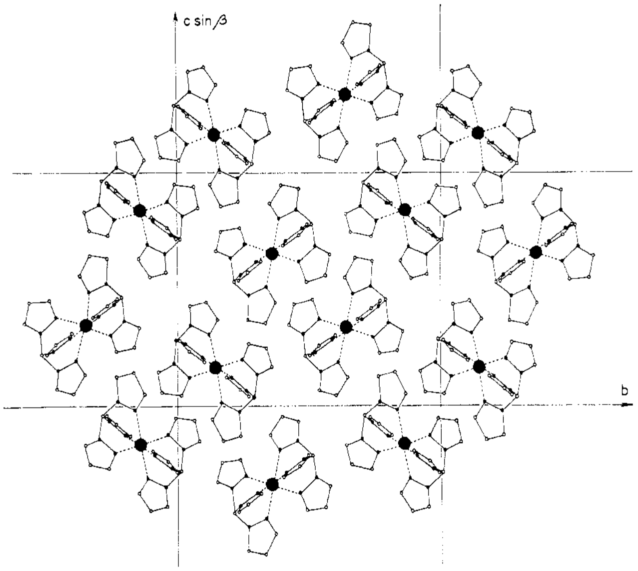

Figure 4.—Packing of $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecules within the unit cell, as viewed down *a*.

(1) = 1.345 Å. [Bond distances obtained from an X-ray structural analysis of pyrazole itself[31] are N(1)–N(2) = 1.36 Å, N(2)–C(3) = 1.31 Å, C(3)–C(4) = 1.41 Å, C(4)–C(5) = 1.34 Å, and C(5)–N(1) = 1.35 Å;[32] this structural analysis is, however, of limited accuracy, since only *hk*0, *h*0*l*, and 0*kl* diffraction data were used.]

Finally, it may be noted that the N(1)–N(2)[25] bonds of the pyrazolyl rings are not parallel to the B(1)···Co···B(2) axis but are canted toward the boron atoms, due to the B–N bond distances being shorter than the Co–N distances. Thus, the average intraligand N(1)···N(1′) distance[25] is 2.513 Å, while the mean intraligand N(2)···N(2′) contact is 2.892 Å.

Intermolecular Contacts

The packing of molecules within the crystal lattice (viewed down *a*) is illustrated in Figure 4. The individual $[HB(C_3N_2H_3)_3]_2Co^{II}$ molecules are separated by normal van der Waals distances, closest approaches (of each type) being: hydrogen···hydrogen, 2.57 Å; carbon···hydrogen, 2.84 Å; nitrogen···hydrogen, 3.00 Å; boron···hydrogen, 3.26 Å.

Acknowledgments.—We thank Dr. S. Trofimenko for providing the sample. This work has been generously supported by the National Science Foundation (Grant No. GP-8077). K. G. gratefully acknowledges the support of an NIH predoctoral fellowship.

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[31] H. W. W. Ehrlich, *Acta Crystallogr.*, **13**, 946 (1960).

[32] We have followed the suggestion of Reimann, *et al.*,[30] that Ehrlich's[31] original assignment of N(1) and N(2) should be reversed.

CONTRIBUTION NO. 3986 FROM THE ARTHUR AMOS NOYES LABORATORY OF CHEMICAL PHYSICS,
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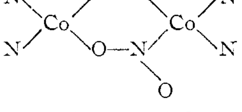
The Structure of μ-Amido-μ-nitro-bis[tetraamminecobalt(III)] Tetrachloride Tetrahydrate

BY ULF THEWALT AND RICHARD E. MARSH

Received December 19, 1969

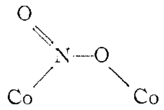
μ-Amido-μ-nitro-bis[tetraamminecobalt(III)] tetrachloride tetrahydrate, $[(NH_3)_4Co(NH_2)(NO_2)Co(NH_3)_4]Cl_4 \cdot 4H_2O$, crystallizes in the monoclinic system, space group $P2_1/m$, with a = 10.328 (2), b = 15.103 (2), c = 7.756 (1) Å, β = 124.10 (2)°, and Z = 2. The crystal structure has been determined from three-dimensional X-ray data using the heavy-atom method and refined by least squares to an R index of 0.048. The cation has mirror symmetry and contains the planar group of atoms



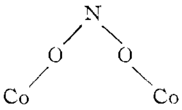
The *exo*-N–O bond length (1.23 ± 0.01 Å) is about equal to the N–O distance in the nitrite ion. The bridging N–O bond, however, is considerably longer (1.31 ± 0.01 Å), approaching the N–O single-bond length. The ions and the water molecules are linked by a network of hydrogen bonds, in which most of the hydrogen atoms take part.

Introduction

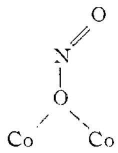
Binuclear cobalt complexes containing one or two bridging NO_2 groups were discovered and formulated by Werner[1] more than 50 years ago. However, the arrangement of the bridging NO_2 group could not be decided at that time. Three possible arrangements are



I



II



III

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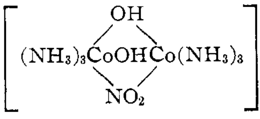
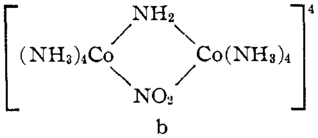
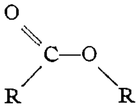
[1] A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).

The first experimental evidence for the arrangement came from infrared studies of cations a[2] and b.[3] The


a


b

frequencies of the infrared-active vibrational modes $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ of these cations were found to be shifted as compared to these of the free nitrite ion, ν_{as} being increased and ν_s lowered. Comparing these shifts (particularly the relatively large one of the antisymmetric stretching frequency, ν_{as}) with the corresponding shifts in nitro and nitrito complexes, Nakamoto, Fujita, and Murata[2] concluded that I is the most probable structure of the bridge. Chatt, *et al.*,[3] reached the same conclusion by comparing the infrared spectrum of b with that of esters of carboxylic acids, where the



group is present.

The objective of the present X-ray diffraction investigation was to check the conclusions drawn from the infrared spectra and to determine the exact geometry of b, the μ-amido-μ-nitro-bis[tetraamminecobalt(III)] cation.

Experimental Section

We prepared μ-amido-μ-nitro-bis[tetraamminecobalt(III)] tetranitrate monohydrate by Werner's[1] method, namely, by the replacement of O_2^- by NO_2^- in the cation of μ-amido-μ-superoxo-bis[tetraamminecobalt(III)] tetranitrate.

The nitrate was then transformed into the chloride as described by Werner. Recrystallization from a water–pyridine solution yielded orange lath-shaped crystals of the tetrachloride tetrahydrate.

Recrystallization from pure water or from dilute HCl solution yielded the same kind of crystals, but usually together with crystals of the orthorhombic monohydrate (which was the only modification reported by Werner to be obtainable under the latter conditions).

Weissenberg photographs around the *a* and the *b* axes confirmed the monoclinic symmetry of the crystal. The only systematic absences are 0*k*0 with *k* odd, indicating $P2_1$ or $P2_1/m$ as possible space groups.

The unit-cell dimensions were obtained from a least-squares treatment of the readings of several independent reflections on Weissenberg photographs of the 0*kl* and *h*0*l* zones, prepared in a special Straumanis-type camera using copper radiation. The density calculated assuming two formula units in the cell is in excellent agreement with the value measured by flotation in a carbon tetrachloride–dibromoethane mixture. The crystal data are given in Table I.

TABLE I
CRYSTAL DATA FOR
μ-AMIDO-μ-NITROBIS[TETRAAMMINECOBALT(III)]
TETRACHLORIDE TETRAHYDRATE

$a = 10.328 \pm 2$ Å	$Co_2N_{10}H_{34}O_6Cl_4$	$a' = 8.775$ Å
$b = 15.103 \pm 2$ Å	mol wt 530.0	$b' = 15.103$ Å
$c = 7.756 \pm 1$ Å	$Z = 2$	$c' = 7.756$ Å
$\beta = 124.10 \pm 2°$	$F(000) = 548$	$\beta' = 102.94°$
Space group $P2_1/m$		
$D_m = 1.76 \pm 0.01$ g cm^{-3}		λ(Cu $K\alpha_1$) 1.54051 Å
$D_x = 1.757 \pm 0.001$ g cm^{-3}		λ(Cu($K\alpha_2$) 1.54433 Å
		λ(Cu $K\alpha$) 1.5418 Å

We have chosen the *a* axis to correspond to the needle axis of the crystals, resulting in an unnecessarily obtuse angle β. Alternate lattice constants (*a'*, *b'*, *c'*), with β as close to 90° as possible, are also given in Table I; they are related to the original set by the transformation

$$(a'b'c') = (abc)\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 1 & 0 & -1\end{pmatrix}$$

Intensity data were collected on a General Electric quarter-circle diffractometer operating with Datex automation and using MnO_2-filtered iron radiation. The diffractometer was equipped with a proportional counter and a pulse-height discriminator. The θ–2θ technique was used with a scanning speed of 2°/min; the scan range varied from 2° (in 2θ) at 2θ = 15° to 4.5° at 2θ = 150°. The background was measured for 50 sec at both sides of the scanning interval, which contained both the α_1 and the α_2 peaks.

A standard reference reflection (002) was measured every 15 reflections. Its intensity decreased continuously over the period of data collection, to about 90% of its initial value. A repetition of the intensity measurements for the first few hundred reflections after all reflections had been recorded indicated that all reflections were probably affected in a similar way. Therefore the recorded intensities were corrected according to the decreasing intensity of the check reflection. The complete data-collection procedure was then repeated with a new crystal; a similar fall-off in intensity was noted. Both crystals were prismatic fragments cut from longer needles; they had approximately rectangular cross sections with dimensions 0.06 × 0.04 × 0.05 mm along *a*, *b*, and *c*. They were mounted with *a* parallel to the φ axis of the diffractometer.

Initial data processing included the calculation of the F_o values and assignment of standard deviations, $\sigma(F_o^2)$, according to

$$F_o = \left[\left(S - \frac{B_1 + B_2}{2t}T_s\right)\frac{1}{Lp}\right]^{1/2}$$

$$\sigma(F_o^2) = \left[S + \frac{B_1 + B_2}{(2t)^2}T_s^2 + (Sd)\right]^{1/2}\frac{1}{Lp}$$

where B_1 and B_2 are background counts, *t* is the time for background count, T_s is the s anning time, *S* is the scan count, *Lp* is the Lorentz–polarization correction factor, and *d* is an empirical constant, taken here as 0.017. No absorption correction was applied (μ = 138 cm^{-1}); we estimate that the transmission coefficients varied by no more than 2% with variations in either the orientation of the crystal or the Bragg angle. The F_o values of the two data sets were then scaled together and averaged. Six high-angle reflections with unusually high background were dropped from the data set; they were clustered within a small region of reciprocal space ($\overline{10}k3$ and $\overline{10}k4$), and we suspect that the primary beam was hitting the brass mounting pin. Of the resulting 1102 independent reflections 29, for which F_o^2 was computed negative, were assigned a value of F_o and a weight equal to zero. All other reflections which were calculated above zero were treated as observed. Finally the structure factors were brought to the absolute scale by Wilson's[4] method.

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(2) K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, **80**, 4817 (1958).

(3) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959).

(4) A. J. C. Wilson, *Nature*, **150**, 151 (1942).

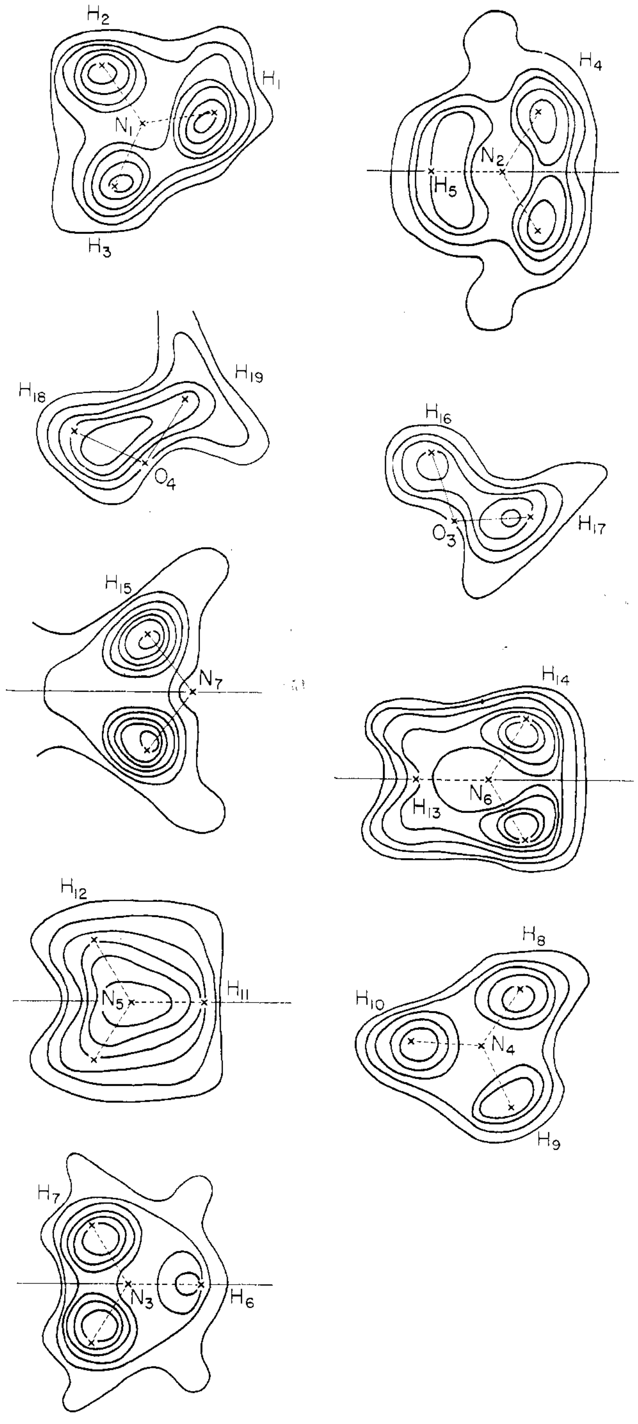

Figure 1.—Final difference Fourier sections, in which the hydrogen contributions were omitted from the F_c's. Contours are at intervals of 0.1 $e^-/Å^3$, beginning with the 0.1-$e^-/Å^3$ contour. Crosses indicate the assumed positions of the hydrogen atoms (Table IV).

Determination and Refinement of the Structure

The statistical test of Howells, Phillips, and Rogers[5] indicated a center of symmetry, and hence the space group $P2_1/m$ was assumed. Since this space group has fourfold general positions, the two cations in the unit cell must lie on mirror planes.

The positions of the cobalt and chlorine atoms were obtained from the sections $v = 0$ and $v = 1/2$ of a three-dimensional Patterson function, and the positions of the remaining nonhydrogen atoms in the asymmetric unit were recovered from subsequent electron-density maps. Six cycles of full-matrix least-squares refinement with individual isotropic temperature factors resulted in an R index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.093. Difference Fourier maps were then calculated in the planes in which the hydrogen atoms of the ammonia groups must lie; all the hydrogen atoms except those on N(5) and N(6) could be located. The hydrogen atoms of the bridging NH_2 group were also found in a difference map. These hydrogen atoms, with isotropic temperature factor $B = 2.5$ Å^2, were included in the subsequent structure factor calculations, but their parameters were not refined. Four cycles of anisotropic refinement then reduced R to 0.059. Whereas the hydrogen atoms attached to N(6) now could be found from a difference map, the hydrogen atoms on N(5) still could not be located; these were then positioned at locations most suitable for the formation of hydrogen bonds. Difference maps through the water oxygen atoms and the potential hydrogen-bond acceptors gave clear indication of the hydrogen positions for O(3), but near O(4) were found only diffuse electron density peaks, and those two hydrogen atoms were therefore positioned from steric considerations.

The refinement was completed with six more cycles of full-matrix least squares. A total of 115 parameters were adjusted: a scale factor k and the coordinates and anisotropic temperature parameters of all nonhydrogen atoms. The quantity minimized was $\Sigma w(F_o^2 - (1/k^2)F_c^2)^2$, with weights taken equal to $1/\sigma^2(F_o^2)$. The final shifts in all parameters were less than 0.05 of the corresponding estimated standard deviations. The final R index for the 1071 reflections of nonzero weight is 0.048, and the goodness of fit, $[\Sigma w(F_o^2 - F_c^2/k^2)^2/(n - p)]^{1/2}$, is 2.1.

Scattering curves for Co^{2+}, Cl^-, N, and O were taken from ref 6; that for H was taken from Stewart, Davidson, and Simpson.[7] The Co^{2+} curve was corrected for anomalous dispersion by subtracting 1.74 electrons. All calculations were performed on an IBM 7094 computer using programs of the CRYRM[8] system.

A three-dimensional difference Fourier synthesis calculated at the end of the refinement showed no positive peak greater than 0.36 e^- Å^{-3} and no negative peak greater than -0.55 e^- Å^{-3}. Difference maps for which the contributions of the hydrogen atoms were omitted from the calculated structure factors are shown in Figure 1.

A list of observed and calculated structure factors is given in Table II. A list of the final heavy-atom parameters and their estimated standard deviations

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[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).

[6] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[8] D. J. Duchamp, American Crystallographic Association Meeting, Bozeman, Mont., Paper B-14 (1964).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (BOTH ×10)[a]

0	K	0
0	---*	5417
-10	K	4
0	221	230
1	---*	23
2	219	-239
-10	K	5
0	108	-81
1	158	-151
2	74	73
3	253	251
-9	K	1
0	---*	-2
1	323	-316
2	---*	-48
3	214	207
-9	K	2
0	145	-132
1	31	26
2	340	342
3	139	154
4	258	-253
5	36	-59
-9	K	3
0	317	314
1	413	418
2	69	-54
3	112	-96
4	88	-81
5	277	278
6	199	-211
7	295	-305
-9	K	4
0	227	236
1	291	-275
2	291	-275
3	54	14
4	125	124
5	115	-107
6	142	-138
7	243	265
-9	K	5
0	456	-463
1	271	-294
2	187	165
3	84	-95
4	---*	-3
5	119	-113
6	322	327
-9	K	6
0	222	-225
1	230	260
2	86	71
3	139	-139
4	61	53
5	120	126
-9	K	7
0	431	452
-8	K	0
1	136	-137
2	26	-31
3	138	132
4	53	-60
5	168	-173
-8	K	1
0	104	99
1	86	-112
2	14	32
3	239	-242
4	95	-93
5	---*	52
6	54	-72
7	168	176
-8	K	2
0	218	-226
1	256	-256
2	192	184
3	68	-43
4	103	-83
5	120	-110
6	83	104
7	244	236
8	216	-213
9	58	-38
-8	K	3
0	164	-176
1	183	189
2	---*	30
3	21	-3
4	68	90
5	165	145
6	114	113
7	141	-118
8	106	-112
9	---*	-2
-8	K	4
0	267	-254
1	15	-17
2	---*	19
3	401	392
4	60	-24
5	98	-89
6	188	181
7	59	-59
8	---*	-14
9	214	-216
-8	K	5
0	38	-23
1	224	230
2	35	44
3	120	-136
4	72	-79
5	52	53
6	48	16
7	264	-262
8	---*	25
-8	K	6
0	118	123
1	---*	-20
2	188	173
3	149	-144
4	204	-210
5	41	-27
6	62	-62
7	53	42
-8	K	7
0	143	151
1	64	-62
2	59	-25
3	145	-154
4	32	-27
-7	K	0
1	105	-97
2	236	224
3	148	-145
4	43	8
5	96	-92
6	474	491
7	54	35
8	369	-368
-7	K	1
0	247	220
1	340	354
2	180	-185
3	128	-132
4	289	280
5	155	163
6	176	-199
7	286	-303
8	51	33
9	269	266
10	225	-220
-7	K	2
0	526	569
1	282	-272
2	102	-112
3	523	497
4	132	-115
5	283	-264
6	403	-419
7	187	184
8	222	220
9	296	-295
10	121	117
-7	K	3
0	111	-110
1	71	-103
2	385	391
3	192	177
4	476	-464
5	97	-80
6	139	130
7	53	40
8	178	-161
9	226	-226
10	368	365
11	12	24
-7	K	4
0	338	-316
1	339	351
2	193	179
3	345	-345
4	164	-150
5	351	343
6	316	309
7	218	-222
8	103	-104
9	289	268
10	88	75
-7	K	5
0	119	109
1	229	-246
2	490	-487
3	159	-149
4	471	473
5	82	-97
6	115	-107
7	250	260
8	312	304
9	73	66
10	363	-365
-7	K	6
0	229	-244
1	221	-210
2	177	172
3	---*	2
4	55	-36
5	186	-173
6	144	146
7	148	146
8	261	-253
-7	K	7
0	69	-30
1	295	280
2	241	230
3	51	67
4	172	-169
5	147	135
-6	K	0
1	252	251
2	275	272
3	467	-475
4	332	-322
5	111	109
6	218	219
7	230	-227
8	208	-208
9	400	401
10	317	326
-6	K	1
0	1037	1058
1	277	279
2	246	-248
3	697	-673
4	88	92
5	251	244
6	680	-693
7	165	-174
8	374	373
9	425	418
10	164	-152
11	247	-246
-6	K	2
0	303	320
1	711	-683
2	104	-115
3	511	515
4	128	108
5	155	-171
6	211	-195
7	688	661
8	63	34
9	514	-508
10	90	-97
11	44	21
12	102	114
-6	K	3
0	1223	1213
1	148	145
2	199	206
3	259	254
4	82	47
5	65	84
6	730	715
7	135	-114
8	464	-439
9	194	-181
10	116	92
11	26	-22
12	188	-190
-6	K	4
0	62	-3
1	804	810
2	303	-304
3	393	-404
4	351	349
5	299	309
6	33	38
7	780	-769
8	194	175
9	461	446
10	270	-255
11	92	-89
-6	K	5
0	645	654
1	276	-279
2	237	-222
3	134	127
4	85	49
5	262	-249
6	422	-416
7	247	246
8	348	345
9	79	-76
10	105	-97
-6	K	6
0	74	56
1	291	-297
2	221	223
3	68	19
4	295	-286
5	136	-134
6	109	-91
7	289	279
8	143	-122
9	87	-81
-6	K	7
0	74	-5
1	245	234
2	89	109
3	220	-207
4	52	-69
5	217	200
6	56	2
-5	K	0
1	180	183
2	27	-14
3	289	-286
4	246	246
5	142	149
6	180	174
7	70	-66
8	178	-173
9	311	307
10	185	-177
11	71	-73
12	40	43
-5	K	1
0	320	318
1	---*	-7
2	321	-322
3	318	308
4	282	294
5	202	-200
6	272	-277
7	155	-160
8	129	143
9	113	-81
10	177	-190
11	184	197
12	250	258
13	26	31
-5	K	2
0	311	306
1	225	223
2	269	280
3	302	323
4	252	-259
5	84	81
6	173	-178
7	223	-228
8	35	-83
9	231	-231
10	166	150
11	65	49
12	43	9
13	101	113
-5	K	3
0	117	-123
1	73	-84
2	227	236
3	337	330
4	381	-404
5	31	40
6	87	75
7	110	82
8	---*	13
9	97	-73
10	301	286
11	87	-57
12	137	-143
13	43	-52
-5	K	4
0	---*	2
1	46	58
2	230	-229
3	527	-533
4	63	23
5	75	100
6	41	57
7	57	-12
8	287	278
9	260	257
10	65	-34
11	149	-142
12	64	-67
-5	K	5
0	70	40
1	335	-355
2	71	-85
3	256	-270
4	264	266
5	129	-130
6	4	-15
7	264	262
8	34	-23
9	49	55
10	235	-228
11	53	12
-5	K	6
0	206	-206
1	149	137
2	118	122
3	---*	10
4	87	54
5	105	121
6	92	68
7	74	-75
8	269	-266
9	38	48
-5	K	7
0	88	94
1	206	193
2	41	-51
3	229	237
4	34	-9
5	46	22
6	113	-107
-4	K	0
1	777	-779
2	113	120
3	109	131
4	158	-153
5	462	-466
6	325	-339
7	589	574
8	98	79
9	125	-146
10	---*	6
11	274	270
12	43	37
13	287	-288
-4	K	1
0	183	-207
1	578	-551
2	566	536
3	102	-95
4	623	-620
5	69	-19
7	540	511
8	370	-381
9	51	63
10	460	461
11	163	-150
12	44	2
13	248	-258
-4	K	2
0	384	379
1	194	195
2	327	-335
3	130	-139
4	236	234
5	191	207
6	281	-278
7	229	-254
8	201	229
9	22	49
10	137	-114
11	279	-278
12	193	196
13	119	107
-4	K	3
0	175	-175
1	346	-360
2	259	-266
3	736	740
4	513	529
5	240	-255
6	165	168
7	159	148
8	95	104
9	471	-451
10	417	-411
11	160	175
12	66	-63
13	22	-17
-4	K	4
0	1064	1072
1	96	-109
2	320	335
3	388	405
4	187	-202
5	189	-192
6	702	694
7	41	39
8	370	-375
9	121	-107
10	157	146
11	275	280
12	291	-290
-4	K	5
0	71	73
1	193	188
2	171	172
3	371	-395
4	276	-286
5	55	1
6	86	-57
7	284	-262
8	48	-53
9	364	368
10	229	229
11	---*	8
-4	K	6
0	781	778
1	72	-84
2	98	-103
3	95	-67
4	43	3
5	58	0
6	530	-535
7	99	92
8	240	225
9	56	17
-4	K	7
0	136	-145
1	206	-194
2	128	141
3	229	222
4	147	-147
5	34	-16
6	103	108
-3	K	0
1	1199	1189
2	396	416
3	331	-310
4	33	33
5	641	-656
6	135	115
7	767	766
8	491	-480
9	251	-258
10	64	4
11	281	287
12	60	69
13	304	-306
14	286	292
-3	K	1
0	108	-102
1	1050	987
2	665	643
3	714	668
4	94	-82
5	383	371
6	70	46
7	746	-724
8	797	-772
9	79	50
10	194	221
11	83	-58
12	84	53
13	268	256
14	324	320
-3	K	2
0	521	496
1	1088	1135
2	373	-386
3	906	892
4	218	-221
5	424	426
6	317	-330
7	855	-813
8	617	632
9	117	-90
10	---*	-8
11	67	-60
12	93	97
13	318	316
14	283	-285
-3	K	3
0	393	361
1	1224	1237
2	561	-570
3	377	401
4	211	215
5	720	-723
6	121	-110
7	746	749
8	571	566
9	562	-559
10	118	-122
11	309	318
12	89	-97
13	282	-270
-3	K	4
0	930	-937
1	329	-316
2	783	802
3	682	-669
4	452	-467
5	23	-20
6	671	655
7	371	376
8	641	-635
9	323	309
10	341	334
11	117	-105
12	377	-368
13	173	-178
-3	K	5
0	127	110
1	441	455
2	83	-89
3	623	-640
4	72	79
5	377	390
6	162	-153
7	305	-295
8	36	17
9	555	539
10	68	-63
11	279	-281
-3	K	6
0	374	379
1	181	-192
2	250	-236
3	356	355
4	238	235
5	184	-191
6	325	-308
7	36	75
8	166	158
9	314	-308
-3	K	7
0	252	-243
1	29	-46
2	208	192
3	423	415
4	90	-79
5	80	-78
-2	K	0
1	402	-407
2	504	505
3	42	9
4	846	-837
5	212	-213
6	132	-131
7	249	252
8	168	-167
9	103	-83
10	571	568
11	129	129
12	56	35
13	85	-66
14	54	40
-2	K	1
0	269	295
1	325	312
2	455	453
3	510	-506
4	268	-266
5	221	208
6	151	-151
7	192	-171
8	204	-202
9	138	127
10	170	137
11	281	-271
12	75	41
13	60	62
14	---*	40
-2	K	2
0	93	89
1	263	260
2	351	-346
3	217	-227
4	420	405
5	575	579
6	23	-35
7	83	45
8	237	239
9	83	81
10	379	-381
11	361	-370
12	19	9
13	66	-29
14	78	-60
-2	K	3
0	1295	1307
1	294	-302
2	30	3
3	108	92
4	73	52
5	134	-144
6	725	709
7	263	249
8	178	-168
9	209	-205
10	59	-8
11	126	124
12	215	-206
13	88	-88
-2	K	4
0	262	-284
1	246	257
2	142	152
3	160	-146
4	77	76
5	134	-112
6	136	139
7	411	-405
8	191	-171
9	236	234
10	---*	-4
11	156	144
12	11	-42
-2	K	5
0	540	548
1	393	399
2	137	133
3	152	-133
4	228	-213
5	196	209
6	351	-341
7	293	-285
8	75	63
9	246	233
10	81	99
11	56	-22
-2	K	6
0	409	400
1	60	-48
2	149	-142
3	57	4
4	48	-27
5	87	99
6	332	-338
7	98	79
8	214	215
-2	K	7
0	247	-260
1	51	-51
2	111	99
3	11	-11
-1	K	0
1	387	369
2	486*	-447
3	475	-466
4	547	512
5	456	438
6	445	-443
7	98	-104
8	138	109
9	464	452
10	401	-395
11	210	-231
12	326	327
13	45	20
14	61	49
15	247	-252
-1	K	1
0	31	-37
1	521	-494
2	61	55
3	1061	1051
4	229	-241
5	571	-519
6	106	-90
7	199	203
8	86	-94
9	689	-673
10	139	150
11	343	336
12	184	180
13	80	-67
14	93	71
15	279	278
-1	K	2
0	46	55
1	380	407
2	365	367
3	817	843
4	183	-179
5	64	-57
6	113	122
7	490	-495
8	189	-172
9	320	-309
10	181	204
11	95	119
12	192	-192
13	225	211
14	44	-27
-1	K	3
0	31	65
1	577	559
2	71	-92
3	319	-337
4	156	-145
5	467	471
6	97	117
7	275	-275
8	278	268
9	386	390
10	70	59
11	219	-218
12	198	-201
13	89	89
-1	K	4
0	133	124
1	648	-645
2	329	-351
3	380	-386
4	144	131
5	297	-299
6	147	-139
7	543	529
8	305	294
9	73	81
10	88	-102
11	32	48
12	97	101
-1	K	5
0	276	-259
1	201	-204
2	443	440
3	238	-218
4	218	-216
5	54	-77
6	165	162
7	155	152
8	452	-455
9	61	33
10	138	128
-1	K	6
0	75	68
1	352	345
2	76	-33
3	134	147
4	146	137
5	231	230
6	78	-85
7	270	-271
0	K	0
2	1211	1145
4	414	376
6	2601	2604
8	1212	1231
10	345	-354
12	721	746
14	627	-662
0	K	1
0	279	-260
1	1005	1032
2	469	480
3	952*	940
4	544	-548
5	57	23
6	147	153
7	989	1035
8	285	-289
9	842	-866
10	377	375
11	46	-17
12	57	-59
13	330	-331
14	118	97
0	K	2
0	1655	1690
1	225	227
2	372	-378
3	75	-77
4	575	556
5	95	115
6	932	973
7	251	-258
8	325	-349
9	56	83
10	51	-75
11	206	-206
12	288	-283
13	112	88
14	238	225
0	K	3
0	92	83
1	186	212
2	516	-549
3	418	-418
4	649	665
5	---*	-17
6	52	45
7	219	-200
8	313	318
9	389	379
10	562	-550
11	17	-9
12	54	-30
13	89	73
0	K	4
0	533	533
1	658	-678
2	276	-278
3	447	456
4	188	179
5	494	-498
6	396	-383
7	523	516
8	223	210
9	302	-301
10	122	-91
11	413	409
0	K	5
0	226	-239
1	107	99
2	581	578
3	105	86
4	604	-587
5	43	-47
6	132	129
7	158	-151
8	417	-421
9	44	-46
0	K	6
0	268	268
1	338	342
2	---*	17
3	84	-74
4	51	-59
5	245	246
1	K	0
0	565	547
1	K	1
0	450	-456
1	83	95
2	90	96
3	1030	1048
4	428	430
5	---*	-16
6	312	323
7	95	-83
8	361	-379
9	501	-485
10	170	-182
11	151	137
12	139	-116
13	49	61
14	183	179
1	K	2
0	550	-535
1	510	497
2	60	47
3	251	217
4	259	-282
5	173	163
6	376	387
7	328	-324
8	88	50
9	120	107
10	237	240
11	---*	-5
12	220	-225
13	71	68
1	K	3
0	578	581
1	86	-53
2	288	-286
3	594	-591
4	74	-64
5	55	-40
6	315	-314
7	48	-25
8	477	474
9	285	285
10	32	11
11	22	-35
12	21	29
1	K	4
0	143	120
1	605	-603
2	307	292
3	70	11
4	230	-211
5	293	-297
6	37	-45
7	541	543
8	221	-216
9	119	-117
10	135	142
1	K	5
0	123	-145
1	186	170
2	80	65
3	43	-51
4	---*	37
5	190	187
6	24	26
7	107	-103
8	197	-187
1	K	6
0	79	-74
2	K	0
0	136	148
2	K	1
0	618	616
1	211	-217
2	6	-34
3	94	-81
4	126	-102
5	51	21
6	285	-293
7	55	41
8	252	256
9	93	-74
10	79	-66
11	235	-229
12	---*	21
13	53	14
14	172	-172
2	K	2
0	586	-579
1	582	-601
2	99	50
3	241	226
4	183	178
5	119	-116
6	464	470
7	548	565
8	120	-131
9	226	-224
10	192	-169
11	---*	6
12	208	-210
13	234	-239
2	K	3
0	775	-787
1	16	-17
2	13	-3
3	102	-106
4	119	101
5	87	-69
6	451	454
7	31	-8
8	216	-202
9	153	146
10	26	15
11	89	100
2	K	4
0	61	51
1	360	358
2	211	208
3	260	-253
4	225	-215
5	88	90
6	---*	-28
7	420	-431
8	152	-155
9	276	269
2	K	5
0	431	440
1	52	-48
2	28	23
3	275	279
4	96	-78
5	70	-46
3	K	0
0	334	-321
3	K	1
0	711	705
1	550	537
2	1202	1222
3	508	511
4	806	833
5	201	204
6	440	-432
7	491	-495
8	822	819
9	244	-219
10	561	-570
11	68	7
12	224	215
13	223	217
3	K	2
0	499	-496
1	737	-746
2	250	249
3	481	501
4	197	-216
5	588	-595
6	410	404
7	470	485
8	139	-122
9	455	-452
10	134	125
11	366	375
12	284	-292
3	K	3
0	189	-199
1	110	106
2	418	413
3	416	-408
4	437	-430
5	116	112
6	187	181
7	45	-22
8	259	-261
9	387	392
10	386	377
3	K	4
0	533	527
1	137	143
2	228	-218
3	377	-369
4	66	59
5	171	157
6	404	-398
7	99	-95
4	K	0
0	632	628
4	K	1
0	391	389
1	305	-294
2	577	-585
3	29	29
4	436	447
5	90	75
6	226	-232
7	452	451
8	489	497
9	171	-161
10	304	-303
11	168	-146
12	69	59
4	K	2
0	532	-527
1	416	-410
2	81	-41
3	224	-194
4	132	112
5	208	-208
6	330	336
7	373	364
8	94	-85
9	36	-13
10	27	-21
4	K	3
0	178	-183
1	242	248
2	179	178
3	290	-291
4	64	-37
5	71	73
6	121	119
7	252	-241
8	214	-226
4	K	4
0	368	373
1	153	155
2	124	-130
3	129	136
4	92	78
5	K	0
0	401	-395
5	K	1
0	309	-312
1	360	375
2	88	82
3	195	201
4	60	65
5	122	122
6	268	260
7	306	-298
8	138	-124
9	17	-1
10	69	-68
11	24	26
5	K	2
0	162	171
1	24	-32
2	146	-152
3	141	126
4	69	-44
5	96	-104
6	77	-82
7	46	28
8	255	262
9	35	20
5	K	3
0	203	208
1	218	-217
2	56	38
3	120	-136
4	155	-151
5	136	-141
6	K	0
0	284	-293
6	K	1
0	213	-205
1	192	193
2	54	-15
3	352	-340
4	76	16
5	174	147
6	184	178
7	126	-117
8	44	18
9	237	236
6	K	2
0	227	221
1	109	-100
2	287	-278
3	269	-267
4	275	256
5	29	21
6	134	-124
7	K	0
0	683	-679
7	K	1
0	111	-117
1	251	244
2	128	-125
3	33	-23
4	90	86
5	87	68
6	98	106
8	K	0
0	218	217

[a] Values of $10F_o$ reported as "..." represent reflections with net counts less than zero; their intensities were arbitrarily set equal to zero. Asterisks indicate reflections assigned zero weight in the least-squares calculations.

TABLE III

THE FINAL HEAVY-ATOM PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	2253 (1)	2500	2995 (2)	50 (2)	16 (1)	92 (3)	...[b]	56 (4)	...
Co(2)	−932 (1)	2500	2971 (2)	52 (2)	23 (1)	89 (3)	...	56 (4)	...
Cl(1)	502 (2)	5838 (1)	2043 (2)	167 (3)	34 (1)	157 (4)	60 (2)	129 (6)	20 (3)
Cl(2)	5039 (2)	3947 (1)	1828 (2)	101 (2)	31 (1)	217 (4)	−11 (2)	171 (5)	12 (3)
N(1)	2336 (5)	3794 (3)	3003 (6)	69 (7)	29 (2)	142 (12)	−8 (7)	96 (15)	−1 (9)
N(2)	4562 (7)	2500	4664 (9)	65 (10)	31 (4)	105 (17)	...	93 (22)	...
N(3)	2114 (7)	2500	370 (9)	74 (10)	24 (3)	130 (19)	...	87 (23)	...
N(4)	−921 (5)	3800 (3)	3054 (7)	92 (7)	30 (3)	200 (14)	29 (7)	125 (17)	8 (10)
N(5)	−1795 (7)	2500	4672 (10)	80 (11)	59 (5)	134 (20)	...	71 (25)	...
N(6)	−3018 (7)	2500	457 (9)	73 (11)	43 (4)	128 (18)	...	119 (24)	...
N(7)	−1 (7)	2500	1409 (9)	66 (10)	16 (3)	111 (17)	...	81 (22)	...
N(8)	2324 (7)	2500	5516 (9)	70 (11)	11 (3)	81 (18)	...	8 (24)	...
O(1)	1064 (5)	2500	5528 (7)	45 (8)	28 (3)	107 (14)	...	59 (18)	...
O(2)	3542 (6)	2500	7262 (7)	68 (9)	41 (3)	91 (15)	...	38 (20)	...
O(3)	3661 (5)	5929 (3)	2235 (7)	232 (9)	33 (3)	458 (12)	2 (8)	418 (22)	−6 (11)
O(4)	2581 (5)	4457 (3)	6770 (6)	170 (8)	35 (2)	206 (12)	−18 (17)	150 (16)	−26 (9)

[a] All values have been multiplied by 10^4. The temperature factors are of the form $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$. [b] b_{ij} terms reported as ... are zero by symmetry.

as calculated from the diagonal elements of the least-squares inverse matrix is given in Table III.

The coordinates assigned to the hydrogen atoms are listed in Table IV. Since the hydrogen atoms were positioned, at least in part, on the basis of structural assumptions, no standard deviations are given for them.

Discussion of the Structure

The Cation.—Figure 2 shows a perspective drawing of the cation. Figure 3 shows a projection along b and summarizes the bond lengths and angles.

The most important result of this structure investigation is the confirmation of the unsymmetrical arrangement of the NO_2 bridge between the Co atoms, as

TABLE IV

POSITIONAL PARAMETERS OF THE HYDROGEN ATOMS ($\times 10^3$)[a]

		x	*y*	*z*
N(1)	H(1)	250	402	430
	H(2)	324	398	297
	H(3)	135	403	179
N(2)	H(4)	495	303	561
	H(5)	493	250	375
N(3)	H(6)	319	250	81
	H(7)	153	303	−32
N(4)	H(8)	0	400	439
	H(9)	−189	401	289
	H(10)	−88	404	190
N(5)	H(11)	−296	250	376
	H(12)	−144	303	556
N(6)	H(13)	−381	250	81
	H(14)	−315	303	−42
N(7)	H(15)	−37	304	54
O(3)	H(16)	394	531	210
	H(17)	264	586	214
O(4)	H(18)	325	503	710
	H(19)	320	427	820

[a] N-Bonded (O-bonded) hydrogen atoms were assigned isotropic temperature factors, $B = 2.5$ Å^2 (4.0 Å^2).

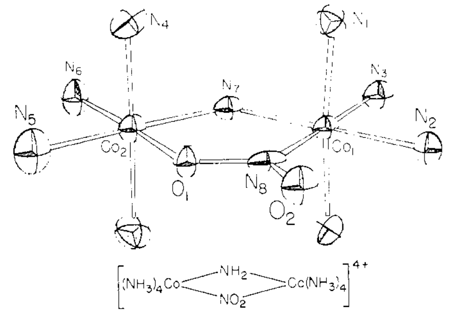


Figure 2.—The μ-amido-μ-nitro-bis[tetramminecobalt(III)] cation and its numbering scheme. This perspective drawing was prepared with a computer program written by C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

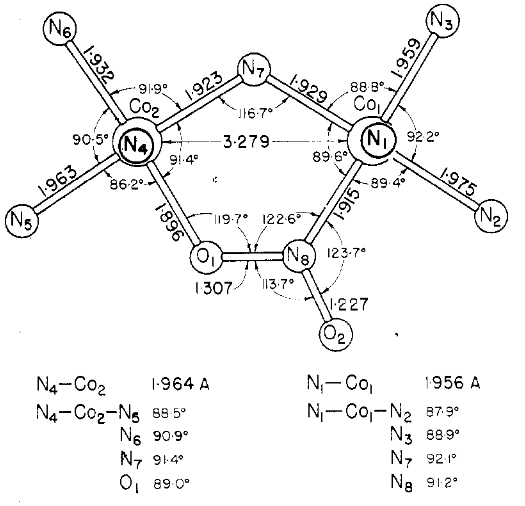
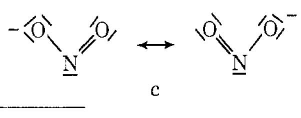


Figure 3.—Bond lengths and angles within the cation. No corrections for thermal motions were applied. Estimated standard deviations are about 0.007 Å for distances between cobalt atoms and their ligands, 0.010 Å for distances between light atoms, 0.3° for angles at the Co atoms, and 0.6° for angles at light atoms.

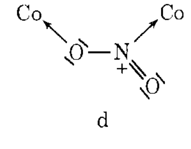
was predicted from the earlier infrared studies. The cation has mirror symmetry. The cobalt atoms, the atoms of the NO_2 group, and the nitrogen atoms of the μ-amido and four ammonia groups lie in the crystallographic mirror plane and are therefore strictly coplanar. All ligand–Co–ligand angles for adjacent ligands are close to the value of 90° expected for regular octahedral coordination.

The six independent Co–N(ammonia) bond lengths vary between 1.932 and 1.975 Å. The rms deviation of these values from the average value (1.958 Å) is 0.010 Å, only slightly larger than the estimated standard deviation (0.007 Å) in the individual values. We conclude that the differences are of doubtful significance. The mean value is in excellent agreement with average Co–N(ammonia) bond lengths in other binuclear cobalt cations—for example, 1.952 ± 0.019 Å in $[(NH_3)_5Co(O_2)Co(NH_3)_5]SO_4(HSO_4)_3$[9] and 1.962 ± 0.011 Å in $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot 4H_2O$[10] and $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$[11]—and with the Co–N bond length in cobalt(III) hexamines, 1.96 ± 0.02 Å.[12] As in nitropentaamminecobalt(III) bromide,[13] the NO_2 group does not seem to exhibit a *trans* effect, the Co(1)–N(3) bond having a normal length of 1.959 ± 0.007 Å. The lengths of the two Co–N bonds to the bridging nitrogen atom N(7) agree well (1.923 ± 0.007 and 1.929 ± 0.007 Å), the average value, 1.926 ± 0.005 Å, being considerably shorter (by about 6σ) than the average Co–N(ammonia) distance, 1.958 Å; similar values were observed in the μ-amido-μ-superoxo-bis[tetraamminecobalt(III)] cation.[11] The shortest Co–N distance, 1.915 ± 0.007 Å, is the one between Co(1) and N(8) of the NO_2 bridge. It compares well with the value 1.921 ± 0.021 Å found for the corresponding distance in nitropentaamminecobalt(III) bromide.[13] Within the NO_2 group, the bond N(8)–O(2), 1.227 ± 0.010 Å, is not significantly shorter than the N–O bond in the free nitrite ion, 1.240 ± 0.003 Å.[14] The N(8)–O(1) bond, however, with a length of 1.307 ± 0.010 Å, is much longer.

A similar observation has been made for the polynuclear complex $[Ni(en)_2(NO_2)]BF_4$, where the nickel atoms are held together by NO_2 bridges;[15] the N–O distances were found to be 1.224 ± 0.025 and 1.276 ± 0.026 Å. These results reflect the change of bond order of the N–O bonds when the free nitrite ion (c) forms a bridge between the metal atoms (d). Structure



c



d

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[9] W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966).

[10] W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

[11] G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *ibid.*, **8**, 291 (1969).

[12] M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

[13] F. A. Cotton and W. T. Edwards, *Acta Crystallogr., Sect. B*, **24**, 474 (1968).

[14] M. I. Kay and B. C. Frazer, *ibid.*, **14**, 56 (1961).

[15] M. G. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 478 (1965).

d, however, does not seem to describe the bonding completely. A comparison with N–O single- and double-bond lengths from other structures (see, *e.g.*, Sutton[16] or Padmanabhan, Smith, and Peterson[17]) suggests that the *exo*-N–O bond is longer than an N–O double bond and that the ring N–O bond is shorter than an N–O single bond.

The Overall Structure. The structure, viewed down the *b* axis, is shown in Figure 4. It is held together by a three-dimensional network of hydrogen bonds among the water molecules, the anions, and the cations. The structure can be regarded as being composed of layers (parallel to the *a*,*c* plane) of cations alternating with layers containing the anions and water molecules.

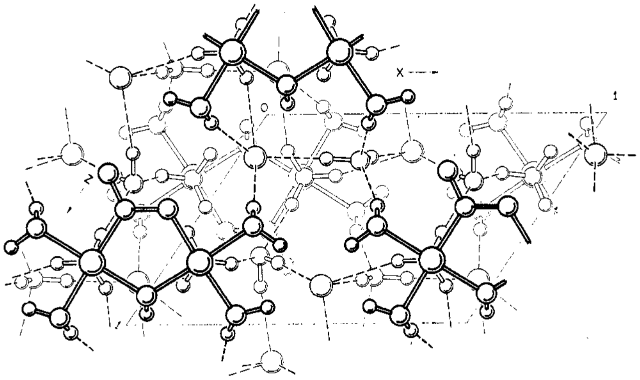
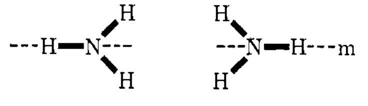


Figure 4.—The structure viewed along the *b* axis. The part between the mirror planes at $y = {}^1/_4$ and $y = {}^3/_4$ is shown.

The hydrogen-bonding scheme is summarized in Table V. The two ammonia groups *outside* the mirror plane, N(1) and N(4), are each linked by one hydrogen bond, of length 2.96 and 3.18 Å, respectively, with water molecules O(4) and O(4g). Whereas the two remaining H atoms of N(4) are not involved in hydrogen bonds, the two remaining H atoms of N(1) point approximately toward chloride ions (Cl(2) and Cl(1h)), the N–Cl distances being 3.39 and 3.37 Å. (See Table VI for short distances not ascribed to hydrogen bonds.)

For the ammonia groups *in* the crystallographic mirror plane, only two conformations are allowed (if no disorder is assumed)



For all these ammonia molecules the out-of-plane hydrogen atoms, as located in the difference maps (and assumed for N(5)), are at such positions that they point to hydrogen-bond acceptors closest to the respective N atom. However, the electron density associated with same of these hydrogen atoms (see Figure 1) is so diffuse that disorder cannot be ruled out.

Both of the water molecules O(3) and O(4) exhibit

TABLE V

HYDROGEN-BOND DISTANCES AND ANGLES

The Donor (D) Is at x, y, z. The Following Designations Are Made for the Positions of the Acceptor (A)

(b) $x, y, z + 1$
(e) $x - 1, y, z$
(f) $-x + 1, -y + 1, -z + 1$
(g) $-x, -y + 1, -z + 1$
(h) $-x, -y + 1, -z$
(j) $-x + 1, y - {}^1/_2, -z + 1$
(k) $-x, y - {}^1/_2, -z$
(l) $-x, y - {}^1/_2, -z + 1$
(p) $x + 1, y, z + 1$

No Corrections for Thermal Motions Were Applied. C Is an Atom Linked with D by a Covalent Bond. Estimated Standard Deviations Are about 0.01 Å and 0.6°

D	A	*d*(DA), Å	A	D	C	∠ADC, deg
N(1)	O(4)	2.96	O(4)	N(1)	Co(1)	108.7°
	Cl(2)	3.39	Cl(2)			96.2
	Cl(1h)	3.37	Cl(1h)			98.8
N(2)	O(3f)	3.13	O(3f)	N(2)	O(3j)	98.3
					Co(1)	118.4
N(3)	Cl(1h)	3.38	Cl(1h)	N(3)	Cl(1k)	95.8
					Co(1)	98.3
N(4)	O(4g)	3.18	O(4g)	N(4)	Co(2)	146.5
N(5)	Cl(1g)	3.28	Cl(1g)	N(5)	Cl(1l)	99.8
					Co(2)	112.4
N(6)	O(3h)	2.98	O(3h)	N(6)	O(3k)	105.6
					Co(2)	113.0

Hydrogen Bonds around the Water Molecules. The N Atoms Are the Donors and the Chloride Ions the Acceptors

	Length, Å		Angle, deg
O(3)–Cl(1)	3.18	Cl(1)–O(3)–Cl(2)	115.3
Cl(2)	3.40	N(2f)	102.3
N(2f)	3.13	N(6h)	100.5
N(6h)	2.98	Cl(2)–O(3)–N(2f)	129.9
O(4)–Cl(2f)	3.16	N(6h)	125.1
Cl(2b)	3.35	N(2f)–O(3)–N(6h)	74.9
N(1)	2.96	Cl(2f)–O(4)–Cl(2b)	80.8
N(4g)	3.18	N(1)	102.5
		N(4g)	71.9
		Cl(2b)–O(4)–N(1)	131.7
		N(4g)	102.2
		N(1)–O(4)–N(4g)	124.8

TABLE VI

SHORT DISTANCES (Å) NOT ASCRIBED TO HYDROGEN BONDS[a]

N(1)–Cl(1)	3.48	N(6)–Cl(2e)	3.51
N(2)–Cl(2)	3.33	N(7)–Cl(1h)	3.49
N(3)–Cl(2)	3.37	O(2)–O(4)	3.07
N(4)–O(4)	3.27	O(2)–N(6p)	2.98
N(5) Cl(2e)	3.50		

[a] For positions see Table V. Estimated Standard Deviations are about 0.01 Å.

TABLE VII

THERMAL MOTIONS OF THE CHLORIDE IONS AND WATER MOLECULES[a]

Atom	Axis i	$(\overline{u_i^2})^{1/2}$, Å	q_{ia}	q_{ib}	q_{ic}
Cl(3)	1	0.292	−0.912	−0.409	0.487
	2	0.191	0.270	−0.545	−0.809
	3	0.163	−0.309	0.732	−0.330
Cl(4)	1	0.218	0.377	−0.408	−0.900
	2	0.200	−0.632	0.544	−0.104
	3	0.172	−0.678	−0.734	0.424
O(3)	1	0.311	−0.230	0.017	−0.677
	2	0.270	−0.972	−0.060	0.734
	3	0.195	−0.054	0.998	0.056
O(4)	1	0.279	−0.993	0.056	0.641
	2	0.220	−0.042	0.644	−0.610
	3	0.186	−0.109	−0.763	−0.467

[a] The magnitudes of the principal axes of thermal motion, $(\overline{u_i^2})^{1/2}$, are rms displacements (Å); the direction cosines q_{ij} are relative to the crystal axes. The estimated standard deviations in the rms displacements are about 0.003 Å for Cl^- and 0.008 Å for O.

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(16) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; Supplement, Special Publication No. 18, The Chemical Society, London, 1965.

(17) V. M. Padmanabhan, H. G. Smith, and S. W. Peterson, *Acta Crystallogr.*, **22**, 928 (1967).

an approximately tetrahedral coordination with two hydrogen-bond acceptors (Cl^- ions) and two hydrogen-bond donors (ammonia molecules). The coordination about the chloride ions is rather irregular. Each has a hydrogen-bonded water molecule as closest neighbor, with distances 3.18 Å for Cl(1)–O(3) and 3.16 Å for Cl(2f)–O(4).

It is interesting to note that neither of the bridging NO_2 and NH_2 groups of the cation is involved in hydrogen bonding.

Thermal Motion.—The ellipsoids of thermal motion for the atoms of the cation are shown in Figure 2. The rms amplitudes along the principal directions range from 0.13 to 0.26 Å. The smallest and most isotropic movements are associated with the Co atoms. The atoms at the periphery of the cation have somewhat more pronounced movements than the atoms of the central ring. The largest thermal vibrations in the structure are displayed by the water molecules and chloride ions, with rms amplitudes up to 0.31 Å; their ellipsoids are described in Table VII. No attempt was made to correct the bond lengths for the effects of thermal vibration.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of Chlorobis(triphenylstibine)tetrakis(trifluoromethyl)rhodiacyclopentadiene–Dichloromethane Solvate, $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$[1]

BY JOEL T. MAGUE

Received December 8, 1969

The structure of chlorobis(triphenylstibine)tetrakis(trifluoromethyl)rhodiacyclopentadiene–dichloromethane solvate, $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$, has been determined from three-dimensional X-ray data collected by counter methods. The final conventional and weighted R factors obtained from a block-diagonal least-squares refinement for 2537 reflections are both 0.044. The material crystallizes in the monoclinic system with space group $P2_1/c$ and a unit cell of dimensions $a = 13.250$ (1), $b = 25.496$ (2), $c = 16.852$ (1) Å; $\beta = 125.4$ (2)°. The calculated density of 1.805 g/cm^3 for four formula units agrees well with the experimental value, 1.80 (2) g/cm^3, determined by flotation. The crystal consists of discrete monomeric molecules interspersed with solvent molecules which do not interact significantly with the metal atoms. The coordination about rhodium is in the form of a slightly distorted trigonal bipyramid with Sb atoms in axial positions and a Cl atom and the 1 and 4 C atoms of the $C_4(CF_3)_4$ moiety occupying equatorial positions. The RhC_4 portion constitutes a five-membered ring which is planar. The chlorine atom and the carbon atoms of the trifluoromethyl groups are also very nearly in the same plane. The average Rh–C distance is 1.98 (1) Å, suggesting Rh–C π bonding. The C–C distances in the ring vary to some extent but are consistent with a considerable degree of delocalization over the four carbon atoms. Distortions from the idealized C_{2v} symmetry are attributed to packing requirements while all other dimensions in the molecule appear normal.

Introduction

In recent years, the search for efficient transition metal catalysts for the polymerization of unsaturated organic molecules has led to the production of a wide variety of novel organometallic complexes.[2,3] During studies on the triphenylstibine analog of the versatile hydrogenation catalyst chlorotris(triphenylphosphine)-rhodium(I), the reaction with hexafluorobutyne-2 was attempted and a yellow crystalline compound of formula $RhCl(Sb(C_6H_5)_3)_2(C_8F_{12})$ was obtained.[4] Chemical and spectroscopic data for this complex were most consistent with the presence of a tetrakis(trifluoromethyl)rhodiacyclopentadiene moiety, but unequivocal proof was not possible. More recently, $IrCl(N_2)(P(C_6H_5)_3)_2$[5] and $Rh(C_6H_4)P(C_6H_5)_2(P(C_6H_5)_3)_2$[6] have been shown to undergo reactions with acetylenes containing electronegative substituents and similar metallocyclic products were postulated. In addition, $Rh(CO)Cl(P(C_6H_5)_3)_2$ was observed to trimerize these same acetylenes, but no intermediate metallocycles could be isolated.[7]

Although such metallocycles have been known for some time,[8] only a limited amount of structural data is

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(1) Supported by National Science Foundation Grant GP-8066.

(2) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, Chapters 8 and 9.

(3) W. Hubel in "Organic Synthesis *via* Metal Carbonyls," Vol. 1, P. Pino and I. Wender, Ed., Wiley-Interscience, New York, N. Y., 1968, p 273.

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