13	10
4	9	13	12
-6	10	13	12
-2	10	17	17
-1	10	19	22
0	10	22	22
1	10	23	24

L= 4

H	K	FO	FC
-8	0	29	31
-7	0	17	15
-6	0	25	26
-5	0	22	22
-4	0	52	54
-2	0	27	30
-1	0	13	1
0	0	32	30
1	0	55	52
2	0	31	31
3	0	11	11
4	0	11	9
5	0	52	51
7	0	25	22
8	0	20	18
9	0	20	19
10	0	14	15
-7	1	13	13
-6	1	29	27
-5	1	25	23
-4	1	51	49
-2	1	17	19
-1	1	122	121
0	1	24	25
1	1	46	46
2	1	27	24
4	1	19	17
5	1	37	17
6	1	24	24
-7	2	17	16
-6	2	27	24
-5	2	24	22
-3	2	22	19
-1	2	62	60
0	2	63	66
1	2	22	22
2	2	15	12
3	2	22	21
6	2	39	36
9	2	15	14
-8	3	25	25
-7	3	22	23
-6	3	50	51
-5	3	58	55
-4	3	44	44
-3	3	85	83
-2	3	98	96
-1	3	100	96
0	3	17	20
1	3	26	24
2	3	13	18
3	3	56	54
4	3	40	40
5	3	37	37
6	3	38	38
7	3	23	21
8	3	16	12
-7	4	19	19
-4	4	20	23
-3	4	35	39
-2	4	35	33
-1	4	16	13
0	4	54	50
4	4	14	13
-7	5	21	20
-6	5	15	16
-5	5	23	24
-4	5	29	29
-3	5	41	40
-2	5	33	35
-1	5	16	19
0	5	33	34
1	5	44	40
2	5	68	65
3	5	29	27
-7	6	14	15
-6	6	30	31
-5	6	17	18
-4	6	29	28
-2	6	18	19
0	6	17	16
2	6	20	20
3	6	18	19
4	6	15	13
-5	8	16	10
-4	8	17	20
-3	8	17	10
6	8	21	21
-5	9	18	14
-4	9	15	16
-3	9	12	12
-2	9	13	14
-1	9	24	24
0	9	17	16
1	9	17	17
2	9	24	25
3	9	14	14
-1	11	13	14
0	11	15	13
1	11	14	14
2	11	16	13

L= 5

H	K	FO	FC
-6	1	44	45
-5	1	64	63
-4	1	47	47
-3	1	51	53
-1	1	35	39
0	1	64	70
2	1	26	21
5	1	10	9
9	1	13	9
-6	2	22	23
-5	2	46	47
-4	2	77	74
-3	2	42	42
-1	2	89	82
0	2	21	22
1	2	50	49
2	2	22	23
3	2	34	31
4	2	46	41
5	2	36	33
6	2	41	39
7	2	25	24
8	2	22	20
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-6	4	28	26
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-1	4	42	43
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1	4	56	55
2	4	70	63
3	4	54	52
4	4	27	27
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6	4	33	34
7	4	31	28
9	4	15	12
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-4	5	22	21
-2	5	37	40
-1	5	23	24
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3	5	15	15
-2	6	20	22
-1	6	14	14
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2	6	17	18
3	6	17	19
5	6	17	17
-6	7	25	28
-5	7	20	20
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-2	7	19	19
-1	7	24	25
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3	7	18	18
-4	8	19	18
-2	8	19	20
-1	8	14	10
3	8	15	19
5	8	16	16
-2	9	18	20
-1	9	17	17
-1	10	19	21
0	10	25	26
1	10	15	18
3	10	19	16

L= 6

H	K	FO	FC
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-5	0	68	69
-4	0	37	38
-3	0	18	20
-2	0	54	52
-1	0	94	107
0	0	88	101
2	0	66	64
4	0	29	31
-5	1	49	45
-4	1	32	27
-3	1	10	8
-2	1	41	44
-1	1	41	40
0	1	16	18
1	1	21	22
2	1	34	34
3	1	17	18
4	1	34	34
5	1	20	28
7	1	14	14
-6	2	42	46
-5	2	63	65
-4	2	41	41
-3	2	65	65
-2	2	28	32
-1	2	18	16
2	2	23	20
3	2	33	32
4	2	28	27
-4	3	27	22
-3	3	54	53
-2	3	76	68
0	3	40	41
2	3	44	47
3	3	47	47
4	3	42	41
5	3	37	36
6	3	49	43
7	3	34	35
8	3	17	16
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-2	4	14	13
-1	4	45	45
1	4	17	20
2	4	31	29
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4	4	21	20
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-4	5	14	9
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1	5	56	54
2	5	59	51
3	5	44	47
5	5	17	18
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7	5	18	19
-6	6	26	26
-4	6	15	14
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-1	6	37	38
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1	6	30	33
2	6	17	21
3	6	15	17
4	6	16	18
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-4	8	23	27
-3	8	26	27
-2	8	18	17
-1	8	20	22
1	8	16	17
2	8	14	15
2	8	19	14

L= 7

H	K	FO	FC
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-5	1	37	38
-4	1	57	58
-3	1	28	32
-2	1	45	42
-1	1	61	58
0	1	40	48
1	1	55	59
2	1	21	25
3	1	51	52
4	1	43	43
5	1	20	19
8	1	12	9
-6	2	18	16
-5	2	13	12
-4	2	10	5
-1	2	16	18
0	2	15	20
2	2	29	29
3	2	41	39
4	2	38	40
5	2	16	17
6	2	26	25
7	2	25	23
8	2	19	14
9	2	13	10
-6	3	14	12
-3	3	50	48
-2	3	46	45
0	3	19	20
-6	4	17	16
-5	4	27	28
-3	4	22	22
-2	4	14	16
0	4	26	27
1	4	18	15
2	4	41	40
3	4	48	46
4	4	22	21
5	4	22	20
6	4	27	25
7	4	22	22
8	4	14	14
-6	5	28	29
-4	5	12	11
-3	5	32	34
-2	5	15	15
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2	6	17	19
3	6	13	11
4	6	15	12
-6	7	20	19
-5	7	25	21
-4	7	26	28
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-2	7	30	31
-1	7	36	35
0	7	25	27
1	7	27	27
2	7	19	20
3	7	24	23
4	7	20	23
-1	8	14	15
0	8	19	18

L= 8

H	K	FO	FC
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-5	0	43	46
-4	0	13	7
-3	0	11	7
-1	0	74	80
0	0	138	149
1	0	108	109
2	0	51	54
3	0	36	33
4	0	65	69
5	0	80	81
7	0	18	15
8	0	14	13
-2	1	14	16
-1	1	16	16
0	1	34	31
2	1	17	19
3	1	56	54
4	1	26	28
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-2	2	52	52
-1	2	51	47
0	2	57	54
2	2	19	19
3	2	43	43
4	2	31	30
5	2	23	23
6	2	15	15
-6	3	19	21
-5	3	51	51
-4	3	12	11
-3	3	27	27
0	3	13	12
3	3	12	11
4	3	18	17
5	3	15	12
6	3	23	23
7	3	18	19
8	3	18	17
-6	4	15	17
-4	4	15	18
-5	4	21	20
-3	4	21	20
-2	4	30	29
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2	4	20	21
3	4	22	11
4	4	24	24
5	4	14	17
-3	5	14	12
1	5	19	19
2	5	20	20
3	5	30	31
-6	6	23	24
-5	6	17	17
-4	6	12	12
-3	6	26	27
-2	6	33	32
-1	6	36	35
0	6	27	26
1	6	46	49
2	6	37	37
3	6	35	36
4	6	13	14
5	6	19	19
7	6	14	13
-2	7	24	25
-1	7	18	18
0	7	13	17
-6	8	14	15
-5	8	14	15
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-3	8	18	17
-2	8	27	30
-1	8	19	17
0	8	25	23
1	8	13	15
4	8	27	19
5	8	17	14

L= 9

H	K	FO	FC
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-3	1	11	14
-2	1	75	76
-1	1	76	74
0	1	111	107
1	1	78	78
2	1	77	86
3	1	57	58
4	1	62	65
5	1	49	50
6	1	17	18
7	1	14	16
-5	2	25	25
-4	2	39	37
-3	2	12	12
-2	2	18	15
-1	2	32	32
0	2	22	20
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-4	3	12	9
-3	3	34	34
-1	3	30	29
0	3	26	24
1	3	27	27
2	3	13	14
3	3	22	23

L=23

H	K	FO	FC
-5	5	13	11
-3	5	14	16
-2	5	15	12

L= 9

H	K	FO	FC
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-6	4	24	24
-5	4	29	28
-3	4	46	45
-2	4	14	13
0	4	28	24
1	4	24	20
2	4	17	17
-5	5	12	15
-4	5	11	10
-3	5	27	26
0	5	42	42
1	5	24	25
2	5	32	33
3	5	20	24
4	5	16	19
5	5	16	15
-5	6	12	9
-4	6	19	18
-6	7	14	15
-5	7	19	21
-4	7	19	20
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-2	7	26	26
-1	7	36	37
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1	7	33	34
2	7	14	14
4	7	25	25
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6	7	15	14
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-2	8	17	21
-1	8	19	25
-5	9	14	13
-1	9	16	17
0	9	16	15

L=10

H	K	FO	FC
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-4	0	23	22
-3	0	39	36
-1	0	96	98
0	0	126	130
1	0	135	134
2	0	26	27
3	0	61	60
4	0	49	49
5	0	42	43
6	0	27	29
-5	1	12	11
-4	1	14	13
-3	1	19	20
-2	1	22	24
-1	1	78	79
0	1	95	94
1	1	66	65
2	1	14	16
-5	2	11	9
-4	2	36	37
-3	2	48	46
-2	2	17	19
-1	2	50	49
0	2	49	50
1	2	30	29
2	2	38	38
3	2	14	12
4	2	38	39
5	2	33	37
6	2	18	18
-6	3	31	35
-5	3	22	22
-4	3	79	80
-3	3	62	61
-2	3	60	60
-1	3	44	47
0	3	30	30
1	3	53	52
2	3	32	32
3	3	34	34
-5	4	18	20
-2	4	20	20
-1	4	14	12
-5	5	27	26
-4	5	21	19
-3	5	30	31
-2	5	29	30
-1	5	24	25
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1	5	31	33
2	5	32	32
3	5	14	12
-3	6	19	18
-2	6	14	12
-1	6	18	20
0	6	15	13
1	6	43	42
2	6	33	34
-2	7	14	14
-1	7	24	26
-5	8	13	14
-3	8	15	10
-2	8	21	21
-1	8	23	21
-5	9	19	19
-4	9	19	20
-2	8	13	14

L=11

H	K	FO	FC
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2	1	12	14
3	1	20	22
4	1	14	12
5	1	17	17
6	1	12	12
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-5	2	67	68
-4	2	58	58
-3	2	69	69
-2	2	70	68
-1	2	68	70
0	2	56	56
1	2	60	61
2	2	35	35
3	2	19	19
4	2	16	12
5	2	14	11
-5	3	28	26
-4	3	26	27
-2	3	12	12
3	3	14	16
-6	4	15	18
-5	4	22	24
-4	4	33	34
-3	4	64	65
-2	4	66	67
-1	4	90	91
0	4	70	68
1	4	68	67
2	4	54	55
3	4	45	44
4	4	16	15
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-5	5	16	17
1	5	34	36
2	5	31	32
3	5	15	15
-4	6	20	22
-3	6	22	25
-2	6	24	26
1	6	18	19
2	6	13	16
4	6	18	17
0	7	20	20
1	7	14	16
5	7	15	18
6	7	14	16
-2	8	18	18
-1	8	14	12

L=12

H	K	FO	FC
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-3	0	38	36
-2	0	50	50
-1	0	25	28
3	0	17	17
-5	1	25	26
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-2	1	43	39
-1	1	65	63
0	1	38	38
1	1	19	22
3	1	24	25
4	1	19	20
-6	2	45	44
-2	2	28	26
-1	2	37	35
0	2	13	11
3	2	14	16
-6	3	16	17
-5	3	29	32
-4	3	55	54
-3	3	87	82
-2	3	66	66
-1	3	65	66
0	3	64	62
1	3	35	32
2	3	52	52
3	3	26	25
4	3	15	19
5	3	14	14
6	3	15	16
7	3	14	13
-6	4	14	16
-4	4	56	55
-3	4	26	23
-1	4	15	15
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-4	6	13	13
-3	6	22	21
-1	6	14	14
-5	9	14	14
0	9	15	15
1	9	16	11
2	9	14	12

L=13

H	K	FO	FC
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-5	1	49	48
-4	1	42	42
-3	1	35	36
-2	1	29	32
-1	1	23	21
0	1	27	27
1	1	21	24
-6	2	18	18
-4	2	37	38
-3	2	56	57
-2	2	32	31
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4	2	15	14
6	2	13	13
-5	3	16	18
-2	3	18	19
-1	3	12	13
3	3	19	20
-6	4	14	14
-5	4	12	10
-4	4	32	32
-3	4	27	26
-2	4	36	37
-1	4	47	44
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1	4	34	32
2	4	32	34
3	4	18	20
4	4	14	15
5	4	15	14
6	4	15	13
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-4	5	24	27
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-2	5	26	27
-1	5	27	27
0	5	14	14
-3	6	19	19
-2	6	17	16
3	6	13	12
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-5	7	21	22
-4	7	25	23
-3	7	20	22
-2	7	26	27
-1	7	15	13

L=14

H	K	FO	FC
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-3	0	43	45
-2	0	40	41
-1	0	35	34
0	0	35	33
1	0	23	20
2	0	20	19
-6	1	23	25
-5	1	16	16
-1	1	15	15
2	1	17	17
3	1	17	16
4	1	17	19
5	1	9	8
-6	2	34	33
-4	2	30	32
-3	2	40	40
-2	2	46	45
-1	2	26	24
1	2	19	18
-3	3	20	21
-2	3	34	38
-1	3	49	45
0	3	35	31
1	3	28	27
4	3	16	16
5	3	18	18
6	3	18	17
7	3	17	18
8	3	15	11
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4	4	17	18
5	4	13	13
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-1	5	20	19
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2	5	27	27
3	5	24	24
-6	6	29	29
-5	6	22	24
-4	6	23	21
-3	6	30	31
-2	6	21	21
-1	6	12	17
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-6	8	14	17
-3	8	13	14
-2	8	20	20
-1	8	18	19
0	8	18	20
1	8	16	16
0	9	14	12

L=15

H	K	FO	FC
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-5	1	60	63
-4	1	49	48
-3	1	52	53
-2	1	48	50
-1	1	34	34
0	1	38	39
1	1	26	30
2	1	15	17
4	1	13	11
-6	2	22	26
-3	2	18	19
0	2	14	17
2	2	22	21
-3	3	28	26
-2	3	28	27
-1	3	22	23
0	3	22	19
2	3	16	14
-5	4	13	11
0	4	14	13
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-3	7	19	18
-3	7	28	29
-2	7	24	23
-1	7	23	20
0	7	19	16
1	7	18	20
3	7	17	19
4	7	14	13

L=16

H	K	FO	FC
-6	0	71	73
-5	0	37	40
-4	0	32	32
-3	0	16	18
-2	0	47	47
-1	0	51	49
0	0	45	46
1	0	31	30
2	0	32	35
3	0	37	39
4	0	24	25
5	0	21	21
-1	1	18	18
-5	2	29	28
-4	2	32	34
-3	2	37	34
-2	2	45	45
-1	2	59	58
1	2	14	17
3	2	23	23
4	2	20	19
-6	3	27	26
-5	3	40	40
-4	3	42	42
-3	4	21	19
-2	4	25	22
0	4	30	27
-6	5	13	15
-2	5	23	22
-1	5	26	25
0	5	14	11
2	5	19	21
-6	6	24	25
-5	6	17	14
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2	6	22	25
-5	7	13	10
-4	7	15	13
-3	8	19	18
-2	8	16	15
-1	8	14	15
5	8	14	9

L=17

H	K	FO	FC
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-1	1	32	34
0	1	24	27
1	1	17	20
2	1	30	32
3	1	27	28
4	1	27	23
5	1	22	22
6	1	15	16
-6	2	22	22
-5	2	30	30
-4	2	18	18
-1	2	25	24
0	2	35	36
-5	3	17	14
-2	3	15	16
-6	4	20	21
-5	4	35	36
-4	4	30	29
-3	4	20	19
-2	4	19	18
-1	4	19	23
0	4	14	12
7	4	15	17
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2	5	14	14
-5	6	14	14
-4	6	22	21
-3	6	13	13
-2	7	21	20
-1	7	23	24
2	7	13	14

L=18

H	K	FO	FC
-5	0	21	20
-1	0	19	21
0	0	25	25
2	0	22	23
3	0	30	33
4	0	35	34
5	0	20	21
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-4	1	18	16
0	1	22	25
1	1	16	18
-1	2	15	14
0	2	15	13
1	2	15	15
-6	3	15	14
-5	3	33	35
-4	3	42	41
-3	3	20	22
-1	3	27	28
0	3	17	19
1	3	32	31
3	3	13	15
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-2	4	16	13
-5	5	18	11
-4	5	15	16
-3	5	19	14
-2	5	12	13
-1	5	14	17
0	5	19	21
-5	6	15	14
-1	6	14	14
2	6	18	19
-1	8	18	19
0	8	15	15

L=19

H	K	FO	FC
-5	1	19	20
-1	1	17	15
3	1	14	19
4	1	14	13
-6	2	14	18
-3	2	14	15
-2	2	16	14
-1	2	36	39
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1	2	26	26
2	2	14	14
3	2	17	16
4	2	14	14
5	2	13	12
-5	4	16	17
-4	4	29	29
-3	4	28	27
-2	4	19	21
0	4	29	31
1	4	32	35
2	4	20	19
3	4	16	16
-6	5	14	18
-3	6	16	15
-8	7	14	12
-1	7	15	17
-5	8	14	14

L=20

H	K	FO	FC
-6	0	20	20
-4	0	14	9
0	0	15	16
-4	1	20	21
0	1	21	20
1	1	15	15
2	1	21	20
4	1	14	12
-2	2	14	15
0	2	24	23
-5	3	14	13
-4	3	18	17
-3	3	46	43
-2	3	29	27
-1	3	27	27
0	3	37	35
1	3	32	34
2	3	27	25
3	3	18	18
5	3	15	11
-5	4	21	19
-3	4	15	16
-4	5	25	24
-3	5	19	17
-2	5	22	22
0	5	17	19
1	5	19	20
2	5	20	18
-6	6	14	15
-3	6	13	12

L=21

H	K	FO	FC
-6	1	22	21
-4	1	13	14
-3	1	17	20
-2	1	27	28
-1	1	22	20
-3	2	24	23
-2	2	26	24
-1	2	25	24
0	2	23	24
1	2	22	23
2	2	19	19
-4	4	24	23
-3	4	31	30
-2	4	20	18
-1	4	15	15
0	4	24	22
1	4	29	28
2	4	21	22
3	4	16	15
-6	5	15	13
-3	5	16	15
-2	5	32	28
-1	5	16	16
-4	6	14	16
-3	6	18	17
-2	4	14	14

L=22

H	K	FO	FC
-5	0	38	36
-4	0	32	33
-2	0	36	33
-1	0	37	38
0	0	30	29
1	0	17	15
2	0	17	18
-6	2	21	17
-5	2	25	20
-3	2	28	28
-2	2	29	30
-1	2	16	17
-5	3	16	14
-3	3	18	14
-2	3	20	20
0	3	16	17
1	3	19	19
-3	4	15	15
-3	5	15	15
-6	6	16	17
-5	6	13	13
-4	5	14	14
-3	6	17	16
-2	6	24	23
-1	6	14	12
0	6	14	12

L=23

H	K	FO	FC
-6	1	22	24
-5	1	33	33
-4	1	26	25
-3	1	32	30
-2	1	34	34
-1	1	28	29
0	1	25	22
2	1	14	13
-4	2	14	15

L=24

H	K	FO	FC
-6	0	20	24
-5	0	30	30
-4	0	25	25
-3	0	14	13
-2	0	27	26
-1	0	29	31
0	0	16	17
1	0	14	16
-4	1	18	17
-4	2	19	17
-3	2	19	20
-2	2	19	20
-1	2	20	19
0	2	16	14
-6	3	17	16
-5	3	19	20
-4	3	19	20
-3	3	15	15
-4	6	15	12
-3	6	13	13

L=25

H	K	FO	FC
-4	1	16	14
-2	1	18	19
-1	1	17	18
-6	2	18	16
-5	2	19	19
-4	2	17	18
-4	4	16	16
-5	4	16	15
-6	4	16	16
-3	4	16	16
0	4	14	9
-4	5	14	10

L=26

H	K	FO	FC
-5	1	20	17
-4	1	21	19
-5	3	21	19
-4	3	24	22
-3	3	24	21
-2	3	13	13

L=27

H	K	FO	FC
-4	1	14	9
-6	2	18	15
-5	2	14	15
-4	2	14	13
-1	2	14	13
-6	4	18	15
-4	4	18	13
-5	4	15	15
1	4	15	15

L=28

H	K	FO	FC
-5	0	16	17

L=30

H	K	FO	FC
-6	0	15	16
-5	0	17	14

L=31

H	K	FO	FC
-2	1	16	14

L=32

H	K	FO	FC
-5	0	16	12

Table IV. Selected Intramolecular Distances and Angles for $[Co(AA)_2(Cha)]_2$

Atoms	Distance, Å	Atoms	Angle, °	Atoms	Angle, °
Co-Co′	3.332(2)	CB6-CB1	1.51(1)	02-C23-C22	124.8(7)
Co-01	2.115(5)	N-CB1	1.49(1)	02-C23-C25	115.2(7)
Co-01′	2.213(5)	N-Co-01	85.8(2)	03-C21-C22	125.8(7)
Co-02	2.047(5)	N-Co-01′	84.3(2)	03-C21-C24	115.1(6)
Co-03	2.043(5)	N-Co-02	94.7(2)	C13-C14-12	127.7(8)
Co-04	2.077(5)	N-Co-04	92.6(2)	C21-C22-C23	127.4(7)
Co-N	2.154(6)	N-Co-03	171.3(2)	C11-C13-C14	117.4(8)
01-C13	1.249(9)	01-Co-01′	79.3(2)	C25-C23-C22	119.9(7)
02-C23	1.267(9)	01-Co-04	90.5(2)	CB1-CB2-CB3	111.4(6)
03-C21	1.268(8)	02-Co-03	89.6(2)	CB2-CB3-CB4	110.4(7)
04-C12	1.228(9)	Co′-Co-N	83.5(2)	C15-C12-C14	117.6(7)
C13-C14	1.41(1)	Co′-Co-03	88.6(1)	C24-C21-C22	119.1(7)
C12-C14	1.42(1)	Co-01-C13	125.5(5)	CB3-CB4-CB5	110.9(7)
C21-C22	1.37(1)	Co-04-C12	126.9(5)	CB4-CB5-CB6	110.7(7)
C22-C23	1.40(1)	Co-02-C23	124.8(5)	CB5-CB6-CB1	112.5(6)
C11-C13	1.51(1)	Co-03-C21	125.2(5)	CB6-CB1-CB2	110.4(6)
C12-C15	1.51(1)	Co-N-CB1	124.5(5)	N-CB1-CB2	111.0(6)
C21-C24	1.52(1)	01-C13-C14	124.9(7)	N-CB1-CB6	110.3(6)
C23-C25	1.52(1)	01-C13-C11	117.6(7)		
CB1-CB2	1.53(1)	04-C12-C14	125.1(7)		
CB2-CB3	1.54(1)	04-C12-C15	117.3(7)		
CB3-CB4	1.50(1)				
CB4-CB5	1.54(1)				
CB5-CB6	1.54(1)				

II; final observed and calculated structure factors are compared in Table III.

Results and Discussion

The structure of $[Co(AA)_2(Cha)]_2$, Figure 1, corresponds to that found for $[Co(AA)_2(H_2O)]_2$. The centrosymmetric dimer consists of two octahedral coordinated cobalts sharing an edge; the edge-sharing creates a four-membered cobalt-oxygen ring which is planar (by symmetry).

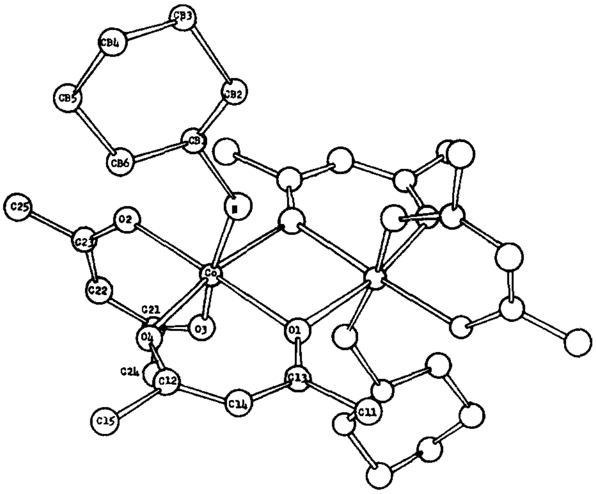

Figure 1. - A perspective drawing of the dimeric structure of $[Co(AA)_2(Cha)]_2$. Atoms of the asymmetric unit are labelled.

Selected intramolecular distances and angles for the structure are given in Table IV. The Co–Co distance of 3.332(2) Å is similar to one of those found[2] for $[Co(AA)_2(H_2O)]_2$, 3.33(4) and 3.22(4) Å, and considerably shorter than the edge-sharing Co—Co distance in $[Co(AA)_2]_4$,[9] 3.57(1) Å. The bond lengths and angles of the acetylacetonate chelate rings appear normal and compare well with those in the literature.[10] The cyclohexyl group shows the expected chair conformation and the bond distances and bond angles are normal; the amine nitrogen occupies an equatorial position on the cyclohexane ring.

The amine nitrogen is bent toward the acetylacetonate oxygen on the adjacent cobalt to give a Co′–Co–N angle of 83.5(2)°; this bending probably results from crystal packing forces but may indicate some interaction between the amine protons and the acetylacetonate oxygen. Although the hydrogen positions are only approximate, the calculated distance from the amine hydrogen to the oxygen, 2.12 Å, appears to be normal non-bonded contact rather than a hydrogen-bonding interaction.

One other feature of the structure should be mentioned—the possibility of π-bonding within the four-membered ring. Although a large number of isomeric structures are possible for such a 1:1 adduct in a dimeric complex, in only two of these structures is it possible to have π-bonding within the four- membered cobalt-oxygen ring. In order to have such π-bonding, the chelate ring which contains the bridging oxygen must be in the same plane as the four-membered ring-this arrangement is possible in one isomer with inversion symmetry (amines on opposite sides of the four-membered ring) and in one isomer with 2-fold symmetry (amines on the same side of the four-membered ring). Of these two isomers, the one with inversion symmetry would seem to minimize steric repulsion and it is this structure which is found for the hydrate and for the cyclohexylamine adduct; it is also the arrangement found for the edge-sharing portion of $[Co(AA)_2]_4$.

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

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

In previous discussions[11,12] of π-bonding in four-membered rings, we showed the planarity of the coordination of the bridging oxygen by calculating the distance of the carbon bonded to the bridging oxygen from the plane of the four-membered ring. In the hydrate structure,[2] the carbon was essentially in the plane (deviations of 0.02 and 0.05 Å but with standard deviations of the order of 0.05 Å). However, the present structure shows some distortion with the carbon 0.25(1) Å out of the plane.

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(11) J.A. Bertrand and J.A. Kelley, *Inorg. Chim. Acta, 4,* 203 (1970).
(12) J.A. Bertrand, J.L. Breece, A R. Kalyanaraman, G.J. Long, and W.A. Baker, Jr., *J. Am. Chem. Soc., 92,* 5233 (1970).