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

The Crystal and Molecular Structure of (1-diacetylmonoximatoimino-3-diacetylmonoximeimino-propane)-methylaquocobalt(III) Perchlorate

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

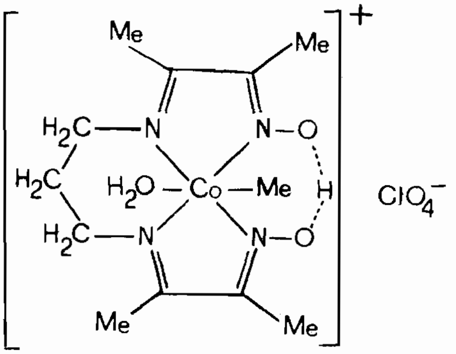
Received January 18, 1969

The crystal and molecular structure of (1-diacetylmonoximato-imino - 3 - diacetylmonoximeimino-propane) methylaquocobalt(III) perchlorate has been determined by X-ray analysis. The final R value was 0.112. The compound belongs to the orthorhombic system, space group Fdd2, with a = 41.96 Å, b = 25.96 Å, and c = 6.89 Å, Z = 16. The crystals are built from organometallic cations and perchlorate anions. The coordination about the Co atom is that of a distorted octahedron. The tetradentate ligand occupies the equatorial sites while the water molecule and the methyl group in the axial positions complete the coordination polyhedron. The Co—CH_3 distance is 1.99±0.04 Å.

Introduction

Recently Costa and Mestroni,[1] using the bis-(diacetyl-monoximeimino)propane-1,3 [$(DOH)_2pn$] as tetradentate ligand, succeeded in preparing novel organo-cobalt complexes which are the first examples of stable water soluble organo-cobalt compounds besides the vitamine B_{12} coenzyme and the alkylcobalamines.

The perchlorate of the methylaquo derivative $[CH_3Co^{III}\{(DO)(DOH)pn\}H_2O]ClO_4$ was formulated as:



The interesting features of this compound prompted us to undertake a three-dimensional X-ray analysis in order to prove the postulated structure.

Experimental Section

Single red orthorhombic crystals elongated along [001], prepared as previously described,[1] were kindly supplied by Prof. G. Costa and Dr. G. Mestroni of this Institute.

The cell dimensions, determined from precession photographs, taken with MoKα radiation, are: a = 41.96±0.05 Å, b = 25.96±0.03 Å, c = 6.89±0.01 Å. The calculated density, assuming 16 formula units, $CoO_3N_4C_{12}H_{24}ClO_4$, in the unit cell is 1.53 g . cm^{-3}.

The density measured by flotation method is 1.53 g . cm^{-3}. The systematic absences, hkl all even or all odd, 0kl with k+1 = 4n and h0l with h+1 = 4n indicated the space group Fdd2.

Intensity data were collected by the equi-inclination Weissenberg method using MoKα radiation. Levels hk0 through hk6 were collected by the multiple film technique. The precession h0l, 0kl, hhl, h3hl, 3hhl levels were recorded with MoKα radiation in order to provide the cross-correlation terms. An approximately cylindrical crystal of mean diameter of ca. 0.15 mm was used. The intensities of 796 independent reflections were measured by visual comparison with a standard scale and were placed in a common scale by cross-level data. Lorentz and polarization factors and the spot-shape correction, for non-zero Weissenberg levels, were applied. No correction for absorption was made (μ = 11 cm^{-1} and $\mu R \cong 0.08$).

All calculations were carried out on an IBM 7044 computer with programs written by A. Domenicano *et al.*[2,3]

The atomic scattering factors used were those of Hanson *et al.*[4] for chlorine, oxygen, carbon and hydrogen, that of Berghuis *et al.*[5] for nitrogen and that listed in the International Tables for X-Ray Crystallography[6] for cobalt.

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(1) G. Costa and G. Mestroni, *Tetrahedron Letters, 41,* 4005 (1967).

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

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

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

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

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

Structure Determination

Approximate coordinates for the cobalt atom were readily determined from peaks location on a three-dimensional Patterson map. A cobalt-phased three-dimensional Fourier synthesis showed the chlorine atom and the six atoms coordinated around the cobalt atom. A three-dimensional electron-density map was then calculated, the phases of the structure factors being determined by the contributions of the atoms located in the previous stage. The two axial substituents were considered as carbon atoms because at this stage it was not possible to distinguish between CH_3 and H_2O groups. The Fourier map revealed the position of the remaining atoms. The peaks around the Cl atom, identified as oxygen atoms, were diffuse and somewhat low in electronic density as expected for an oxygen atom. The possible hydrogen bond formation between the water molecules and the perchlorate oxygen atoms indicated the water molecule location. The structure factors calculation, phased by all the non-hydrogen atoms, gave a R-value of 0.25. The atomic parameters were then refined by isotropic block-diagonal least-squares method. The R-value fell to 0.135 after five cycles. The weighting scheme used was: $w = 1/(40.0+1.0\,|F_o| + 0.01\,|F_o|^2)$. A final block-diagonal least-squares refinement, using anisotropic temperature factors for Co and Cl atoms, lowered the R-value to 0.112.

No region of electronic density exceeded ± 0.6 e $Å^{-3}$ on the final $|F_o-F_c|$ synthesis.

No attempt was made to include the hydrogen atom contribution. The final parameters of all non-hydrogen atoms are listed in Table I together with their estimated standard deviations. Observed and calculated structure factors are listed in Table II.

Discussion

The bond lengths, together with the numbering scheme for the atoms of the cation, are shown in Figure 1.

All the bond lengths and angles are given in Table III, together with their standard deviations. The standard deviations are quite large. In fact, it would have been necessary to measure more intensities ($\sin\vartheta/\lambda \leqslant 0.5$) in order to obtain greater precision, but in this determination we were more interested in the elucidation of the overall geometry.

The coordination about the cobalt atom is that of a distorted octahedron, the cobalt atom and the four nitrogen atoms lying in the equatorial plane. The water molecule and the methyl group occupy the axial positions. The cobalt atom and the four nitrogen atoms of the tetradentate ligand are planar within 0.05 Å. The geometry of the tetradentate ligand was analyzed by considering the equations of the best least-square planes calculated according to Schomaker *et al.*[7] with unitary weights for all the atoms. The equations of the best planes are given in Table IV together with the distances of the individual atoms from the planes.

The planes passing through the two halves of the chelate make a dihedral angle of 2.7°.

Table I. Atomic parameters with their estimated standard deviations in parentheses

	x/a	y/b	z/c	B($Å^2$)
Co	0.0520(1)	0.1210(1)	0.0041(12)	^{a}
O(1)	0.0872(6)	0.1510(9)	−0.3356(38)	4.6(5)
O(2)	0.0368(5)	0.1929(8)	−0.3006(36)	3.9(5)
O(3)	0.0287(5)	0.0628(8)	−0.1630(36)	3.7(5)
N(1)	0.0873(8)	0.1209(11)	−0.1602(53)	5.0(7)
N(2)	0.0783(6)	0.0703(10)	0.1358(39)	2.9(6)
N(3)	0.0171(6)	0.1227(9)	0.1849(37)	2.8(5)
N(4)	0.0280(7)	0.1719(10)	−0.1220(44)	3.5(6)
C(1)	0.1377(10)	0.0824(14)	−0.2632(73)	5.4(9)
C(2)	0.1094(9)	0.0890(13)	−0.1271(59)	3.9(8)
C(3)	0.1045(7)	0.0583(12)	0.0573(49)	3.1(7)
C(4)	0.1299(10)	0.0219(15)	0.1531(69)	5.5(9)
C(5)	0.0681(8)	0.0461(13)	0.3216(56)	4.1(8)
C(6)	0.0303(9)	0.0394(14)	0.3463(61)	4.4(8)
C(7)	0.0138(9)	0.0934(14)	0.3656(60)	4.3(8)
C(8)	−0.0356(9)	0.1645(13)	0.2512(66)	4.7(8)
C(9)	−0.0061(8)	0.1532(13)	0.1355(55)	3.7(7)
C(10)	−0.0003(8)	0.1820(11)	−0.0516(46)	2.8(6)
C(11)	−0.0221(9)	0.2199(13)	−0.1446(63)	4.3(8)
C(12)	0.0755(8)	0.1748(13)	0.1514(56)	4.0(8)
Cl	0.1872(2)	0.1843(3)	0.0727(16)	^{a}
O(4)	0.1675(10)	0.1505(15)	0.1538(71)	10.4(11)
O(5)	0.2028(11)	0.1523(19)	−0.0580(84)	13.0(14)
O(6)	0.2103(9)	0.2046(14)	0.1961(63)	9.8(11)
O(7)	0.1711(9)	0.2227(14)	−0.0270(72)	10.1(10)

	10^5B_{11}	10^5B_{22}	10^5B_{33}	10^5B_{12}	10^5B_{13}	10^5B_{23}
Co	15(2)	52(4)	1515(66)	5(7)	31(26)	−109(46)
Cl	40(5)	86(11)	3019(252)	−12(13)	60(63)	−158(99)

[a] For the cobalt and chlorine atoms temperature factors of the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$ were used; resulting thermal coefficients (with standard deviations in parentheses) are given in the lower part of the Table.

Table II. Observed and calculated structure factors

H	L	FO	FC
******K=		0******	
2	2	220	298
2	6	237	211
4	0	360	369
6	2	121	69
6	6	110	91
8	0	356	565
8	4	207	223
10	2	194	126
10	6	135	129
12	0	196	154
12	4	218	246
14	2	207	146
14	6	118	110
16	4	129	135
18	2	398	436
18	6	102	68
20	4	236	276
22	2	249	299
24	4	145	178
26	2	125	117
26	6	107	94
28	0	113	113
28	4	126	116
30	2	235	238
30	6	89	85
32	4	80	97
34	2	158	126
36	0	219	194
36	4	85	53
38	2	224	217
******K=		1******	
1	1	591	606
1	3	118	86
1	5	84	71
3	1	239	216
3	3	201	207
3	5	70	73
5	1	49	49
5	3	104	100
5	5	95	95
7	1	355	375
7	3	148	152
9	1	312	286
9	3	142	150
9	5	117	118
11	3	159	147
11	5	102	108
13	1	224	219
13	3	132	124
15	1	133	149
15	3	217	203
15	5	161	115
17	1	320	299
17	3	115	89
17	5	78	55
19	3	98	111
19	5	118	124
21	1	290	250
21	3	220	229
21	5	55	64
23	1	89	96
23	3	150	161
25	1	67	62
25	3	88	81
25	5	109	131
27	1	89	85
27	3	78	65
27	5	94	107
29	1	89	68
29	3	91	104
29	5	90	73
31	1	103	122
31	3	91	85
33	3	87	43
33	5	94	91
35	1	199	210
37	1	129	146
******K=		2******	
0	2	228	219
0	6	54	59
2	2	209	214
2	4	127	130
2	6	124	119
4	0	366	509
4	2	147	117
4	4	98	64
6	0	330	452
6	2	308	345
6	6	157	150
8	0	143	115
8	2	217	200
8	4	117	120
8	6	66	98
10	0	215	203
10	2	294	308
10	6	78	70
12	0	153	163
12	2	135	122
12	4	211	238
14	0	159	118
14	2	397	443
16	2	156	162
16	4	210	212
18	0	67	12
18	2	151	122
20	0	87	65
20	2	92	65
22	0	103	99
22	2	259	273
24	0	211	205
24	4	189	232
26	0	63	70
26	2	123	131
26	6	96	98
28	0	60	81
28	2	83	48
30	0	63	46
30	2	113	87
32	0	213	216
32	2	95	79
32	4	93	96
34	2	152	135
36	0	221	215
******K=		3******	
1	1	358	374
1	3	63	65
1	5	65	42
3	1	257	243
3	3	141	144
3	5	45	42
5	1	436	422
5	3	147	159
5	5	111	132
7	1	245	209
7	3	164	145
7	5	57	71
9	1	254	200
9	3	104	103
9	5	108	113
11	1	179	184
11	3	206	224
11	5	98	100
13	1	183	162
13	3	234	268
15	1	143	137
15	3	180	188
15	5	100	111
17	1	343	317
17	3	92	99
19	3	95	102
19	5	121	137
21	1	206	165
21	3	213	248
23	1	83	52
23	3	165	180
23	5	67	77
25	1	122	133
25	3	95	99
25	5	77	93
27	1	95	103
27	3	75	72
27	5	80	79
29	1	93	101
29	3	99	105
31	1	96	120
33	1	106	116
35	1	142	168
37	1	89	110
39	1	104	104
******K=		4******	
0	0	799	887
0	4	125	134
2	0	54	28
2	2	230	207
2	6	129	119
4	0	166	155
4	2	171	156
4	4	87	83
6	0	383	343
6	2	196	175
6	6	74	66
8	0	260	290
8	2	200	175
8	4	172	164
10	0	390	422
10	2	281	291
10	4	129	105
10	6	86	81
12	2	221	220
12	4	222	259
14	0	165	144
14	4	106	118
16	0	108	85
16	2	112	84
16	4	106	105
18	2	270	254
18	4	115	110
18	6	90	98
20	0	317	334
20	2	152	130
20	4	165	164
22	2	123	112
22	4	97	92
22	6	72	68
24	2	116	65
26	2	109	101
26	6	69	66
28	0	276	282
28	4	124	132
30	0	123	72
30	2	164	156
30	6	97	108
32	0	164	147
34	0	130	103
36	0	179	148
38	2	160	168
******K=		5******	
1	1	140	117
1	3	112	82
1	5	149	141
3	1	533	538
3	5	99	110
5	1	506	525
5	3	129	108
5	5	141	145
7	1	477	499
7	3	50	35
7	5	75	52
9	1	125	108
9	3	64	67
9	5	118	125
11	1	234	244
11	3	204	235
11	5	86	75
13	1	206	195
13	3	81	48
13	5	113	121
15	1	212	231
15	3	113	116
17	3	140	133
17	5	99	112
19	1	131	156
19	3	155	186
19	5	105	92
21	1	180	167
21	3	109	109
23	5	96	83
25	1	73	45
25	3	110	111
27	1	94	120
27	3	146	179
27	5	63	69
29	1	94	89
29	3	109	123
29	5	84	84
31	1	141	162
31	3	98	110
33	1	80	79
33	3	84	92
35	1	115	136
35	3	87	96
39	1	84	93
******K=		6******	
0	2	335	345
0	6	64	58
2	0	104	100
2	2	198	172
2	4	158	153
2	6	53	86
4	0	358	421
4	2	65	55
4	4	158	221
6	0	212	251
6	2	375	364
6	4	76	59
6	6	107	98
8	0	70	59
8	2	112	67
8	4	101	116
8	6	63	75
10	0	160	178
10	2	124	115
12	0	215	282
12	2	58	85
12	4	176	151
12	6	55	37
14	2	370	379
14	6	100	89
16	0	181	152
16	2	155	143
16	4	131	135
18	0	128	154
18	2	157	153
18	6	81	51
20	0	188	189
22	0	150	137
22	2	137	97
22	6	118	119
24	0	326	377
24	2	118	96
24	4	126	123
26	0	166	161
26	2	157	154
26	6	105	93
28	0	78	66
30	0	70	51
32	0	264	252
32	2	51	59
32	4	82	93
34	2	134	143
******K=		7******	
1	1	233	201
1	3	140	164
1	5	55	99
3	1	357	375
3	3	88	95
3	5	111	95
5	1	247	253
5	3	135	139
5	5	147	172
7	1	352	368
7	3	216	244
7	5	85	87
9	1	145	192
9	3	151	149
9	5	89	84
11	1	435	432
11	3	157	168
13	1	52	101
13	3	122	121
13	5	112	127
15	1	220	199
15	3	157	155
15	5	92	65
17	1	260	259
19	1	145	162
19	3	113	99
21	1	201	176
23	1	83	85
23	3	79	76
23	5	110	125
25	1	207	226
25	3	131	146
27	1	134	141
27	3	65	102
29	1	109	113
31	3	69	72
33	1	115	138
33	3	97	102
35	3	115	126
******K=		8******	
0	0	282	270
0	4	230	261
2	0	78	57
2	2	359	362
2	4	97	103
2	6	64	67
4	0	83	60
4	2	121	107
4	4	95	77
6	2	243	233
6	4	99	104
8	2	120	116
8	4	213	229
10	0	90	101
10	2	422	492
12	0	91	59
12	4	112	122
14	0	80	74
14	6	85	87
16	0	138	87
16	2	115	124
16	4	107	95
18	2	185	202
18	6	84	90
20	0	280	315
20	2	60	46
20	4	108	109
22	0	123	99
22	2	135	122
22	6	101	102
24	0	111	100
24	2	82	76
24	4	130	143
26	2	164	183
28	0	385	420
28	4	111	117
30	0	133	121
30	2	134	119
32	0	213	218
34	2	107	96
38	2	125	99
******K=		9******	
1	1	95	77
1	3	168	196
1	5	110	118
3	1	105	125
3	3	87	84
3	5	88	91
5	1	149	133
5	3	158	164
5	5	107	90
7	1	310	230
7	3	125	139
7	5	64	54
9	1	61	73
9	3	228	257
9	5	78	104
11	1	331	306
11	3	137	163
13	1	103	123
13	3	97	84
13	5	102	103
15	1	80	73
17	1	81	82
17	3	192	211
19	1	142	161
19	3	132	136
21	1	168	113
21	3	107	137
23	1	71	73
25	1	218	222
25	3	65	65
27	1	95	109
27	3	108	97
29	1	154	170
31	1	144	155
33	1	101	111
35	1	94	99
******K=		10******	
0	2	107	99
0	6	63	67
2	0	109	88
2	2	192	176
2	4	113	108
2	6	54	36
4	0	241	262
4	2	132	116
4	4	239	255
6	0	94	103
6	2	236	179
6	6	100	89
8	0	182	148
8	2	203	203
8	4	137	128
10	2	310	341
10	4	81	77
12	0	253	360
12	2	247	244
12	4	180	142
14	0	65	40
14	2	244	210
14	6	122	120
16	0	267	292
16	2	108	69
16	4	108	125
18	0	86	70
18	2	122	113
20	0	169	192
20	2	84	54
22	0	111	118
22	2	127	101
22	6	58	108
24	0	230	343
24	2	73	62
26	2	172	167
30	0	167	133
30	4	94	75
32	0	153	144
32	2	106	81
32	4	78	111
34	2	186	191
******K=		11******	
1	1	118	111
1	3	75	70
1	5	55	93
3	1	191	192
3	3	81	51
3	5	112	123
5	1	118	137
5	3	156	170
5	5	121	131
7	1	157	149
7	3	165	190
7	5	65	72
9	1	60	51
9	3	182	194
9	5	100	108
11	1	303	390
11	3	62	64
13	1	129	156
13	5	135	163
15	1	189	224
15	3	111	110
17	1	109	121
17	3	55	102
19	1	156	167
19	3	119	121
21	1	89	101
23	5	90	96
25	1	193	184
27	1	190	171
29	1	104	102
31	1	83	87
35	3	127	140
******K=		12******	
0	0	236	203
0	4	200	222
2	0	81	53
2	2	174	174
2	4	78	67
2	6	99	106
4	0	142	135
4	2	128	134
4	4	83	61
6	0	242	213
6	2	151	135
6	4	70	65
8	0	293	268
8	2	118	100
8	4	151	158
10	0	141	115
10	2	299	301
10	4	119	133
10	6	77	100
12	0	259	215
12	4	88	82
14	0	212	229
14	2	76	80
14	4	87	95
18	0	133	97
18	2	197	211
20	0	208	191
20	2	135	97
20	6	114	128
22	0	158	151
22	2	149	158
26	2	142	112
28	0	212	224
30	2	111	124
32	0	78	82
32	2	69	78
38	2	116	124
******K=		13******	
1	1	137	148
1	3	185	231
1	5	64	88
3	1	75	44
3	3	184	215
3	5	45	36
5	1	71	79
5	3	70	106
7	1	149	130
7	3	123	141
9	1	117	105
9	3	176	195
11	1	134	108
11	3	131	145
11	5	58	74
13	1	84	97
13	3	185	213
15	1	86	63
17	1	118	122
17	3	162	169
19	1	88	90
19	3	106	118
19	5	81	93
21	1	236	259
21	3	78	76
23	1	63	79
25	1	207	201
29	1	144	177
31	1	81	46
******K=		14******	
0	2	145	147
2	0	113	102
2	2	148	142
2	4	111	109
2	6	64	52
4	0	136	151
4	2	79	41
4	4	166	175
6	0	96	55
6	2	125	100
6	4	97	105
8	0	185	187
8	2	100	110
8	4	85	86
10	0	93	62
10	2	142	122
12	2	125	100
12	4	72	82
14	0	74	89
14	2	233	269
16	0	164	180
16	2	143	122
16	4	129	148
22	0	144	110
22	2	236	224
24	0	167	144
24	2	130	99
24	4	81	103
26	2	132	114
28	0	108	80
28	4	121	34
30	2	85	77
32	0	124	118
34	2	142	137
36	0	92	107
******K=		15******	
1	1	193	209
1	3	95	102
1	5	76	82
3	1	81	82
3	3	87	78
3	5	76	80
5	1	189	200
5	3	96	79
5	5	44	69
7	1	130	158
7	3	117	98
7	5	69	66
9	1	125	137
11	5	66	51
13	1	84	88
13	3	170	204
13	5	72	65
15	1	94	117
15	3	162	178
15	5	89	55
17	1	93	90
17	3	137	136
21	1	85	92
21	3	77	75
23	1	162	184
25	1	99	111
31	1	139	160
******K=		16******	
0	0	306	313
0	4	172	174
2	2	142	118
2	6	96	97
4	0	102	101
4	2	105	79
4	4	84	93
6	0	148	151
6	2	70	67
8	0	304	313
8	2	108	72
8	4	113	99
10	0	96	70
10	2	129	120
10	6	102	115
12	0	139	146
12	4	93	88
14	0	62	63
14	2	130	99
16	0	187	166
16	2	115	85
16	4	78	76
18	2	183	155
20	0	145	168
20	4	128	131
22	0	112	106
22	2	180	161
24	0	114	82
24	2	100	77
28	0	117	109
30	2	132	143
36	0	108	83
38	2	141	148
******K=		17******	
1	1	223	267
1	5	102	101
3	1	125	132
3	3	63	64
3	5	80	77
5	1	140	129
7	1	72	96
7	3	80	100
7	5	77	78
9	1	184	201
9	5	44	88
11	3	110	118
11	5	75	98
13	1	79	73
13	3	118	130
15	3	108	98
17	1	107	108
17	3	111	118
19	3	128	158
21	1	108	125
21	3	120	140
23	3	91	92
31	1	99	96
******K=		18******	
0	2	142	119
2	0	168	172
2	2	185	163
2	4	76	67
4	0	217	177
4	4	122	130
6	2	188	107
6	6	72	63
8	0	186	148
10	0	120	102
10	2	120	92
12	2	78	80
12	4	79	101
14	2	208	208
16	0	111	96
16	4	121	130
18	2	147	120
20	0	98	66
20	2	133	108
22	0	70	36
22	2	160	152
24	0	136	138
24	4	107	112
28	0	126	112
32	0	132	105
36	0	123	150
******K=		19******	
1	1	121	119
1	5	65	53
3	1	132	155
3	3	87	96
5	1	155	178
5	3	67	90
7	1	51	103
7	3	72	77
9	1	123	97
9	5	67	40
11	3	54	86
13	1	83	71
13	3	144	172
15	1	80	89
15	3	145	163
17	1	100	90
17	3	122	132
19	1	75	75
19	3	103	87
21	1	85	90
21	3	57	105
23	3	50	114
25	3	54	105
******K=		20******	
0	0	275	243
0	4	68	87
2	2	138	115
4	0	95	48
4	2	158	170
8	0	103	155
10	2	148	139
12	0	105	97
12	2	127	103
16	0	172	112
18	0	115	87
18	2	103	137
20	2	198	95
20	4	114	128
22	2	142	98
26	0	97	109
28	0	132	135
34	0	83	112
38	0	103	61
******K=		21******	
1	1	163	167
1	5	85	65
3	1	114	119
3	5	85	92
7	1	116	139
9	1	100	125
9	5	70	86
11	1	132	167
11	3	77	54
19	3	121	137
21	3	84	102
25	1	100	72
******K=		22******	
2	0	115	115
4	0	175	161
6	0	121	116
6	2	143	142
8	2	94	86
10	0	131	139
12	0	145	145
14	2	121	114
18	2	88	84
24	0	142	123
******K=		23******	
3	1	122	142
5	1	122	136
5	3	74	78
9	1	90	86
13	3	78	98
15	3	105	119
23	1	96	116
******K=		24******	
2	2	108	105
6	2	100	77
10	2	193	152
12	0	139	103
12	2	85	67
18	2	95	109
20	0	94	86
******K=		25******	
7	3	84	65
9	3	85	114
11	3	95	106
******K=		26******	
4	0	158	168
10	0	75	76
12	0	144	114
20	0	117	111
22	0	106	67
******K=		27******	
2	0	81	87
******K=		28******	
12	0*	91	86
14	0	84	111
20	0	116	88
******K=		29******	
0	2	95	104
******K=		30******	
0	0	106	130

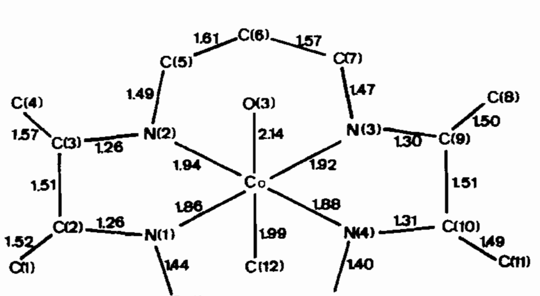

Figure 1. Numbering scheme for the atoms of the complex cation.

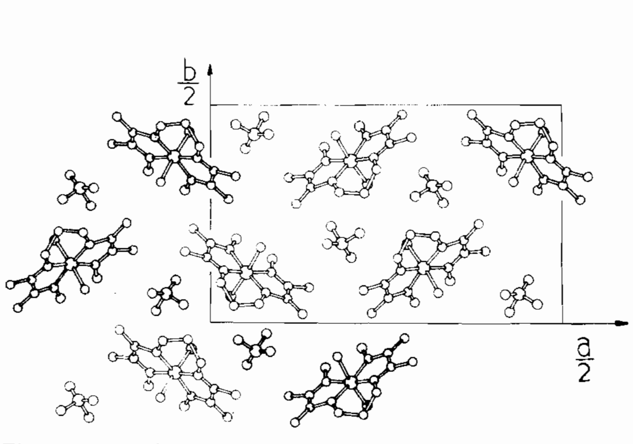

Figure 2. Projection of the structure on (001).

The propylene bridge has the expected conformation, the torsional angles about C(5)–C(6) and C(6)–C(7) bonds being respectively –67.6° and 65.7°.

The Co–C bond length of 1.99 Å is in good agreement with that of 2.04 Å found in the O-methylcarboxymethyl(bisdimethylglyoximato)pyridinatecobalt[8] and with that of 2.05 Å reported by Lenhert[8] for the B_{12} coenzyme. Furthermore, it agrees well with the average value of 1.97 Å in the cyanocobalamin structures.[9,10] Finally it results somewhat longer than the Co–C distance of 1.89 Å found in the ethylene-bis-(acetylacetoneiminato)vinylaquo-cobalt.[11] The Co–N average bond length involving the chemically equivalent N(1) and N(4) atoms and that involving the other

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[10] D. G. Hodgkin, J. Lindsey, R. A. Sparks, K. N. Trueblood, and J. C. White, *Proc. Roy. Soc.*, *A266*, 494 (1962).

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Table III. Bond lengths (Å) and angles (°) with their estimated standard deviations

Co—N(1)	1.86(4)	N(3)—Co—N(4)	82.8(12)
Co—N(2)	1.94(3)	N(3)—Co—O(3)	91.0(10)
Co—N(3)	1.92(3)	N(3)—Co—C(12)	91.8(13)
Co—N(4)	1.88(3)	N(4)—Co—O(3)	90.2(11)
Co—C(12)	1.99(4)	N(4)—Co—C(12)	90.5(13)
Co—O(3)	2.14(2)	Co—N(1)—C(2)	118.3(28)
O(1)—N(1)	1.44(4)	Co—N(1)—O(1)	120.5(22)
O(2)—N(4)	1.40(4)	O(1)—N(1)—C(2)	120.6(32)
N(1)—C(2)	1.26(5)	Co—N(2)—C(3)	117.5(22)
N(2)—C(3)	1.26(4)	Co—N(2)—C(5)	121.6(20)
N(2)—C(5)	1.49(5)	C(3)—N(2)—C(5)	120.9(26)
N(3)—C(7)	1.47(5)	Co—N(3)—C(7)	127.6(21)
N(3)—C(9)	1.30(4)	Co—N(3)—C(9)	114.5(22)
N(4)—C(10)	1.31(4)	C(7)—N(3)—C(9)	117.9(28)
C(1)—C(2)	1.52(6)	Co—N(4)—C(10)	117.2(23)
C(2)—C(3)	1.51(5)	Co—N(4)—O(2)	122.8(20)
C(3)—C(4)	1.57(5)	O(2)—N(4)—C(10)	119.2(26)
C(5)—C(6)	1.61(5)	N(1)—C(2)—C(1)	122.3(36)
C(6)—C(7)	1.57(5)	N(1)—C(2)—C(3)	113.4(32)
C(8)—C(9)	1.50(5)	C(1)—C(2)—C(3)	124.3(30)
C(9)—C(10)	1.51(5)	N(2)—C(3)—C(2)	110.3(27)
C(10)—C(11)	1.49(5)	N(2)—C(3)—C(4)	124.0(31)
Cl—O(4)	1.33(4)	C(2)—C(3)—C(4)	125.3(29)
Cl—O(5)	1.39(5)	N(2)—C(5)—C(6)	114.9(28)
Cl—O(6)	1.39(4)	C(5)—C(6)—C(7)	110.4(28)
Cl—O(7)	1.39(4)	N(3)—C(7)—C(6)	110.5(30)
O(1) - - - O(2)	2.39(3)	N(3)—C(9)—C(8)	126.7(33)
N(1)—Co—N(2)	80.3(13)	N(3)—C(9)—C(10)	113.9(29)
N(1)—Co—N(3)	176.8(14)	C(8)—C(9)—C(10)	119.3(30)
N(1)—Co—N(4)	98.4(14)	N(4)—C(10)—C(9)	111.3(28)
N(1)—Co—O(3)	92.0(12)	N(4)—C(10)—C(11)	122.0(30)
N(1)—Co—C(12)	85.2(14)	C(9)—C(10)—C(11)	126.6(30)
N(2)—Co—N(3)	98.4(11)	O(4)—Cl—O(5)	99.8(28)
N(2)—Co—N(4)	177.6(11)	O(4)—Cl—O(6)	115.2(27)
N(2)—Co—O(3)	91.9(9)	O(4)—Cl—O(7)	112.3(25)
N(2)—Co—C(12)	87.5(13)	O(5)—Cl—O(6)	107.1(26)
		O(5)—Cl—O(7)	109.8(30)
		O(6)—Cl—O(7)	111.7(23)

two chemically equivalent N(2) and N(3) atoms, are 1.87 and 1.93 Å respectively. However this difference is hardly significant because of the high estimated standard deviations of the Co—N bond lengths.

Table IV. Best least-square planes defined by atomic positions. In the following equations x, y, z refer to atomic fractional coordinates

(i) Plane defined by O(1), N(1), C(1), C(2), C(3), C(4), N(2), C(5)

$18.817\,x + 19.055\,y + 3.514\,z = 3.314$

Distances of atoms from this plane (Å)

O(1)	0.02	C(3)	—0.04
N(1)	0.06	C(4)	0.09
C(1)	—0.07	N(2)	—0.03
C(2)	—0.01	C(5)	—0.03

(ii) Plane defined by O(2), N(4), C(10), C(11), C(8), C(9), N(3), C(7)

$18.656\,x + 19.162\,y + 3.496\,z = 3.325$

Distances of atoms from this plane (Å)

O(2)	0.00	C(8)	0.05
N(4)	0.05	C(9)	—0.03
C(10)	—0.02	N(3)	—0.02
C(11)	—0.02	C(7)	—0.01

Table IV. (Continued)

(iii) Plane defined by Co, N(1), N(2), N(3), N(4), O(1), O(2), C(1), C(2), C(3), C(4), C(5), C(7), C(8), C(9), C(10), C(11)

$18.780\,x + 19.094\,y + 3.504\,z = 3.315$

Distances of atoms from this plane (Å)

Co	—0.01	C(3)	—0.04
N(1)	0.07	C(4)	0.08
N(2)	—0.03	C(5)	—0.03
N(3)	0.00	C(7)	0.01
N(4)	0.06	C(8)	0.04
O(1)	0.03	C(9)	—0.03
O(2)	0.01	C(10)	—0.03
C(1)	—0.08	C(11)	—0.04
C(2)	—0.01		

The C(6) atom is displaced —0.78 Å from this plane

(iiii) Plane defined by Co, N(1), N(2), N(3), N(4)

$25.967\,x + 25.960\,y + 5.144\,z = 4.558$

Distances of atoms from this plane (Å)

Co	—0.05	N(3)	0.02
N(1)	0.02	N(4)	0.00
N(2)	0.00		

The O(1) . . . . . O(2) distance of 2.39 Å indicates a strong hydrogen bond.

Table V. Non-bonded intermolecular distances below 4 Å with their e.s.d., in parentheses

O(1)—C(5)	I	3.69(4)	C(3)—O(7)	III	3.38(5)	C(8)—O(5)	IX	3.53(7)
O(1)—C(7)	I	3.99(5)	C(4)—C(12)	III	3.59(6)	O(3)—Cl	X	3.84(2)
O(1)—C(12)	I	3.62(5)	C(4)—O(7)	III	3.87(6)	O(3)—O(5)	X	3.46(5)
O(2)—C(7)	I	3.59(4)	C(5)—O(6)	III	3.71(5)	O(3)—O(6)	X	3.00(4)
O(3)—C(5)	I	3.94(4)	C(6)—O(6)	III	3.55(6)	N(3)—O(6)	X	3.52(5)
O(3)—C(6)	I	3.44(5)	C(5)—O(7)	IV	3.39(6)	N(4)—O(5)	X	3.91(6)
O(3)—C(7)	I	3.40(5)	C(6)—O(7)	IV	3.73(6)	C(7)—O(6)	X	3.87(6)
C(6)—C(6)	II	3.26(5)	C(1)—C(8)	V	3.61(6)	C(8)—O(4)	X	3.53(6)
C(6)—C(7)	II	3.92(5)	O(1)—C(4)	VI	3.87(5)	C(8)—O(6)	X	3.74(5)
O(3)—Cl	III	3.63(2)	C(8)—C(11)	VII	3.92(5)	C(9)—Cl	X	3.93(4)
O(3)—O(6)	III	2.94(4)	C(9)—C(11)	VII	3.81(5)	C(9)—O(4)	X	3.84(6)
O(3)—O(7)	III	3.24(4)	C(10)—C(11)	VII	3.90(5)	C(9)—O(5)	X	3.79(7)
N(1)—O(7)	III	3.95(5)	C(12)—C(11)	VII	3.80(5)	C(9)—O(6)	X	3.39(5)
N(2)—O(6)	III	3.65(5)	O(2)—C(8)	VIII	3.72(4)	C(10)—O(5)	X	3.43(6)
N(2)—O(7)	III	3.81(5)	O(2)—C(10)	VIII	3.99(4)	C(10)—O(6)	X	3.91(5)
C(1)—O(7)	III	3.77(5)	O(2)—C(11)	VIII	3.34(5)	C(11)—O(5)	X	3.53(6)
C(2)—O(7)	III	3.44(5)	C(7)—O(5)	IX	3.41(6)			
C(3)—O(6)	III	3.90(5)						

Asymmetric Units

No label	x	y	z
I	x	y	z—1
II	—x	—y	z
III	1/4—x	y—1/4	z—1/4
IV	1/4—x	y—1/4	z+3/4
V	x+1/4	1/4—y	z—3/4
VI	1/4—x	y+1/4	z—3/4
VII	—x	1/2—y	z+1/2
VIII	—x	1/2—y	z—1/2
IX	x—1/4	1/4—y	z+3/4
X	x—1/4	1/4—y	z—1/4

Although the perchlorate ion is somewhat distorted, it is still a fair approximation to the tetrahedral ion expected. The average Cl-O distance of 1.38 Å is smaller than the expected value. This may be ascribable to high vibrational motion of the oxygen atoms or to highly hindered rotational motions, as suggested by the high values of the thermal parameters of these atoms.

The crystals are built from organometallic cations and perchlorate anions. The crystal packing is shown in Figure 2, where the projection of the structure down the c-axis is represented. In Table V are reported the non-bonded interatomic distances below 4 Å. The water molecule is so arranged that it forms hydrogen bonds with oxygen atoms of two perchlorate ions (O(3)—O(6)III = 2.94 Å, O(3)—O(6)X = 3.00 Å). The O(6)III—O(3)—O(6)X angle of 85.8° suggests that the hydrogen bonds are bent.

All other contact distances, besides the C(6)—C(6)II distance of 3.26 Å, are equal or greater than the sum of the Van der Waals radii of the respective atoms.

Acknowledgments. This work was supported in part by the Consiglio Nazionale delle Ricerche, Roma (Italy) and in part by the S.N.A.M.-Progetti, Milano (Italy).

We are grateful to Prof. A. Ripamonti for helpful discussions.