Contribution from the Istituto di Chimica, Università di Trieste, Trieste, Italy

The Crystal Structure of the Lattice Compound of NN'-ethylene-bis-(acetylacetoneiminato)cobalt(II) with Benzene

S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio

Received July 31, 1968

NN'-ethylenebis-(acetylacetoneiminato)cobalt(II), Co-(BAE) crystallizes from benzene with an equal mole ratio of solvent. The monoclinic unit cell, space group $P2_1/m$, with a = 11.74 Å, b = 7.35 Å, c = 10.60 Å, β = 99.0°, *contains two formula units, Co-BAE.C_6H_6. Least-squares refinement resulted in a final R-value of* 0.075 *for* 836 *independent observed reflections. The complex molecule has an exact tetracoordinate planar geometry. The average Co—O and Co—N bond lengths are* 1.85 *and* 1.87 (±0.01) *Å. The complex molecules are packed in such a way to make large channels where benzene molecules are accomodated.*

Introduction

Recently some stable organometallic derivatives of cobalt(III) complex of bis(salicylaldehyde)ethylendiimine (salenH_2) and bis(acetylacetone)-ethylenediimine (BAEH_2) have been studied in this Institute.[1-2] These compounds are of particular interest because their physico-chemical properties and reactivity show strong analogies with the vitamin B_{12} group compounds. The crystal structure determination of the lattice compound of NN'-ethylenebis(acetylacetoneiminato)cobalt(II) (CoBAE) with benzene and that of NN'-ethylenebis(acetylacetoneiminato)vinylaquocobalt-(III), described in the following paper, are part of a program aimed to provide data on the coordination configuration and on the structure of the tetradentate ligands able to stabilize the cobalt-carbon bond.

Experimental Section

Single orange monoclinic crystals elongated along [010], prepared as previously described,[3] were kindly supplied by Professor G. Costa and Dr. G. Mestroni of this Institute. Co(BAE) crystallizes from benzene with an approximately equal mole ratio of benzene. Crystals were enclosed in thin-walled glass capillary tubes under nitrogen to prevent loss of benzene and contact with air. The cell dimensions, determined from precession photographs, taken with MoK_α radiation, are: $a = 11.74 \pm 0.02$ Å, $b = 7.35 \pm 0.02$ Å, $c = 10.60 \pm 0.02$ Å, $\beta = 99.0 \pm 0.3°$.

The calculated density assuming two formula units Co(BAE).C_6H_6 per unit cell, is 1.32 g.cm^{-3} in agreement with approximate density measurements which were limited by the rapid loss of benzene. The only systematic absences observed, 0k0 with k odd, indicated that the possible space group is either $P2_1$ or $P2_1/m$. Intensity data were collected by the equi-inclination Weissenberg method using MoK_α radiation. Levels h0l through h8l were recorded by the multiple film technique. An approximately cylindrical crystal of mean diameter of *ca.* 0.15 mm was used. The precession zero-levels hk0 and 0kl, recorded with MoK_α radiation, were used to place the reflections in a common scale. The intensities of 838 independent reflections were measured by visual comparison with a standard scale. No correction for absorption was made. Lorentz and polarisation factors and the spot shape correction for non-zero levels were applied. All calculations were carried out on an IBM 7044 computer with programs written by A. Domenicano *et al.*[4,5]

The atomic scattering factors used were those of Hanson *et al.*[6] for oxygen, carbon, and hydrogen, that of Berghuis *et al.*[7] for nitrogen and that, listed in the International Tables for X-ray Crystallography,[8] for cobalt.

Structure Determination

The systematic absences cannot distinguish between the space groups $P2_1$ or $P2_1/m$, which have a twofold and a fourfold general position respectively. However, the mostlikely gauche conformation of ethylendiamine bridge suggests the choice of the non-centrosymmetric space group $P2_1$. In fact the space group $P2_1/m$ with two formula units per unit cell demands that the molecule of Co(BAE) possesses

---

(1) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem.*, *6*, 181 (1966); G. Costa and G. Mestroni, *J. Organomet. Chem.*, *11*, 325 (1968).

(2) G. Costa, G. Mestroni, and L. Stefani, *J. Organomet. Chem.*, 7, 493 (1967); H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organomet. Chem.*, *11*, 167 (1968).

(3) G. Morgan and J. Smith, *J. Chem. Soc.*, 2030 (1925).

(4) V. Albano, A. Domenicano, and A. Vaciago, *Gazz. Chim. Ital.*, 96, 922 (1966).

(5) A. Domenicano and A. Vaciago, private communication.

(6) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, *17*, 1040 (1964).

(7) J. Berghuis, I. J. M. Haanappell, M. Potters, B. O. Loopstra, C. H. Gillavry, and A. L. Veencdaal, *Acta Cryst.*, *8*, 478 (1955).

(8) «International Tables for X-ray Crystallography», vol. III, Kynoch Press, Birmingham (1962).

exact *m* symmetry. Therefore the interpretation of the Patterson synthesis, for the location of the metal atom was originally based on the space group $P2_1$ in which the y coordinate of the cobalt can be chosen arbitrarily as zero. The heavy atom-phased three-dimensional Fourier synthesis was calculated. Because of the false symmetry introduced into the synthesis by inclusion of only cobalt contribution to the structure factors, peaks corresponding to the remaining non-hydrogen atoms together with an equally weighted collection of peaks reflected through the $y=0$ plane were expected. However, the electron distribution was such to indicate that the complex molecule as well as the benzene molecule, had exact *m* symmetry coinciding with the crystallographic mirror symmetry in the space group $P2_1/m$. y coordinates were then reassigned to agree with the standard setting of the centrosymmetric space group. A structure factor calculation including all non-hydrogen atoms and using an over-all temperature factor, B of 3 Å^2, gave a reliability index of 0.23. Three cycles of block-diagonal least-squares refinement of positional and isotropic thermal factors reduced R to 0.130. Three further cycles of refinement were carried out, allowing all positional parameters and the anisotropic thermal parameters to vary, and the R-value fell to 0.091. At this stage an electron density difference function, with all the atoms except hydrogen subtracted out, was calculated using the results of this refinement for the terms with $(\sin\theta)/\lambda \leqslant 0.4$.

Estimated positions of the hydrogen atoms all occurred in regions of positive electron-density on this map. Therefore the hydrogen atoms with an over-all isotropic temperature factor B of 5 Å^2 were included, but they were held fixed in the last cycles of refinement. Finally two reflections, 020 and $11\bar{1}$, which seemed to be affected by extinction were removed from the refinement scheme. Block diagonal least-squares refinement, using anisotropic temperature factors for each non-hydrogen atom, was continued until no parameter showed any significant change between successive cycles, giving $R=0.075$. The weighting scheme used was: $w=1/(a+b|F_o|+c|F_o|^2)$, where $a=7.10$, $b=1.0$, and $c=0.01$.

Table I. Positional parameters of non-hydrogen atoms and their estimated standard deviations in parentheses, both multiplied by 10^4

	x	y	z
Co	1305 (2)	2500	4121 (2)
O(1)	1094 (8)	2500	2351 (10)
O(2)	2857 (7)	2500	3978 (10)
N(1)	− 269 (10)	2500	4206 (12)
N(2)	1557 (10)	2500	5920 (12)
C(1)	287 (17)	2500	184 (19)
C(2)	127 (13)	2500	1555 (17)
C(3)	− 914 (13)	2500	1920 (17)
C(4)	−1135 (12)	2500	3199 (17)
C(5)	−2372 (13)	2500	3467 (19)
C(6)	− 554 (13)	2500	5522 (16)
C(7)	501 (12)	2500	6545 (15)
C(8)	2631 (17)	2500	8100 (18)
C(9)	2589 (14)	2500	6646 (16)
C(10)	3637 (13)	2500	6155 (15)
C(11)	3736 (11)	2500	4886 (16)
C(12)	4893 (13)	2500	4415 (18)
C(13)	−2874 (12)	1619 (21)	7842 (14)
C(14)	−3303 (13)	691 (20)	8707 (16)
C(15)	−3785 (10)	1613 (22)	9611 (13)

Table II. Fractional coordinates of hydrogen atoms multiplied by 10^3

	x	y	z
H(1C1)	− 45	250	−39
H(2C1)	80	130	0
H(1C5)	−289	250	255
H(2C5)	−250	130	403
H(1C8)	350	250	858
H(2C8)	215	130	838
H(1C12)	563	250	512
H(2C12)	490	130	385
H(C3)	−167	250	120
H(C6)	−105	130	550
H(C7)	45	130	713
H(C10)	443	250	681
H(C13)	−252	80	708
H(C14)	−329	−80	868
H(C15)	−424	80	1041

Atomic parameters and their standard deviations are listed in Tables I, II, and III. The final observed and calculated structure factors are listed in Table IV. Bond lengths and angles are listed in Table V. The scheme for the labelling of atoms is shown in Figure 1. The atoms of the benzene molecules related to the reference atoms C(13), C(14), and C(15) by the mirror symmetry are primed.

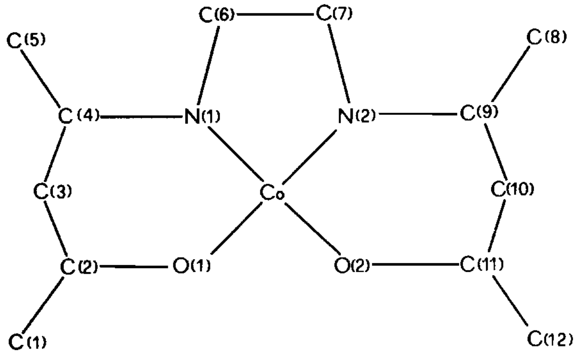

Figure 1. Numbering scheme for the atoms of the complex molecule.

Results and Discussion

The crystal packing of Co(BAE).C_6H_6 is very similar to that of the lattice compound of NN′ ethylenebis(acetylacetoneiminato)copper(II)[9] with methylammonium perchlorate. The refinement of the molecular parameters for this compound, assuming the space group $P2_1/m$, led to unacceptable values of some bond lengths and angles and of some thermal parameters. These effects were ascribed to some real distortion from $P2_1/m$ symmetry. On the contrary, no indication of distortion from $P2_1/m$ symmetry was obtained for the compound Co(BAE).C_6H_6 and no

---

(9) N. F. Curtis, E. N. Baker, D. Hall, and T. N. Waters, *Chem. Comm.*, 675 (1966).

difficulties were encountered in the refinement of the structure. Therefore it can be deduced that the choice of the centrosymmetric space group $P2_1/m$ is correct.

Symmetry demands that all non-hydrogen atoms of the complex molecule lie on the crystallographic mirror plane. The same plane relates one-half of

Table III. Anisotropic temperature factors in the form: $\exp-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$. These factors and their estimated standard deviations (given in parentheses) are multiplied by 10^4

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	46 (1)	148 (3)	86 (2)	0	48 (2)	0
O(1)	77 (8)	262 (21)	126 (12)	0	75 (15)	0
O(2)	50 (7)	288 (22)	135 (13)	0	25 (15)	0
N(1)	86 (10)	148 (19)	123 (14)	0	80 (19)	0
N(2)	63 (9)	215 (23)	110 (15)	0	13 (20)	0
C(1)	143 (20)	314 (41)	130 (22)	0	20 (34)	0
C(2)	76 (13)	212 (29)	146 (21)	0	−14 (27)	0
C(3)	63 (12)	286 (36)	160 (25)	0	−32 (29)	0
C(4)	63 (11)	172 (25)	187 (23)	0	51 (29)	0
C(5)	70 (12)	294 (37)	208 (25)	0	96 (27)	0
C(6)	96 (12)	190 (27)	152 (19)	0	122 (23)	0
C(7)	83 (11)	255 (32)	134 (18)	0	118 (22)	0
C(8)	133 (19)	383 (47)	100 (20)	0	−4 (33)	0
C(9)	118 (15)	162 (25)	132 (20)	0	68 (28)	0
C(10)	88 (13)	271 (32)	106 (22)	0	−1 (28)	0
C(11)	49 (10)	228 (29)	143 (20)	0	31 (22)	0
C(12)	51 (11)	414 (49)	166 (24)	0	20 (28)	0
C(13)	135 (13)	438 (39)	191 (18)	62 (39)	28 (26)	−103 (46)
C(14)	160 (15)	279 (30)	262 (24)	−8 (39)	−147 (31)	73 (47)
C(15)	107 (11)	574 (48)	181 (17)	−173 (34)	17 (23)	207 (44)

Table IV. Observed and calculated structure factors (x10)

K	L	FO	|FC|
******H=		0******	
2	0	1412	1958
4	0	953	860
6	0	540	464
8	0	264	197
0	1	519	727
1	1	228	230
2	1	711	903
3	1	419	442
4	1	415	542
5	1	163	196
6	1	162	250
7	1	70	98
8	1	129	133
0	2	254	240
1	2	533	514
2	2	215	196
3	2	147	145
4	2	133	122
5	2	155	159
6	2	73	77
7	2	72	81
8	2	68	40
1	3	387	398
2	3	163	145
3	3	321	311
5	3	145	159
7	3	90	96
0	4	362	355
1	4	391	405
2	4	209	218
3	4	327	298
4	4	237	216
5	4	174	178
6	4	132	147
7	4	97	100
8	4	88	56
0	5	595	648
1	5	168	162
2	5	555	551
3	5	149	146
4	5	298	295
5	5	138	129
6	5	144	143
8	5	128	82
0	6	226	237
2	6	212	220
4	6	137	148
6	6	103	92
0	7	157	164
1	7	196	187
2	7	116	124
3	7	130	122
4	7	114	118
1	8	199	194
3	8	145	156
5	8	105	103
******H=		1******	
0	0	626	670
1	0	417	455
2	0	636	766
3	0	754	641
4	0	589	458
5	0	382	284
6	0	251	221
7	0	112	141
8	0	101	117
0	1	578	593
0	-1	272	223
1	1	172	156
1	-1	818	1156
2	1	77	49
2	-1	340	285
3	-1	522	583
4	1	80	84
4	-1	166	170
5	1	45	40
5	-1	302	367
6	1	100	117
6	-1	80	90
7	-1	135	167
8	1	68	53
0	2	248	245
0	-2	93	54
1	2	295	274
1	-2	141	130
2	2	178	165
2	-2	204	192
3	-2	257	260
4	2	168	174
4	-2	100	105
5	-2	139	155
6	2	63	80
7	2	38	17
7	-2	90	91
8	2	66	58
0	3	238	213
0	-3	385	386
1	3	186	170
1	-3	114	107
2	3	164	166
2	-3	228	216
3	3	72	74
3	-3	123	119
4	3	155	132
4	-3	197	206
5	3	120	122
5	-3	65	72
6	3	82	91
6	-3	135	143
7	3	74	65
7	-3	52	53
8	-3	67	54
0	4	167	165
0	-4	417	450
1	4	464	437
1	-4	128	126
2	4	56	63
2	-4	480	456
3	4	344	360
4	4	69	63
4	-4	313	296
5	4	150	176
6	4	49	45
6	-4	156	154
7	4	106	103
7	-4	60	9
8	-4	117	92
0	-5	672	666
1	5	397	365
1	-5	274	252
2	-5	571	571
3	5	288	281
3	-5	215	202
4	-5	352	330
5	5	183	179
5	-5	172	171
6	5	60	55
6	-5	179	181
7	5	95	93
7	-5	89	70
8	-5	127	98
0	6	186	171
0	-6	147	154
1	-6	383	372
2	6	188	189
2	-6	127	121
3	6	98	97
3	-6	282	280
4	6	96	99
4	-6	143	145
5	6	101	93
5	-6	162	150
6	-6	84	94
7	-6	110	79
0	7	298	316
1	-7	190	214
2	7	247	272
3	-7	153	162
4	7	190	191
5	-7	102	100
6	7	115	122
0	8	188	185
1	8	152	153
1	-8	168	161
2	8	151	162
3	8	129	116
3	-8	123	136
4	8	136	137
5	-8	104	95
6	8	71	86
1	9	150	137
3	9	112	111
1	10	144	146
3	10	113	111
******H=		2******	
0	0	176	144
1	0	486	508
2	0	115	112
3	0	100	106
4	0	76	74
5	0	122	148
7	0	66	80
0	1	114	105
0	-1	124	114
1	1	385	384
1	-1	283	246
2	1	88	81
2	-1	304	279
3	1	188	201
3	-1	272	279
4	1	87	90
4	-1	177	208
5	1	81	88
5	-1	149	163
6	1	35	47
6	-1	57	75
7	1	60	55
7	-1	75	87
0	2	821	862
0	-2	68	57
1	2	444	428
1	-2	191	177
2	2	324	325
3	2	142	140
4	2	145	164
4	-2	88	75
5	2	98	106
6	2	112	129
6	-2	94	95
7	2	58	52
8	2	61	55
0	3	130	120
0	-3	200	198
1	-3	278	252
2	3	370	361
2	-3	130	142
3	-3	148	132
4	3	243	275
4	-3	96	97
6	3	128	137
6	-3	67	72
8	3	102	89
0	4	445	458
0	-4	169	165
1	4	265	250
1	-4	152	143
2	4	320	316
2	-4	185	200
3	4	144	140
4	4	220	210
4	-4	106	104
5	4	140	125
5	-4	106	97
6	4	127	138
6	-4	75	67
7	4	65	57
8	4	84	63
0	5	213	208
0	-5	145	135
1	5	338	344
1	-5	331	335
2	5	136	144
2	-5	81	84
3	5	289	275
3	-5	266	249
4	5	114	107
4	-5	138	139
5	5	128	123
5	-5	150	159
6	-5	87	96
7	5	82	76
7	-5	110	96
1	6	293	266
1	-6	364	363
3	6	235	225
3	-6	292	262
5	6	162	163
5	-6	154	149
7	6	99	87
7	-6	106	95
0	7	243	255
0	-7	118	115
1	7	220	213
1	-7	84	96
2	7	216	241
2	-7	93	102
3	7	183	166
4	7	135	132
4	-7	84	80
5	7	129	118
5	-7	84	80
0	8	145	130
0	-8	127	121
2	8	109	121
2	-8	117	124
0	9	116	107
******H=		3******	
0	0	296	286
1	0	259	230
2	0	176	132
3	0	168	146
4	0	155	144
5	0	85	96
6	0	70	60
7	0	59	51
8	0	53	48
0	1	457	452
0	-1	793	647
1	1	643	616
1	-1	145	125
2	1	76	65
2	-1	362	363
3	1	228	216
4	-1	220	234
5	1	162	170
6	-1	154	157
7	1	84	85
8	-1	87	69
0	2	82	69
0	-2	119	127
1	2	175	174
1	-2	313	294
2	2	80	71
2	-2	118	90
3	2	375	385
3	-2	200	196
4	-2	104	99
5	2	182	194
6	-2	73	77
7	2	115	117
0	3	341	343
0	-3	242	197
1	3	135	120
1	-3	202	199
2	3	105	106
2	-3	187	175
3	-3	124	125
4	3	65	74
5	3	83	73
5	-3	122	133
6	3	87	80
7	-3	69	66
0	4	161	171
1	4	65	66
1	-4	128	138
2	4	240	248
3	-4	150	155
4	4	154	157
4	-4	71	68
5	-4	107	111
6	4	60	84
6	-4	60	56
0	5	263	292
1	-5	269	249
2	5	213	208
3	-5	171	160
4	5	168	162
5	-5	93	78
6	5	114	114
0	6	234	228
0	-6	281	287
1	6	215	205
1	-6	118	110
2	6	195	198
2	-6	231	243
3	6	175	156
3	-6	124	114
4	6	141	145
4	-6	168	174
5	-6	90	91
6	6	65	81
6	-6	105	100
0	7	109	93
0	-7	127	131
1	7	96	100
2	7	85	97
2	-7	117	134
3	7	83	81
4	-7	98	98
6	-7	72	67
0	-8	141	145
2	-8	114	116
******H=		4******	
0	0	354	352
1	0	85	91
2	0	271	248
4	0	200	201
6	0	138	136
8	0	83	66
0	-1	332	321
1	1	147	146
1	-1	429	404
2	1	378	335
2	-1	241	247
3	1	69	74
3	-1	342	333
4	1	249	277
4	-1	209	197
5	-1	139	154
6	1	120	132
6	-1	115	118
7	-1	104	94
8	1	100	81
8	-1	92	56
0	2	394	426
0	-2	153	118
1	2	130	128
1	-2	171	172
2	2	81	75
2	-2	160	166
3	-2	223	218
5	2	75	79
5	-2	175	193
6	2	50	61
7	-2	110	110
0	3	98	89
1	3	314	291
3	-3	116	123
5	-3	127	127
7	-3	75	70
0	4	138	120
0	-4	79	59
1	4	177	179
1	-4	239	229
3	-4	165	162
4	-4	69	60
6	-4	53	47
0	5	171	163
0	-5	112	116
1	5	106	99
2	5	216	224
2	-5	114	116
3	5	101	98
4	5	142	149
4	-5	130	125
5	-5	75	61
6	-5	90	80
0	6	240	232
0	-6	282	304
1	-6	163	138
2	6	191	180
2	-6	263	275
3	-6	109	118
4	6	152	154
4	-6	148	174
6	6	91	107
6	-6	108	104
0	-7	154	148
1	-7	176	159
2	-7	122	130
3	-7	138	132
4	-7	94	90
5	-7	86	87
1	-8	105	101
3	-8	98	103
0	-9	108	108
1	-9	150	152
3	-9	91	104
0	-10	108	91
0	-11	115	134
******H=		5******	
0	0	431	449
1	0	346	322
2	0	309	273
3	0	356	331
4	0	178	170
5	0	169	172
6	0	97	104
7	0	112	98
0	1	533	537
1	1	313	283
1	-1	695	722
2	1	421	380
2	-1	84	86
3	1	62	72
3	-1	476	492
4	1	223	232
5	1	96	89
5	-1	270	298
6	1	134	140
7	-1	151	156
8	1	102	69
0	2	93	76
0	-2	406	394
1	2	104	114
1	-2	528	512
2	2	151	131
2	-2	415	383
3	-2	429	391
4	2	147	137
4	-2	185	191
5	-2	276	268
6	2	78	76
6	-2	90	86
7	-2	140	132
0	3	272	275
0	-3	132	133
1	3	111	116
1	-3	350	339
2	3	56	65
2	-3	131	117
3	-3	186	200
4	-3	118	123
6	-3	103	103
7	-3	81	54
0	-4	161	152
1	4	201	201
2	-4	134	142
3	4	213	233
4	-4	155	158
5	4	127	120
6	-4	105	101
0	5	187	166
0	-5	209	231
1	5	321	289
1	-5	164	144
2	5	95	117
2	-5	188	196
3	5	183	184
3	-5	138	114
4	-5	120	100
5	5	140	146
5	-5	96	89
0	6	186	163
0	-6	158	158
1	6	162	155
1	-6	409	420
2	6	172	176
2	-6	134	134
3	6	128	136
3	-6	308	315
4	6	99	104
4	-6	108	88
5	-6	207	202
7	-6	119	110
1	-7	264	272
3	-7	237	231
5	-7	170	161
7	-7	127	95
1	-8	134	139
3	-8	94	94
0	-10	129	135
******H=		6******	
1	0	382	364
2	0	58	43
3	0	334	301
5	0	168	182
7	0	104	98
0	1	275	257
0	-1	397	385
1	1	311	295
1	-1	354	320
2	1	119	109
2	-1	368	337
3	1	301	288
3	-1	275	255
4	-1	200	176
5	1	160	163
5	-1	180	191
6	-1	90	83
7	1	107	96
7	-1	93	89
0	2	220	205
0	-2	700	661
1	2	232	229
1	-2	233	213
2	2	158	177
2	-2	604	565
3	-2	134	122
4	2	123	124
4	-2	358	356
6	2	93	75
6	-2	176	192
8	-2	125	94
0	3	162	144
0	-3	383	381
1	-3	160	163
2	3	224	239
2	-3	346	322
3	3	114	100
3	-3	110	94
4	3	172	185
4	-3	280	277
6	3	97	96
6	-3	166	169
8	-3	101	77
0	4	386	403
0	-4	245	230
1	4	97	102
1	-4	262	268
2	4	238	229
2	-4	188	206
3	4	79	82
3	-4	209	196
4	4	136	140
4	-4	112	103
5	-4	120	124
6	4	94	103
6	-4	72	61
7	-4	104	74
1	5	187	199
1	-5	401	391
2	5	125	115
3	5	189	193
3	-5	304	311
4	5	91	93
5	5	111	113
5	-5	193	199
7	-5	110	101
0	-6	242	244
1	6	195	204
1	-6	436	434
2	-6	215	227
3	6	139	139
3	-6	342	330
4	-6	155	158
5	6	124	116
5	-6	207	217
6	-6	100	91
7	-6	128	125
0	-7	421	411
1	-7	255	261
2	-7	361	345
3	-7	197	199
4	-7	212	229
5	-7	119	120
6	-7	132	130
0	-8	132	123
2	-8	126	135
4	-8	105	120
0	-9	124	100
******H=		7******	
0	0	267	244
1	0	108	98
2	0	295	255
3	0	111	91
4	0	172	178
5	0	102	97
6	0	87	95
7	0	83	48
0	1	198	192
0	-1	226	221
1	1	302	293
2	1	97	93
2	-1	189	206
3	1	255	259
4	1	99	74
4	-1	125	132
5	1	148	160
6	1	68	64
6	-1	72	83
7	1	94	93
0	2	154	164
0	-2	180	166
1	2	215	237
1	-2	221	215
2	2	62	44
2	-2	144	145
3	2	252	241
3	-2	166	161
4	-2	167	167
5	2	145	151
5	-2	79	73
6	-2	99	110
7	2	92	89
0	3	134	112
0	-3	144	120
1	3	336	353
1	-3	225	204
2	3	127	139
2	-3	111	115
3	3	182	183
3	-3	187	140
4	3	107	111
5	3	128	136
5	-3	94	103
0	4	188	182
1	-4	157	154
2	4	205	215
3	4	132	110
3	-4	166	162
4	4	158	167
5	-4	113	129
6	4	104	101
0	5	298	319
0	-5	134	112
1	-5	168	176
2	5	203	219
2	-5	130	120
3	-5	142	136
4	5	161	152
4	-5	87	89
5	-5	100	100
6	5	109	103
0	6	121	104
0	-6	296	301
1	6	132	123
1	-6	175	155
2	6	121	123
2	-6	229	254
3	-6	137	126
4	-6	174	173
6	-6	89	101
0	-7	322	284
1	7	98	105
2	-7	242	278
4	-7	215	222
6	-7	124	137
0	-8	146	135
1	8	103	95
1	-8	186	161
2	-8	121	118
3	-8	113	102
******H=		8******	
0	0	416	414
1	0	141	139
2	0	375	374
3	0	111	108
4	0	217	236
5	0	99	94
6	0	126	134
0	1	294	282
0	-1	187	183
1	1	136	119
1	-1	291	290
2	1	243	252
2	-1	139	139
3	1	80	70
3	-1	215	212
4	1	183	176
4	-1	148	142
5	-1	130	126
6	1	109	105
6	-1	83	100
7	-1	70	71
0	2	174	144
0	-2	98	83
1	2	190	188
1	-2	309	296
3	2	170	170
3	-2	197	207
5	-2	92	117
0	-3	109	98
1	3	200	200
1	-3	154	146
3	3	176	175
3	-3	138	148
5	-3	117	121
0	-4	129	140
1	4	208	253
1	-4	82	80
2	4	72	64
2	-4	122	126
3	4	158	147
4	-4	103	87
0	5	142	139
0	-5	181	180
1	5	108	107
2	5	95	134
2	-5	140	156
3	5	136	134
4	5	101	94
4	-5	106	112
0	6	148	138
0	-6	125	108
2	6	93	89
2	-6	110	106
1	-7	125	114
2	-7	94	90
******H=		9******	
1	0	284	261
3	0	196	212
5	0	141	138
1	-1	320	348
3	-1	230	256
5	-1	118	149
7	-1	101	94
0	-2	156	130
1	-2	147	160
2	-2	96	119
3	-2	175	162
4	-2	92	89
5	-2	118	134
0	3	139	132
0	-3	150	140
2	-3	124	133
4	-3	113	91
0	-4	168	171
2	4	96	87
2	-4	141	158
4	-4	122	125
0	-5	145	130
1	-5	141	131
2	-5	102	119
3	-5	141	121
4	-5	125	95
1	-6	156	158
3	-6	125	107
******H=		10******	
1	0	91	94
0	-1	201	175
1	1	92	74
1	-1	90	82
2	-1	138	162
4	-1	138	133
0	-2	171	143
2	-2	142	131
4	-2	98	87
0	3	147	129
0	4	166	152
2	4	114	119
1	-5	159	167
3	-5	121	133
1	-6	154	134
3	-6	111	115
0	-7	131	138
2	-7	108	112
0	-8	129	126
2	-8	118	118
******H=		11******	
0	0	114	95
1	0	88	70
2	0	111	88
0	-1	253	241
1	1	113	107
2	-1	188	210
4	-1	112	131
0	-2	164	154
1	2	115	145
2	-2	134	141
3	2	121	118
3	-2	87	83
4	-2	112	112
1	3	110	131
1	-3	96	102
3	3	101	102
0	4	154	117
1	-4	98	102
0	-6	183	169
2	-6	122	161
0	-7	165	148
2	-7	125	133
1	-8	125	120
2	-8	87	81
******H=		12******	
0	0	150	149
2	0	117	135
0	1	147	126
0	-1	105	108
1	-1	124	118
2	1	105	116
3	-1	101	107
0	2	143	104
1	-2	155	168
3	-2	123	132
0	-3	106	107
1	-3	110	120
0	-4	114	104
2	-4	91	102
0	-5	136	148
2	-5	107	132
0	-6	133	133
2	-6	109	118
1	-7	126	140
******H=		13******	
1	-1	152	145
3	-1	123	113
0	-2	133	122
0	-3	133	137
******H=		14******	
0	-2	147	138
0	-3	141	114

Table V. Bond lengths (in Å) and bond angles (°), with their estimated standard deviations in parentheses

Co—O(1)	1.854 (0.011) Å	Co—O(1)—C(2)	128.3°(1.1)
Co—O(2)	1.852 (0.009)	O(1)—C(2)—C(1)	113.6 (1.5)
Co—N(1)	1.864 (0.012)	O(1)—C(2)—C(3)	123.7 (1.6)
Co—N(2)	1.884 (0.013)	C(1)—C(2)—C(3)	122.7 (1.5)
O(1)—C(2)	1.304 (0.017)	C(2)—C(3)—C(4)	126.0 (1.5)
O(2)—C(11)	1.297 (0.016)	C(3)—C(4)—C(5)	120.0 (1.4)
N(1)—C(4)	1.354 (0.019)	C(3)—C(4)—N(1)	121.7 (1.4)
N(1)—C(6)	1.484 (0.022)	C(5)—C(4)—N(1)	118.3 (1.6)
N(2)—C(9)	1.330 (0.019)	C(4)—N(1)—Co	126.1 (1.1)
N(2)—C(7)	1.494 (0.020)	C(4)—N(1)—C(6)	119.3 (1.3)
C(1)—C(2)	1.494 (0.028)	C(6)—N(1)—Co	114.6 (0.9)
C(2)—C(3)	1.338 (0.023)	N(1)—C(6)—C(7)	113.2 (1.3)
C(3)—C(4)	1.420 (0.026)	C(6)—C(7)—N(2)	109.0 (1.3)
C(4)—C(5)	1.523 (0.022)	C(7)—N(2)—Co	116.0 (0.9)
C(6)—C(7)	1.513 (0.020)	C(7)—N(2)—C(9)	119.2 (1.3)
C(8)—C(9)	1.534 (0.026)	C(9)—N(2)—Co	124.8 (1.2)
C(9)—C(10)	1.409 (0.024)	N(2)—C(9)—C(8)	117.7 (1.5)
C(10)—C(11)	1.368 (0.024)	N(2)—C(9)—C(10)	123.7 (1.5)
C(11)—C(12)	1.519 (0.022)	C(8)—C(9)—C(10)	118.6 (1.4)
C(13)—C'(13)	1.295 (0.022)	C(9)—C(10)—C(11)	125.8 (1.3)
C(13)—C(14)	1.305 (0.023)	C(10)—C(11)—C(12)	122.7 (1.3)
C(14)—C(15)	1.366 (0.022)	C(10)—C(11)—O(2)	123.4 (1.3)
C(15)—C'(15)	1.304 (0.023)	C(12)—C(11)—O(2)	113.9 (1.4)
O(1)—Co—O(2)	84.0°(0.4)	C(11)—O(2)—Co	128.2 (1.0)
O(1)—Co—N(1)	94.1 (0.5)	C'(13)—C(13)—C(14)	121.5 (1.5)
O(2)—Co—N(2)	94.7 (0.5)	C(13)—C(14)—C(15)	118.8 (1.4)
N(1)—Co—N(2)	87.2 (0.5)	C(14)—C(15)—C'(15)	119.7 (1.4)

Table VI. Non-bonded intermolecular distances below 4 Å

Co—C(6)I	3.81
O(1)—C(14)I	3.79
O(1)—C(13)I	3.70
O(2)—C(13)I	3.59
O(2)—C(14)I	3.79
N(1)—N(2)I	3.97
N(1)—C(6)I	3.80
N(1)—C(7)I	3.76
N(2)—C(5)I	3.83
N(2)—C(4)I	3.84
C(1)—C(9)I	3.68
C(2)—C(7)I	3.75
C(3)—C(15)II	3.90
C(1)—C(1)III	3.75
C(1)—C(8)II	3.79
C(1)—C(7)II	3.90
C(8)—C(15)IV	3.98
C(12)—C(5)V	3.51
C(12)—C(12)VII	3.87
C(15)—C(15)VI	3.90

I	$\bar{x}, \bar{y}, 1-z$
II	$x, y, z-1$
III	$\bar{x}, \bar{y}, \bar{z}$
IV	$\bar{x}, \bar{y}, 2-z$
V	$1+x, y, z$
VI	$-1-x, \bar{y}, 2-z$
VII	$1-x, \bar{y}, 1-z$

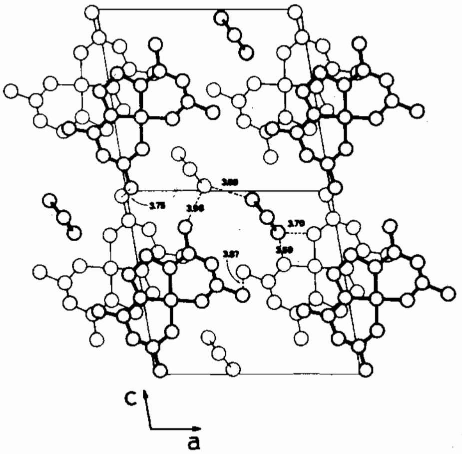

Figure 2. Projection of the structure on (010).

the benzene molecule to the other. The structure is most readily described as molecular units separated by van der Waals distances (Table VI). The projection of the contents of two unit cells onto (010) is shown in Figure 2. Close intermolecular contacts are involved between methyl groups of the complex molecule, which make large channels where the benzene molecules are accomodated .

The benzene ring shows no significant deviations from planarity. The equation of the best least-squares plane through the benzene carbon atoms is $9.456x+4.872z=1.108$ in which x and z are crystallographic fractional coordinates. The deviations from this plane are 0.010, –0.005, and –0.005 Å for C(13), C(14), and C(15) respectively. The observed values of the bond lengths within the benzene ring are considerably smaller than the expected values. This may be ascribable to considerable librational movement and possible fractional occupancy of the sites, as suggested by the high thermal parameters for these atoms and by the easy loss of the solvent molecules.

The complex molecule adopts an exact tetracoordinate planar geometry in spite of the steric effects of the ethylenediamine bridge for which a gauche conformation is clearly more stable. A similar situation has been found in the crystal of the lattice

(10) R. G. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc.*, (A), 223 (1968).

compound Cu(BAE).$CH_3NH_3ClO_4$ [9] and of Cu(BAE).½H_2O.[10] In the latter compound the observed angle between the planes passing through the atoms of the two planar acetylacetoneiminato-rings is 3.5°. Although it has been reported that the ethylendiamine ring is in the usual gauche conformation, the angle of rotation around the C–C bond is only 11.7°. A more marked distortion from planarity has been found in the anhydrous Cu(BAE),[11] in which strong interactions between pairs of complex molecules are involved. Thus it appears likely that, when no marked intermolecular interactions take place, the ligand planar conformation is essentially determined by the nature of the metal-ligand bonding.

The two acetylacetoneiminato rings are related by an approximate mirror plane normal to the molecular plane and passing through the cobalt atom and the middle point of the C–C bond of the ethylendiamine bridge. The average values of Co–O and Co–N bond lengths are 1.85 and 1.87 Å, respectively. The bond lengths and angles of the ligand have the expected values for a conjugated system.

Acknowledgments. We are grateful to prof. A. Ripamonti for helpful discussions. This research was supported by the Consiglio Nazionale delle Ricerche, Rome, Italy.

---

(11) D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 5897 (1963).