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The Crystal and Molecular Structure of N,N'-Ethylene-bis-(acetylacetoneiminato)methylcobalt(III)

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The crystal structure of N,N'-ethylene-bis-(acetylacetoneiminato)methyl-cobalt(III), $CoO_2N_2C_{13}H_{23}$, has been determined by the heavy atom method and refined to a conventional R*-value of 0.090 by the least-squares method using three-dimensional data. The crystals are orthorhombic, space group* $P2_12_12_1$*, with four molecules in the unit cell of dimensions* $a = 5.99 \pm 0.01$ Å, $b = 13.02 \pm 0.02$ Å, $c = 17.69 \pm 0.03$ Å. *The measured and calculated densities were 1.44 and 1.43 g . cm*$^{-3}$*, respectively.*

The crystal consists of monomeric molecules with a five-coordinate stereochemistry. The nearly planar tetradentate ligand occupies the four basal positions of a distorted rectangular-based pyramid, whose axial position is occupied by the methyl group.

The bond lengths are 1.87 ± 0.01 Å *(mean) for Co–O,* 1.87 ± 0.01 Å *(mean) for Co–N,* 1.95 ± 0.02 Å *for Co–*CH_3*.*

Introduction

One of the more remarkable features of organometallic derivatives of cobalt(III) complexes of bis-(acetylacetone)-ethylendiimine ($BAEH_2$) is the stability of the cobalt-carbon (alkyl or aryl) bond. In order to elucidate the nature of this bond we have recently reported the crystal structure of the vinylaquo(BAE)-Co^{III}[VACo(BAE)][1].

As part of this study we have now undertaken the crystal structure analysis of the low-spin pentacoordinate N,N' - ethylene - bis - (acetylacetoneiminato) - methyl-cobalt(III)[MeCoBAE].

Experimental Section

The needle-like dark-green crystals elongated along the *b*-axis, were kindly supplied by Professor G. Costa and Dr. G. Mestroni of this Institute.[2]

The cell dimensions, determined from precession photographs, taken with MoKα radiation, are: $a = 5.99 \pm 0.01$ Å, $b = 13.02 \pm 0.02$ Å, $c = 17.69 \pm 0.03$ Å. The calculated density, assuming four formula units, $CoO_2N_2C_{13}H_{23}$, per unit cell is 1.43 g.cm^{-3} in agreement with the value of 1.44 g.cm^{-3} of the density measured by the flotation method. The systematic absences, *h00* with *h* odd, *0k0* with *k* odd and *00l* with *l* odd, indicated the space group $P2_12_12_1$.

Intensity data were collected by the equi-inclination Weissenberg method using CoKα radiation. Levels *0kl* through *5kl* and *h0l* through *h9l* were recorded by the multiple film technique. The intensities of 819 independent reflections were measured by visual comparison with a standard scale and were placed in a common scale by cross-correlation terms.

The usual Lorentz and polarization corrections and the spot shape correction for non-zero levels were applied. No correction for absorption was made ($\mu = 27$ cm^{-1}, $\mu R = 0.1$-0.4).

All calculations were carried out on an IBM 7044 computer with programs written by A. Domenicano *et al.*[3,4]

The atomic scattering factors used were those of Hanson[5] *et al.* for oxygen, carbon and hydrogen, that of Berghuis[6] *et al.* for nitrogen and that listed in the International Tables of X-Ray Crystallography[7] for cobalt.

Structure determination

The coordinates of Co atom were easily determined from the Harker sections inspection on the three-dimensional Patterson synthesis. A set of structure factors calculated using only the cobalt atom gave an *R*-value of 0.41. From the cobalt-phased three-dimensional Fourier synthesis the remaining non-hydrogen atoms were located.

A structure factors calculation including all non-hydrogen atoms and using an overall temperature factor, *B* of 3 Å,^{2} gave an *R* value of 0.20. The atomic parameters were then refined by isotropic block-diagonal least-squares method. The *R*-value fell to 0.110 after five cycles.

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[1] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta, 2,* 416 (1968).

[2] G. Costa and G. Mestroni, *J. Organometal. Chem., 11,* 325 (1968).

[3] A. Domenicano and A. Vaciago, private communication.

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

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

[6] J. Berghuis, I. J. M. Haanappell, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst., 8,* 478 (1955).

[7] « International Tables for *X*-Ray Crystallography », vol. III, Kynoch Press, Birmingham (1962).

Table I. Positional parameters of non-hydrogen atoms and their estimated standard deviations in parentheses ($\times 10^4$).

	x	y	z
Co	0.0713(4)	−0.1082(2)	0.1232(1)
O(1)	−0.1195(19)	0.0025(8)	0.1030(6)
O(2)	−0.1237(17)	−0.1346(7)	0.2038(6)
N(1)	0.2421(21)	−0.0895(9)	0.0352(7)
N(2)	0.2308(21)	−0.2301(9)	0.1375(7)
C(1)	−0.2740(45)	0.1502(15)	0.0503(10)
C(2)	−0.0993(28)	0.0680(12)	0.0468(9)
C(3)	0.0461(27)	0.0620(13)	−0.0097(9)
C(4)	0.2136(31)	−0.0114(13)	−0.0136(9)
C(5)	0.3839(38)	−0.0082(15)	−0.0843(9)
C(6)	0.4314(32)	−0.1585(15)	0.0274(11)
C(7)	0.4263(35)	−0.2438(14)	0.0859(10)
C(8)	0.3544(32)	−0.3902(15)	0.1988(11)
C(9)	0.2059(32)	−0.2965(13)	0.1933(10)
C(10)	0.0296(25)	−0.2869(14)	0.2475(10)
C(11)	−0.1085(26)	−0.2072(13)	0.2513(8)
C(12)	−0.2966(35)	−0.2025(13)	0.3124(9)
C(13)	0.2772(31)	−0.0273(13)	0.1848(10)

Anisotropic block-diagonal least-squares refinement gave an R-value of 0.095 after three cycles. On a successive three-dimensional difference Fourier synthesis, estimated positions of the hydrogen atoms all occurred in regions of positive electron density. Three more cycles of refinement lowered the R-value to 0.090. The contribution of the hydrogen atoms was held constant with an overall temperature factor of 6 Å.^{2}

The weighting scheme used was:

$$w = 1/(5.0+1.0\,|Fo|+0.006\,|Fo|^2).$$

where the constant values were chosen so that the $w(|F_o|-|F_c|)^2$ value was essentially constant over all ranges of F_o.

No region of electron density exceeded ±0.4 e. Å^{-3} on the final $|F_o-F_c|$ synthesis.

Table II. 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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	293(5)	63(1)	32(1)	−7(7)	0(5)	5(2)
O(1)	348(35)	67(8)	35(4)	−73(32)	38(20)	−37(9)
O(2)	346(33)	52(7)	32(3)	18(28)	38(21)	−8(9)
N(1)	291(35)	56(9)	26(4)	72(37)	57(23)	4(10)
N(2)	304(38)	34(8)	30(4)	−36(33)	−38(27)	16(10)
C(1)	754(96)	71(13)	37(6)	−82(73)	−42(52)	−22(15)
C(2)	303(46)	60(11)	36(5)	−20(48)	−50(33)	3(13)
C(3)	272(47)	76(13)	33(5)	−7(48)	22(32)	−15(14)
C(4)	384(55)	81(14)	25(5)	77(52)	36(32)	4(14)
C(5)	560(74)	94(16)	34(5)	2(73)	103(41)	7(17)
C(6)	336(52)	89(14)	49(7)	−61(59)	37(47)	−18(17)
C(7)	390(56)	61(13)	43(6)	−31(62)	−16(44)	33(15)
C(8)	445(63)	74(14)	50(7)	−6(62)	−53(40)	−10(20)
C(9)	538(59)	54(12)	52(6)	−79(53)	−246(33)	11(17)
C(10)	197(40)	86(14)	45(6)	61(44)	29(31)	22(17)
C(11)	302(46)	72(12)	28(5)	44(48)	−37(33)	−10(13)
C(12)	579(68)	51(12)	35(5)	−6(56)	140(36)	−31(14)
C(13)	396(57)	60(13)	38(6)	−31(53)	−79(37)	−11(15)

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

	x	y	z
H(1C1)	−270	200	98
H(2C1)	−431	112	52
H(3C1)	−265	195	2
H(C3)	32	115	−54
H(1C5)	380	−80	−110
H(2C5)	547	10	−65
H(3C5)	334	50	−123
H(1C6)	581	−112	34
H(2C6)	434	−188	−28
H(1C7)	578	−243	119
H(2C7)	420	−316	59
H(1C8)	373	−427	145
H(2C8)	278	−444	236
H(3C8)	512	−371	219
H(C10)	7	−347	285
H(1C12)	−309	−275	336
H(2C12)	−451	−182	287
H(3C12)	−258	−147	354
H(1C13)	240	50	180
H(2C13)	439	−41	167
H(3C13)	257	−49	242

Atomic parameters and their standard deviations are listed in Table I, II, and III. The final observed and calculated structure factors are listed in Table IV. The e.s.d.'s in coordinates are derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle.

Discussion

Bond lengths are shown in Figure 1 together with the numbering scheme for the atoms. The bond lengths and angles are given in Table V together with their estimated standard deviations.

The crystal consists of monomeric molecules with a five-co-ordinate stereochemistry resulting from bonding to Co atom of a nearly planar tetradentate BAE ligand and a methyl group in the axial position. The projection of the structure onto (100) is shown in Figure 2. The geometry about the cobalt atom is closely represented by a rectangular-based pyramid, with the Co atom on the pyramidal axis, 0.12 Å above the basal plane of N(1), N(2), O(1), O(2) atoms.

Table IV. Observed and calculated structure factors (×10)

H	K	FO	|FC|
******L= 0******			
2	0	107	40
4	0	115	116
6	0	270	270
1	1	322	360
3	1	80	99
4	1	98	99
5	1	282	334
6	1	144	125
0	2	207	205
1	2	580	657
3	2	141	122
4	2	134	132
5	2	158	180
1	3	532	866
2	3	312	302
3	3	394	371
4	3	347	428
5	3	70	83
0	4	221	225
1	4	150	192
2	4	422	457
3	4	73	49
4	4	118	129
6	4	90	101
1	5	364	354
2	5	98	90
3	5	407	426
4	5	128	128
5	5	209	209
6	5	34	34
0	6	301	278
1	6	792	817
2	6	214	225
5	6	98	79
6	6	95	92
3	7	231	267
4	7	222	250
0	8	491	489
1	8	326	306
2	8	129	117
4	8	121	100
5	8	140	102
1	9	145	154
2	9	197	212
3	9	103	91
0	10	388	406
1	10	240	221
2	11	127	150
******L= 1******			
1	0	886	1020
2	0	118	109
3	0	49	21
4	0	135	136
5	0	178	193
6	0	164	149
0	1	1106	966
1	1	790	831
2	1	213	270
3	1	103	105
4	1	148	180
5	1	201	228
6	1	127	119
0	2	830	813
1	2	639	784
2	2	251	251
3	2	236	260
4	2	146	153
5	2	267	244
6	2	147	150
0	3	341	346
1	3	257	306
2	3	47	73
3	3	300	337
4	3	67	39
5	3	54	86
6	3	54	74
0	4	102	82
1	4	281	305
2	4	462	463
3	4	122	112
4	4	242	288
5	4	124	108
0	5	44	49
1	5	560	582
2	5	615	623
3	5	126	135
4	5	252	262
5	5	130	118
6	5	47	50
0	6	348	298
1	6	65	81
2	6	392	438
3	6	248	241
4	6	171	158
5	6	107	108
6	6	52	49
0	7	636	584
1	7	228	215
2	7	136	166
3	7	227	247
4	7	90	68
5	7	72	87
0	8	204	186
1	8	245	236
2	8	108	87
3	8	137	107
4	8	89	63
5	8	98	89
0	9	70	71
1	9	220	223
2	9	137	149
3	9	103	79
4	9	132	95
0	10	185	225
1	10	261	236
0	11	224	241
2	12	91	106
******L= 2******			
0	0	233	171
1	0	683	746
2	0	84	95
3	0	158	172
4	0	78	81
5	0	357	346
6	0	83	82
0	1	1236	1189
1	1	596	600
2	1	225	264
3	1	87	87
4	1	112	105
6	1	207	186
0	2	1137	914
1	2	841	707
2	2	407	515
3	2	64	65
4	2	352	402
5	2	136	128
6	2	43	57
0	3	381	336
1	3	599	729
2	3	348	384
3	3	294	313
4	3	73	55
5	3	177	182
6	3	84	70
0	4	43	55
1	4	204	231
2	4	340	400
3	4	550	585
4	4	216	234
5	4	100	108
0	5	699	677
1	5	328	321
2	5	291	324
3	5	106	97
5	5	87	80
6	5	135	113
1	6	481	477
2	6	265	271
3	6	246	263
4	6	172	177
5	6	114	112
0	7	176	151
1	7	421	433
2	7	89	103
3	7	102	96
5	7	101	108
1	8	68	65
2	8	267	283
3	8	172	175
4	8	110	132
5	8	143	122
0	9	420	428
1	9	186	173
2	9	180	176
0	10	118	105
1	10	154	143
3	10	128	116
1	11	251	248
0	12	208	243
2	12	122	146
******L= 3******			
1	0	302	369
3	0	99	92
4	0	308	353
5	0	118	135
0	1	930	836
1	1	891	836
2	1	245	283
3	1	280	339
4	1	155	195
5	1	182	201
6	1	79	80
0	2	612	519
1	2	975	963
2	2	374	375
3	2	328	298
4	2	128	125
5	2	194	199
6	2	121	102
0	3	873	726
1	3	559	628
2	3	588	685
3	3	335	342
4	3	231	241
5	3	135	146
6	3	56	55
0	4	193	223
1	4	292	344
2	4	201	244
3	4	348	345
4	4	238	232
5	4	104	86
6	4	85	76
0	5	40	57
1	5	399	386
2	5	260	255
4	5	214	200
5	5	94	91
0	6	408	340
1	6	180	160
2	6	237	258
3	6	199	193
4	6	112	104
5	6	84	68
0	7	492	462
1	7	348	345
2	7	193	205
3	7	200	205
4	7	97	92
5	7	114	145
0	8	453	467
1	8	242	227
3	8	155	167
4	8	131	127
5	8	87	71
0	9	92	101
1	9	303	305
2	9	224	234
4	9	144	170
0	10	100	104
1	10	363	269
2	10	123	114
0	11	131	133
0	12	119	138
******L= 4******			
0	0	234	267
1	0	771	820
2	0	259	243
3	0	196	171
4	0	132	156
6	0	126	134
0	1	271	257
1	1	390	380
2	1	543	508
3	1	402	456
4	1	185	226
5	1	88	87
0	2	285	216
1	2	906	859
2	2	416	446
3	2	352	389
4	2	225	216
5	2	151	132
0	3	743	613
1	3	582	546
2	3	548	531
3	3	246	276
4	3	410	435
5	3	111	108
6	3	82	83
0	4	146	170
1	4	472	475
2	4	479	406
3	4	69	54
4	4	124	91
5	4	119	118
6	4	52	67
0	5	115	105
1	5	225	221
2	5	156	202
3	5	418	422
4	5	105	94
5	5	52	88
0	6	352	329
1	6	357	351
2	6	146	134
3	6	115	99
4	6	51	53
5	6	131	133
0	7	322	281
1	7	186	151
2	7	270	318
4	7	152	162
0	8	548	514
1	8	310	303
2	8	156	221
3	8	53	71
4	8	85	63
1	9	219	197
3	9	253	263
0	10	157	233
2	10	166	180
0	11	105	110
2	11	125	166
3	11	106	94
******L= 5******			
1	0	250	265
2	0	251	305
3	0	103	90
4	0	216	214
5	0	51	43
0	1	241	249
1	1	174	183
2	1	488	466
3	1	267	189
4	1	241	251
5	1	106	107
6	1	81	81
0	2	677	574
1	2	413	401
2	2	276	300
3	2	462	505
4	2	50	64
0	3	47	30
1	3	225	197
2	3	511	526
3	3	414	409
4	3	166	167
5	3	66	61
6	3	70	66
0	4	63	104
1	4	507	506
2	4	853	757
3	4	332	311
4	4	312	300
5	4	115	92
0	5	255	232
1	5	221	220
2	5	237	224
3	5	264	239
4	5	201	197
5	5	63	58
0	6	166	162
1	6	332	303
2	6	267	273
3	6	203	212
4	6	120	104
0	7	436	386
1	7	130	132
2	7	197	215
3	7	211	215
5	7	81	83
0	8	155	147
1	8	307	296
2	8	235	239
3	8	123	104
4	8	102	79
5	8	76	94
0	9	176	144
1	9	256	229
2	9	154	150
3	9	114	93
0	10	145	158
1	10	125	120
1	11	229	189
3	11	108	140
******L= 6******			
1	0	191	185
2	0	443	446
3	0	547	542
4	0	230	209
5	0	163	179
0	1	420	362
1	1	483	449
2	1	428	422
3	1	144	143
4	1	129	118
5	1	117	117
6	1	55	51
0	2	125	121
1	2	207	163
2	2	615	607
3	2	212	202
4	2	313	311
6	2	54	64
0	3	113	126
1	3	645	653
2	3	291	247
3	3	135	143
4	3	72	70
5	3	116	127
6	3	37	30
0	4	237	223
1	4	327	327
2	4	305	245
3	4	507	506
4	4	220	187
5	4	90	84
0	5	70	74
1	5	198	176
2	5	478	453
3	5	188	167
4	5	93	70
1	6	141	123
2	6	285	295
3	6	322	331
4	6	234	266
5	6	75	77
0	7	131	142
1	7	368	358
2	7	86	93
3	7	107	98
5	7	65	70
0	8	125	133
1	8	240	202
2	8	144	136
3	8	52	87
4	8	115	103
0	9	570	534
1	9	122	95
2	9	127	97
2	10	170	202
3	10	145	168
1	11	157	137
2	12	86	106
******L= 7******			
1	0	827	899
2	0	748	702
4	0	207	223
5	0	109	86
0	1	213	194
1	1	305	319
2	1	319	294
3	1	222	231
4	1	200	194
5	1	67	76
6	1	52	95
0	2	357	370
1	2	379	344
2	2	287	290
3	2	323	306
4	2	107	130
6	2	75	78
0	3	161	152
1	3	137	91
2	3	315	294
3	3	330	301
4	3	172	142
6	3	72	63
0	4	125	108
1	4	215	204
2	4	340	329
3	4	212	171
4	4	155	176
5	4	54	79
0	5	84	56
1	5	207	190
2	5	413	419
3	5	170	157
4	5	231	273
5	5	77	71
0	6	260	288
1	6	143	144
2	6	240	226
3	6	315	321
4	6	122	110
0	7	221	224
1	7	167	155
2	7	102	105
3	7	233	250
5	7	47	82
0	8	266	273
1	8	260	214
2	8	220	275
4	8	57	107
1	9	203	177
1	10	276	285
2	10	57	81
2	11	84	105
******L= 8******			
0	0	459	459
1	0	253	213
2	0	581	553
1	1	259	362
2	1	257	279
3	1	303	336
4	1	210	201
5	1	110	116
0	2	78	85
1	2	483	405
2	2	43	49
3	2	124	119
5	2	111	115
0	3	225	194
1	3	430	417
2	3	458	419
3	3	59	101
4	3	136	134
5	3	52	75
0	4	157	184
1	4	181	156
2	4	217	244
3	4	88	73
5	4	77	62
0	5	95	85
1	5	248	227
2	5	197	191
3	5	492	550
4	5	95	93
5	5	77	94
0	6	347	320
1	6	232	209
2	6	113	105
3	6	336	359
0	7	191	164
2	7	284	339
4	7	153	171
0	8	199	204
1	8	267	262
1	9	153	144
2	9	145	126
0	10	179	218
2	10	121	142
2	11	122	136
******L= 9******			
1	0	313	325
2	0	298	247
3	0	103	92
4	0	209	207
0	1	485	447
1	1	588	552
2	1	142	161
3	1	72	78
4	1	89	88
5	1	112	128
0	2	496	445
1	2	250	215
2	2	147	133
3	2	263	238
5	2	78	88
0	3	446	366
1	3	240	226
2	3	237	191
3	3	344	313
4	3	123	109
5	3	109	96
0	4	99	119
1	4	143	147
2	4	264	242
4	4	219	198
5	4	63	53
0	5	197	207
1	5	273	260
2	5	252	248
3	5	150	144
4	5	141	155
5	5	63	46
0	6	210	187
1	6	328	315
2	6	263	259
3	6	207	193
4	6	133	139
5	6	84	86
0	7	297	304
1	7	210	195
2	7	206	219
3	7	87	87
4	7	78	78
0	8	272	285
1	8	113	105
2	8	130	110
3	8	196	125
1	9	235	215
2	9	132	113
******L= 10******			
0	0	284	275
1	0	150	153
3	0	275	308
4	0	115	123
0	1	509	474
1	1	306	315
2	1	222	236
4	1	75	87
5	1	92	95
0	2	302	295
1	2	134	122
2	2	343	313
3	2	105	95
4	2	187	186
0	3	455	401
1	3	428	356
2	3	176	133
3	3	112	88
4	3	73	62
5	3	100	68
1	4	274	262
2	4	192	198
3	4	268	257
4	4	159	128
5	4	163	142
0	5	387	397
2	5	170	175
4	5	100	47
0	6	187	153
1	6	253	224
2	6	171	161
3	6	112	114
4	6	152	134
5	6	51	66
1	7	326	338
2	7	156	184
3	7	206	238
4	7	71	62
0	8	150	165
2	8	150	157
3	8	115	105
4	8	124	146
0	9	254	285
1	9	145	110
2	9	116	111
******L= 11******			
1	0	246	228
2	0	306	312
0	1	172	213
1	1	194	202
3	1	115	133
4	1	114	110
5	1	79	82
0	2	553	516
1	2	311	293
2	2	213	203
3	2	167	174
5	2	127	114
0	3	186	160
1	3	198	175
2	3	284	250
3	3	193	180
4	3	93	91
5	3	155	135
0	4	156	145
1	4	317	293
2	4	66	41
3	4	161	140
4	4	120	91
5	4	57	49
1	5	219	192
2	5	221	231
4	5	89	93
0	6	270	284
1	6	164	157
3	6	92	87
4	6	93	90
0	7	211	253
2	7	143	164
3	7	82	98
0	8	109	105
1	8	242	215
2	8	160	183
0	9	138	115
1	9	170	138
2	9	116	128
1	11	108	74
******L= 12******			
0	0	414	473
0	1	64	84
2	1	197	219
3	1	104	102
4	1	123	123
5	1	111	108
0	2	68	65
1	2	351	387
2	2	127	126
5	2	73	68
0	3	101	89
1	3	163	130
2	3	201	178
3	3	141	125
4	3	230	197
5	3	84	102
0	4	455	640
1	4	205	194
2	4	183	182
4	4	55	72
0	5	74	77
1	5	124	114
2	5	135	158
3	5	114	131
4	5	55	76
0	6	234	227
1	6	255	257
3	6	78	86
4	6	71	54
0	7	135	138
1	7	56	114
2	7	106	108
0	8	176	170
1	8	154	148
2	8	88	75
1	9	125	112
1	10	115	108
******L= 13******			
1	0	192	203
4	0	136	134
0	1	209	214
1	1	291	298
2	1	144	170
4	1	67	75
0	2	116	115
1	2	165	172
2	2	126	120
3	2	175	156
0	3	367	375
1	3	52	76
2	3	51	97
3	3	155	143
4	3	105	88
1	4	246	248
2	4	120	93
3	4	85	80
4	4	51	87
0	5	121	132
1	5	162	158
4	5	84	85
0	6	183	155
1	6	122	114
2	6	142	135
3	6	70	67
4	6	64	95
0	7	175	206
3	7	67	77
0	8	110	113
2	8	71	72
1	9	152	162
2	9	88	103
******L= 14******			
0	0	216	208
1	0	161	205
3	0	125	117
0	1	344	388
1	1	152	218
2	1	82	95
3	1	45	43
4	1	31	35
2	2	188	165
3	2	74	84
4	2	184	178
0	3	64	55
1	3	155	140
2	3	150	124
3	3	148	115
2	4	123	130
3	4	215	195
4	4	62	55
0	5	158	232
1	5	210	210
2	5	135	155
2	6	122	115
3	6	76	69
1	7	152	184
2	7	68	70
0	8	90	53
2	8	55	52
0	9	128	121
******L= 15******			
1	0	258	285
0	1	171	141
1	1	113	131
2	1	42	75
3	1	55	57
4	1	75	84
0	2	123	136
2	2	83	52
3	2	72	48
0	3	86	89
1	3	224	232
2	3	152	159
3	3	174	140
1	4	104	103
3	4	61	54
0	5	84	73
1	5	144	148
2	5	163	155
0	6	120	86
1	6	149	131
2	6	125	124
3	6	70	79
0	7	55	108
2	7	61	67
******L= 16******			
0	0	265	290
0	1	156	193
2	1	85	95
3	1	141	138
1	2	175	207
2	2	78	90
3	2	90	47
0	3	127	125
1	3	62	65
2	3	121	105
3	3	72	71
0	4	133	123
2	4	138	133
3	4	58	46
1	5	82	76
0	6	105	84
1	6	141	138
2	6	94	98
******L= 17******			
1	1	102	116
2	1	105	116
3	1	44	57
0	2	153	140
1	2	88	113
2	2	53	66
3	2	108	125
0	3	76	88
2	3	55	71
1	4	86	83
2	4	122	131
1	5	91	89
1	6	61	53
1	7	43	44
******L= 18******			
1	1	82	92
2	1	69	82
0	2	100	104
2	2	102	122
0	3	62	73
1	3	135	140
2	3	60	65
0	4	72	71
1	4	57	55
0	5	128	130
******L= 19******			
0	1	72	93
0	2	80	92
0	3	55	79

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

Co—O(1)	1.874(11) Å	N(1)—Co—N(2)	86.7(5)°
Co—O(2)	1.871(11)	N(1)—Co—C(13)	92.6(6)
Co—N(1)	1.876(13)	N(2)—Co—C(13)	93.4(6)
Co—N(2)	1.870(12)	Co—O(1)—C(2)	125.9(10)
Co—C(13)	1.952(18)	O(1)—C(2)—C(1)	111.6(14)
O(1)—C(2)	1.313(19)	O(1)—C(2)—C(3)	126.1(15)
O(2)—C(11)	1.266(19)	C(1)—C(2)—C(3)	122.1(15)
N(1)—C(4)	1.342(20)	C(2)—C(3)—C(4)	123.6(15)
N(1)—C(6)	1.453(23)	C(3)—C(4)—C(5)	118.6(14)
N(2)—C(7)	1.494(23)	C(3)—C(4)—N(1)	125.6(15)
N(2)—C(9)	1.318(21)	C(5)—C(4)—N(1)	115.7(14)
C(1)—C(2)	1.498(28)	C(4)—N(1)—C(6)	120.5(14)
C(2)—C(3)	1.325(23)	C(4)—N(1)—Co	124.0(11)
C(3)—C(4)	1.387(24)	Co—N(1)—C(6)	115.0(10)
C(4)—C(5)	1.611(25)	N(1)—C(6)—C(7)	111.9(15)
C(6)—C(7)	1.516(26)	C(6)—C(7)—N(2)	110.0(15)
C(8)—C(9)	1.513(26)	C(7)—N(2)—Co	114.8(10)
C(9)—C(10)	1.430(25)	C(7)—N(2)—C(9)	117.7(14)
C(10)—C(11)	1.329(24)	Co—N(2)—C(9)	126.8(11)
C(11)—C(12)	1.560(24)	C(8)—C(9)—C(10)	117.5(15)
O(1)—Co—O(2)	84.5(4)°	N(2)—C(9)—C(10)	121.7(16)
O(1)—Co—N(1)	94.3(5)	N(2)—C(9)—C(8)	120.7(16)
O(1)—Co—N(2)	172.1(5)	C(9)—C(10)—C(11)	124.2(16)
O(1)—Co—C(13)	94.4(6)	C(10)—C(11)—C(12)	121.0(15)
O(2)—Co—N(1)	173.3(5)	C(10)—C(11)—O(2)	126.5(15)
O(2)—Co—N(2)	93.5(5)	O(2)—C(11)—C(12)	112.0(13)
O(2)—Co—C(13)	94.1(6)	C(11)—O(2)—Co	126.5(10)

The C(13) atom is 2.07 Å above this plane and lies, within the experimental errors, at the apex of the rectangular-based pyramid. The planes through the two chemically equivalent halves make an angle of 4.0°.

The C(6) and C(7) atoms lie above the plane passing through all the other atoms of the tetradentate ligand (0.20 and 0.15 Å respectively). The ethylendiamine bridge, as in the tetracoordinate parent compound Co(BAE), is in eclipsed conformation, the torsional angle around the C(6)-C(7) bond being 2.3°. The least-squares planes of interest are given in Table VI, together with the distances of the individual atoms from these planes. These planes were calculated according to Schomaker *et al.*[8] with unitary weights for all the atoms. The equations are referred to the crystal axes and *x*, *y*, *z* are fractional coordinates.

Table VI. Equations of least-squares planes and distances of atoms (in Å) from the planes

1) Plane through O(1), O(2), N(1) and N(2)

$3.719\,x - 7.077\,y + 9.958\,z = 0.608$

O(1)	0.009 Å	N(1)	−0.009 Å
O(2)	−0.009	N(2)	0.009

2) Plane through O(1), O(2), N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(8), C(9), C(10), C(11) and C(12)

$3.740\,x - 7.088\,y + 9.876\,z = 0.565$

O(1)	0.023 Å	C(4)	0.018 Å
O(2)	0.031	C(5)	−0.021
N(1)	0.052	C(8)	−0.043
N(2)	0.025	C(9)	0.012
C(1)	−0.029	C(10)	−0.044
C(2)	0.007	C(11)	0.042
C(3)	−0.049	C(12)	−0.025

3) Plane through O(1), N(1), C(1), C(2), C(3), C(4) and C(5)

$3.716\,x - 7.419\,y + 9.501\,z = 0.566$

O(1)	−0.013 Å	C(3)	−0.027 Å
N(1)	0.004	C(4)	0.014
C(1)	0.008	C(5)	−0.001
C(2)	0.014		

4) Plane through O(2), N(2), C(8), C(9), C(10), C(11) and C(12)

$3.750\,x - 6.783\,y + 10.228\,z = 0.720$

O(2)	−0.012 Å	C(10)	−0.023 Å
N(2)	−0.008	C(11)	0.039
C(8)	−0.004	C(12)	−0.010
C(9)	0.019		

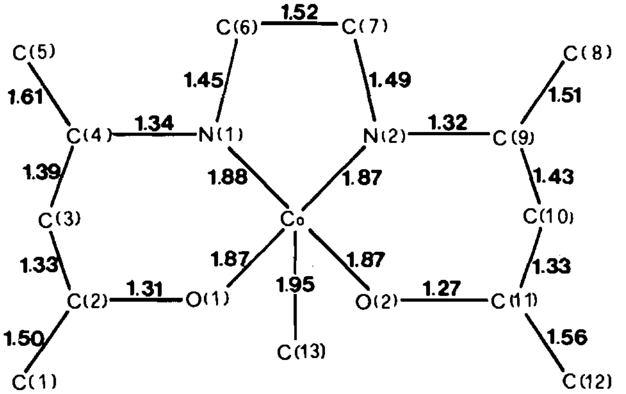

Figure 1. Bond lengths and numbering scheme for the atoms of the molecule.

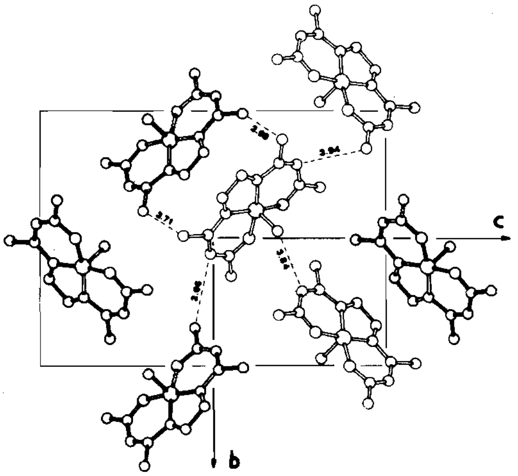

Figure 2. Projection of the structure onto (100).

The displacement of the Co atom above the basal plane is smaller than that found in other square-pyramidal structures involving the cobalt atom [0.39 Å in {(paphyl)Co}Cl$_2$ [9] and 0.54 Å in Co(NO)-(S$_2$CN(CH$_3$)$_2$)$_2$ [10]]. This can be explained in terms of the partecipation of the cobalt electrons in the π-orbitals of the conjugate system of the chelate rings. In fact, Furlani[11] recently reported that a square complex represents perhaps the best condition for efficient π-back-bonding as well as a « regular » square pyramid, while a distorted pyramid (central atom out of plane) is in a worse situation. The geometry of MeCoBAE seems to be due to a compromise between the necessity of planarity for optimum π-bonding and the best σ-overlap in the Co—C bond. In fact, the Co—CH$_3$ bond of 1.95 Å seems relatively strong as compared with the other values found for the Co—C σ-bond. The eclipsed conformation of the ethylendiamine bridge is in agreement with this hypothesis. This conformation is very similar to that found for the tetracoordinate Co-(BAE),[12] which adopts an exact planar geometry in spite of the more stable gauche conformation of the ethylendiamine bridge. It seems likely that in the octahedral VACo(BAE)[1] the π-effect imposes less strict conditions (the ethylendiamine bridge is twisted) because of the steric effects of the σ-bonded vinyl group on the tetradentate ligand.

After correction for the different covalent radii of the sp^2 and sp^3 carbon atom, the value of the Co—CH$_3$ bond length is greater than that of the Co—C(sp^2) bond found in the VACo(BAE). This lengthening, if significant (~0.04 Å), can be discussed *via* electrostatic model or *via* $d_\pi \rightarrow p_\pi$ back-donation (metal to ligand).

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Table VII. Non-bonded distances below 4 Å

C(8)—C(12)	I	3.79(3)
C(9)—C(12)	I	3.85(3)
O(1)—C(6)	II	3.66(2)
O(1)—C(13)	II	3.91(2)
O(2)—C(7)	II	3.69(2)
O(2)—C(13)	II	3.87(2)
C(1)—C(4)	II	3.89(3)
C(1)—C(5)	II	3.75(3)
C(2)—C(5)	II	3.99(3)
C(3)—C(12)	III	3.93(2)
C(13)—C(8)	IV	3.50(3)
C(1)—C(3)	V	3.96(3)
O(1)—C(10)	VI	3.84(2)
O(2)—C(8)	VI	3.87(2)
C(1)—C(10)	VI	3.94(3)
C(5)—C(8)	VII	3.71(3)
C(5)—C(9)	VII	3.73(3)
C(6)—N(1)	VII	3.93(2)
C(6)—N(2)	VII	3.71(2)
C(6)—C(6)	VII	3.95(3)
C(6)—C(7)	VII	3.79(3)
C(7)—N(1)	VII	3.58(2)
C(7)—C(4)	VII	3.84(3)
C(7)—C(6)	VII	3.84(3)
C(8)—C(5)	VII	3.99(3)

no label	x,	y,	z
I	$1+x$,	y,	z
II	$-1+x$,	y,	z
III	$-\frac{1}{2}-x$,	$-y$,	$-\frac{1}{2}+z$
IV	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
V	$-\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	$-z$
VI	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
VII	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$

However, we believe that many factors, which are usually neglected, as the different co-ordination about the metal atom and the different nature of of the other coordinated ligands, affect the metal-carbon distances. Therefore it is not surprising that, for example, the Co—CH_3 distance of 1.95 Å is very different from the Co—CH_2COOCH_3 distance of 2.05 Å in the octahedral O-methyl-(Co—C)carboxymethyl-(bis-dimethylglyoximato)pyridinate-cobalt(III).[13]

If one considers that the lengthening of the Co—O distances in VACo(BAE) can be ascribed to the intermolecular hydrogen bonds in which these oxygen atoms are involved, no significant difference can be noted in the bond lengths and angles of the tetradentate ligand and in those involving the cobalt atom, for this and related complexes.

Non-bonded intermolecular distances below 4 Å are given in Table VII.

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