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The Crystal Structure of Trinitrotriamminecobalt(III). A Redetermination

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Received September 14, 1970

The crystal structure of trinitrotriamminecobalt(III), $Co(NO_2)_3(NH_3)_3$, has been redetermined and shows that a previously published structure was incorrect. The final value of the conventional R was 0.090 for 670 data collected by normal film techniques. The compound is orthorhombic, of space group $P2_12_12_1$; $a = 10.14$, $b = 11.68$, $c = 6.82$ Å; $d_{obsd} = 2.00$, $d_{calcd} = 2.01$ g/cm^3; $Z = 4$. The molecule is the meridial isomer (mer) with one pair of trans nitro groups and one pair of trans ammine groups. The average bond lengths are as follows: Co–NH_3, 1.96 Å; Co–NO_2, 1.92 Å (esd 0.01 Å); N–O, 1.24 Å (esd 0.02 Å). There are a large number of intermolecular hydrogen bonds and nonbonded contacts, with the O···N separations ranging between 2.95 and 3.22 Å.

The present redetermination is a result of a project to study the preparations, structures, and infrared spectra of the various compounds in the cobalt–nitro–ammine series $Co(NO_2)_6{}^{3-}$ to $Co(NH_3)_6{}^{3+}$. Although two forms of the neutral compound $Co(NH_3)_3(NO_2)_3$ had been reported[1] with different infrared absorption spectra and X-ray powder patterns, only one could be prepared. X-Ray photographs showed the material to be identical with that studied by Tanito, *et al.*[2] Their structure was determined from two projections using a total of 142 data. The coordinates of the cobalt atom were found from the Patterson projections and those of the nitrogen atoms from the subsequent Fourier maps. However, the coordinates of the oxygen atoms had to be calculated by assuming reasonable values for N–O bond lengths and O–N–O angles. Then (presumably) the acceptable appearance of the final Fourier projection, the correspondence of F_o with F_c, and reasonable intermolecular atom–atom distances were taken to confirm the correctness of the oxygen atom positions. It was decided to collect full three-dimensional X-ray data and to refine the published structure. Most unexpectedly, it was found that the new observed data did not fit the published results and hence it was necessary to redetermine the structure.[3]

Experimental Section

$Co(NO_2)_3(NH_3)_3$ crystallizes in the orthorhombic form with $a = 10.14 \pm 0.02$, $b = 11.68 \pm 0.02$, $c = 6.82 \pm 0.02$ Å; space group $P2_12_12_1$; $d_{obsd} = 2.00 \pm 0.02$, $d_{calcd} = 2.01$ g/cm^3; $Z = 4$; λ(Mo Kα) 0.7107, λ(Cu Kα) 1.5418 Å; μ(Mo Kα) = 22, μ(Cu Kα) = 163 cm^{-1}.

The material was prepared by Miss B. Wise by a variation of the method of Duval[4] using charcoal as a catalyst.[5] Recrystallization from water, slightly acidified with acetic acid, yielded well-formed parallelepipeds elongated parallel to c (in contrast to the plates obtained by Tanito[2]). The density, measured by flotation in aqueous zinc bromide solution, was found to be 2.00 ± 0.02 g/cm^3.

Oscillation, Weissenberg, and precession photographs showed the crystal to be orthorhombic and extinction conditions $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$ showed the space group to be $P2_12_12_1$. Accurate unit cell dimensions were obtained from a- and c-axis zero-layer Weissenberg photographs which had been calibrated with CeO_2 powder patterns ($a_0 = 5.411$ Å). The crystal chosen for the initial data collection measured 0.2 × 0.2 × 0.5 mm.

Using zirconium-filtered Mo Kα radiation, unintegrated data were collected by the precession method for layers $0kl$–$3kl$ and $h0l$–$h3l$, and integrated data were collected by the equiinclination Weissenberg method for layers $hk0$–$hk7$. To obtain a reasonable range of intensities, six exposures were made for each layer of precession data: 10, 30, and 90 min; 5, 12, and 36 hr. For the Weissenberg data single 24-hr exposures were made using packs of four sheets of film, interleaved with three pieces of 0.0025-mm brass shimstock. The intensities were estimated visually by comparison with suitable time-calibrated intensity strips. Lorentz and polarization corrections were calculated and applied to the data. The three sets of data were scaled together by comparing common reflections. The agreement between the values obtained and those previously published[2] for the $0kl$ and $hk0$ data left no doubt that the compound was the same in both cases.

Determination of the Structure

A three-dimensional Patterson synthesis (calculated with program MIFR 1, on an IBM 704 at the CSIR facility, Pretoria, South Africa) confirmed that the approximate coordinates of the cobalt atom were 0.317, 0.25, 0.25. Structure factor calculations and Fourier projections yielded nitrogen atom coordinates similar to those published previously,[2] but it soon became evident that the reported positions of the oxygen atoms were not correct. After many trials the three projections yielded a self-consistent set of coordinates for all atoms.[3] Structure factor calculations using an overall $B = 3.0$ Å^2 gave a discrepancy index R ($R = \Sigma[(|F_o| - |F_c|)/|F_o|]$) of 0.32 compared with $R = 0.42$ from the coordinates of Tanito, *et al.*[2]

All calculations had been done on an IBM 1620 computer, using the set of programs of R. Shiono and D. Hall, IBM library numbers 8.4.004 to 8.4.007; it was now impossible to proceed by conventional three-dimensional Fourier methods, because of the severe limitations of the computational facilities available, and so the work was terminated at this stage.[3]

An attempt was made to refine the new postulated structure by least squares, using program ORFLS on an IBM 360/40 computer at the CSIR, Pretoria, South Africa. R dropped only to 0.25 while the isotropic B's of four of the oxygen atoms increased markedly. It was obvious that the structure still was not correct.

At this stage an 8k-core, single-disk IBM 1130 computer became available in Durban, South Africa, enabling three-dimensional Fourier summations to be done. All subsequent calculations were done on this machine using the local set of programs.[6]

A series of three-dimensional observed and difference Fourier maps showed that atoms O(3), O(4), O(5), and

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(1) R. Duval, *C. R. Acad. Sci.*, **206**, 1652 (1938).

(2) Y. Tanito, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **25**, 188 (1952).

(3) C. G. S. Baines, M.Sc. Thesis, University of Natal, Durban, South Africa, 1967.

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(6) M. Laing and A. Sale, *Acta Crystallogr., Sect. B*, **25**, 1674 (1969).

Table I

Final Positional and Thermal Parameters[a]

	x	y	z		x	y	z
Co	0.3171 (2)	0.2432 (2)	0.2597 (7)	O(5)	0.173 (1)	0.409 (1)	0.064 (3)
N(1)	0.488 (1)	0.314 (1)	0.288 (3)	O(6)	0.353 (2)	0.368 (1)	−0.084 (3)
N(2)	0.361 (2)	0.136 (2)	0.459 (4)	H(14)	0.14	0.09	0.20
N(3)	0.278 (2)	0.350 (2)	0.053 (4)	H(24)	0.09	0.21	0.14
N(4)	0.143 (1)	0.171 (1)	0.223 (3)	H(34)	0.10	0.16	0.35
N(5)	0.243 (2)	0.349 (2)	0.448 (4)	H(15)	0.21	0.31	0.57
N(6)	0.384 (2)	0.135 (2)	0.061 (4)	H(25)	0.16	0.39	0.39
O(1)	0.586 (1)	0.271 (1)	0.214 (3)	H(35)	0.30	0.41	0.48
O(2)	0.499 (1)	0.402 (1)	0.385 (3)	H(16)	0.32	0.12	−0.04
O(3)	0.319 (2)	0.034 (1)	0.453 (3)	H(26)	0.46	0.16	0.01
O(4)	0.429 (2)	0.159 (1)	0.608 (3)	H(36)	0.41	0.06	0.12

Anisotropic Thermal Parameters[b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0025 (2)	0.0019 (1)	0.0125 (8)	0.0003 (4)	−0.0011 (9)	0.000 (1)
N(1)	0.002 (1)	0.004 (1)	0.016 (7)	0.000 (2)	0.004 (5)	0.009 (5)
N(2)	0.005 (2)	0.002 (1)	0.022 (8)	−0.001 (2)	−0.003 (6)	0.011 (5)
N(3)	0.005 (2)	0.001 (1)	0.027 (8)	0.000 (2)	−0.011 (6)	0.000 (4)
N(4)	0.003 (1)	0.004 (1)	0.006 (5)	0.003 (2)	0.001 (5)	0.000 (5)
N(5)	0.006 (2)	0.006 (2)	0.007 (6)	0.000 (3)	−0.005 (5)	−0.002 (5)
N(6)	0.004 (2)	0.006 (2)	0.020 (7)	0.001 (3)	0.000 (6)	−0.003 (6)
O(1)	0.004 (1)	0.005 (1)	0.030 (7)	0.002 (2)	−0.006 (5)	0.000 (5)
O(2)	0.006 (1)	0.006 (1)	0.031 (6)	−0.009 (2)	0.008 (6)	−0.002 (5)
O(3)	0.011 (2)	0.002 (1)	0.029 (6)	0.001 (2)	−0.012 (6)	0.004 (5)
O(4)	0.010 (2)	0.006 (1)	0.027 (7)	−0.003 (3)	−0.011 (6)	0.010 (5)
O(5)	0.006 (1)	0.004 (1)	0.033 (6)	0.004 (2)	0.000 (6)	0.007 (4)
O(6)	0.010 (2)	0.007 (1)	0.015 (6)	0.005 (3)	0.014 (6)	0.005 (5)

[a] The estimated standard deviations are given in parentheses. The approximate errors for the hydrogen atoms are ±0.01 in x and y and ±0.02 in z. All hydrogen atoms were assigned an isotropic $B = 4.0$ Å^2. [b] The general form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

O(6) were incorrectly placed, and adjustment of their positional coordinates reduced R to 0.21. However the final Fourier map still showed small ghost peaks related to the four oxygens by pseudomirror planes at $y = 0.25$ and $z = 0.25$ (presumably due to the cobalt atom having these coordinates). In addition, there were only relatively few data with large h and k indices, so it was decided to re-collect full three-dimensional data for the compound using Ni-filtered Cu Kα radiation, in spite of the absorption and fluorescence problems.

A crystal, of dimensions 0.1 × 0.1 × 0.3 mm, was mounted parallel to c and multiple-film nonintegrated intensity data were collected by the equiinclination Weissenberg method for layers $hk0$–$hk5$. The data were estimated visually and, after Lorentz and polarization corrections had been applied, were used in all subsequent calculations. A three-dimensional observed Fourier map, phased on the cobalt and six nitrogen atoms, still showed the mirror planes, but once oxygens O(1) and O(2) were included in the structure factor calculations, it was possible to destroy the pseudosymmetry and correctly locate the four remaining oxygen atoms. The atom parameters were adjusted by the method of Booth,[7] yielding $R = 0.185$.

The structure was then refined anisotropically by least-squares using the CRYM system at the California Institute of Technology. A Hughes weighting scheme[8] was used, with $4F_{\min} = 20.0$. Neutral atom scattering factors for O, N, and H were taken from ref 9; the scattering factor for cobalt was taken from the tabulation of Hanson, *et al.*,[10] and adjusted for the real part of the dispersion correction.[9] Neither extinction nor absorption corrections were applied so the values of the anisotropic thermal motion parameters, especially for the cobalt atom, are not of great physical significance. When R had dropped to 0.094, a difference Fourier was calculated to check whether the ammonia hydrogens were observable. Areas of positive electron density were found in reasonable positions, and the nine hydrogen atoms were therefore included in the calculations, but their parameters were not refined. After two further cycles of least-squares refinement, the structure converged to a conventional $R = 0.090$.

The final positional and thermal parameters are given in Table I. The values for the observed and calculated structure factors are given in Table II. Intramolecular bond lengths are given in Table III and bond angles are given in Table IV. The numbering system and more important bond lengths and angles are illustrated in Figures 1 and 2. Intermolecular nonbonded contacts are listed in Table V and the nitro oxygen to

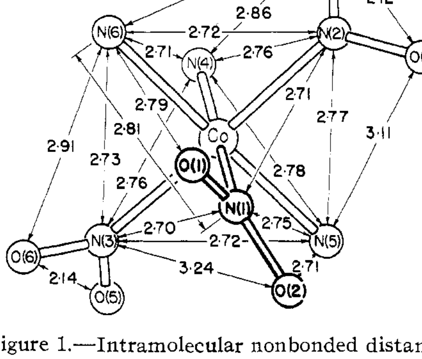

Figure 1.—Intramolecular nonbonded distances.

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TABLE II
FINAL VALUES OF THE OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)[a]

0		K	0
2	1238	1417	179
4	421	415	179
6	252	252	179
8	626	646	0
10	561	557	179
12	277	279	0
1		K	0
3	100	103	89
4	172	177	-89
5	508	513	89
6	100	109	89
7	194	184	-89
8	183	178	-89
9	120	132	89
10	100	120	-89
11	228	236	-89
12	180	120	89
2		K	0
0	712	751	179
1	876	889	0
2	278	256	0
3	115	61	179
4	290	294	179
5	102	43	0
6	219	226	0
7	258	258	179
8	379	396	179
9	664	647	0
10	433	416	0
11	199	197	179
12	186	144	179
3		K	0
1	478	541	89
2	485	517	89
3	891	825	-89
4	274	280	89
6	197	198	89
7	305	292	89
8	274	285	-89
9	106	124	-89
10	219	206	89
11	63	90	-89
13	111	114	89
14	128	105	89
4		K	0
0	355	379	179
1	680	722	179
2	162	143	0
3	786	806	0
4	44	11	0
5	724	751	179
7	440	470	0
8	191	200	179
9	629	621	179
10	89	109	0
11	211	207	0
13	137	122	179
5		K	0
1	195	163	-89
2	267	249	89
3	211	197	89
4	140	103	-89
5	198	203	-89
6	333	357	-89
7	84	96	-89
8	197	207	89
11	130	126	89
12	102	106	89
13	69	68	-89
6		K	0
0	733	723	0
1	369	371	0
2	168	182	179
3	407	426	179
4	205	242	0
5	315	323	0
6	412	443	179
8	190	204	0
9	107	111	0
11	169	195	179
12	156	154	0
13	167	183	0
7		K	0
2	177	191	89
4	84	84	-89
5	161	156	89
10	155	117	-89
12	78	109	89
8		K	0
0	234	225	179
1	120	144	0
2	323	318	0
3	195	193	179
4	688	632	179
5	200	191	0
6	434	440	0
7	123	93	179
8	196	218	179
9	93	85	0
10	240	221	0
9		K	0
2	200	175	89
5	152	145	-89
7	113	127	89
8	130	92	-89
10		K	0
0	163	166	0
1	163	143	179
2	137	148	179
3	298	295	0
4	230	230	0
5	274	251	179
6	208	217	179
7	130	120	0
9	174	193	179
0		K	0
14	188	176	179
3		K	0
14	113	105	89
12		K	0
0	219	196	0
1	221	238	0
2	132	116	179
3	263	244	179
4	93	103	0
5	178	210	0
6	128	120	179
0		K	1
2	183	151	0
5	121	116	-89
7	227	232	-89
10	208	211	179
12	173	136	0
14	103	66	179
1		K	1
0	592	695	-89
1	1091	1019	-88
2	747	652	47
3	565	460	105
4	597	524	-68
5	649	523	-63
6	442	430	95
7	392	417	66
8	246	244	-63
9	372	377	-102
11	367	331	115
13	277	228	-85
14	95	98	67
2		K	1
0	277	305	89
1	220	228	-50
2	368	365	17
3	277	247	-74
4	333	327	141
5	207	207	105
6	251	244	-22
7	215	218	145
8	209	173	-153
9	346	336	22
10	99	90	-4
11	294	239	169
13	114	94	-15
14	89	94	-32
3		K	1
0	208	197	89
1	563	610	129
2	574	568	-78
3	426	404	-62
4	897	867	97
5	265	236	110
6	526	547	-103
7	265	260	-131
8	526	522	84
9	197	194	78
10	388	412	-92
11	188	180	-41
12	148	150	86
14	128	122	-103
4		K	1
0	98	84	-89
1	372	354	-120
2	619	609	-28
3	188	227	-66
4	222	223	-137
5	78	81	117
6	251	228	118
7	183	149	56
8	78	99	3
9	82	105	145
11	76	103	-23
13	142	111	-152
5		K	1
0	736	689	-89
1	448	482	92
2	639	548	115
3	341	319	-77
4	329	346	-107
5	270	310	61
6	209	248	80
7	265	246	-53
8	191	220	-86
9	201	196	114
10	227	219	106
11	149	193	-133
12	206	215	-90
13	135	138	89
6		K	1
0	103	78	89
2	115	120	133
4	183	226	13
5	150	172	-59
6	167	144	-143
10	143	170	169
11	84	54	-130
12	191	186	0
13	48	68	9
7		K	1
0	114	112	89
1	542	549	-100
2	310	268	-38
3	509	512	79
4	123	161	74
5	539	525	-90
7	298	312	88
9	211	183	-83
10	84	120	-60
11	141	192	102
8		K	1
0	147	157	89
4	114	118	-114
6	129	130	17
8	92	117	175
9	98	97	75
9		K	1
1	129	98	114
2	154	162	-100
3	193	201	-88
4	317	301	90
5	274	292	91
6	183	214	-109
7	244	264	-92
8	158	174	102
9	196	180	91
10	177	171	-66
10		K	1
0	197	192	-89
5	115	122	-144
7	108	121	12
11		K	1
0	397	396	-89
1	89	122	-144
2	388	341	99
3	96	124	17
4	282	263	-92
5	87	87	-10
6	189	205	84
7	45	61	168
12		K	1
5	61	75	48
0		K	2
1	341	303	89
2	1231	1216	0
3	606	557	-89
4	1217	1291	179
5	76	115	-89
6	688	640	0
7	195	196	89
8	179	179	179
10	171	150	0
12	310	325	179
14	288	255	0
1		K	2
1	227	210	-126
2	547	483	-93
3	643	577	118
4	320	271	54
5	138	123	-133
6	84	58	-134
7	142	186	51
8	147	179	-37
9	166	137	-61
10	114	78	149
11	126	85	142
2		K	2
0	187	184	179
1		K	2
13	195	227	-102
2		K	2
1	283	383	79
2	423	490	137
3	551	589	-14
4	482	496	-8
5	657	639	-172
6	447	466	-163
7	416	436	-4
8	280	285	-9
10	161	152	-163
11	222	179	16
12	135	162	-8
13	208	211	176
14	121	121	170
3		K	2
0	145	158	179
1	240	221	50
2	220	202	81
3	287	284	-83
4	268	278	69
5	96	109	-50
6	155	191	-131
7	190	176	93
8	172	184	88
10	98	91	-61
12	129	129	101
14	86	81	-68
4		K	2
0	61	60	0
1	598	642	6
2	239	223	138
3	685	694	175
4	220	221	-41
5	521	591	-5
7	639	613	-168
8	147	129	92
9	291	255	14
10	98	97	157
11	218	266	160
12	131	124	-22
13	199	193	-9
5		K	2
0	137	140	179
1	363	336	-179
2	84	78	74
3	89	100	-144
4	206	188	-72
5	99	91	152
6	91	87	-165
7	166	162	-68
10	181	183	62
11	86	95	86
12	228	234	-74
13	82	80	173
6		K	2
0	378	368	179
1	472	480	-176
2	458	507	-5
3	199	232	-14
4	236	263	176
5	131	99	-165
6	147	116	28
7	197	223	-7
8	160	166	-173
9	96	150	163
10	171	230	-21
11	150	124	15
12	203	200	172
7		K	2
0	89	72	0
1	309	285	173
2	167	169	-96
3	132	148	174
4	109	148	69
5	211	170	15
8	55	80	-74
9	136	135	-99
8		K	2
0	414	373	0
1	184	205	135
2	436	414	175
3	149	134	-20
4	279	272	6
5	150	146	-157
6	287	321	-171
7	94	129	-19
8	344	372	0
10	229	253	-170
9		K	2
4	137	153	143
6	73	75	-46
7	109	119	-92
9	169	157	59
10		K	2
0	197	193	179
1	288	261	4
2	186	198	-18
3	158	145	175
4	103	116	163
5	128	133	-23
6	136	123	25
7	237	226	-176
8	117	125	-170
9	165	190	6
12		K	2
0	122	138	179
1	294	290	176
2	143	146	21
3	155	190	-13
4	68	83	-167
0		K	3
1	115	115	89
2	267	228	0
3	41	7	-89
4	108	94	179
7	96	131	-89
8	172	122	179
10	109	112	179
12	106	135	179
14	281	242	0
1		K	3
0	310	342	89
1	398	396	78
2	588	498	-76
3	814	736	-86
4	351	321	77
5	454	409	99
6	183	180	-79
7	344	332	-84
8	91	118	67
9	189	187	99
10	133	101	-78
11	240	226	-85
12	132	117	82
13	230	200	101
2		K	3
0	177	210	-89
1	451	413	15
2	395	340	118
3	235	219	123
4	301	276	-17
5	279	295	-151
6	91	96	174
7	313	279	35
9	94	94	-149
11	52	77	28
12	189	153	-32
13	128	151	175
3		K	3
0	435	434	-89
2	447	404	83
3	371	327	115
4	372	359	-97
5	383	382	-93
6	680	690	88
7	304	275	112
8	401	400	-99
10	161	152	79
11	48	102	-4
12	240	241	-98
4		K	3
0	117	118	-90
1	251	274	146
2	360	334	-17
5	66	95	-9
6	267	256	-171
7	104	103	166
9	109	119	-12
10	157	162	-15
11	106	96	-171
12	139	113	153
13	99	86	3
5		K	3
0	332	359	89
1	404	368	-66
2	450	432	-107
3	357	342	110
4	287	288	82
5	151	132	-54
6	290	287	-79
7	121	142	78
8	227	233	110
9	131	178	-109
10	150	170	-87
11	183	192	88
12	155	148	89
6		K	3
1	199	200	138
2	98	94	110
3	252	260	-18
4	73	71	9
5	92	93	79
7	109	154	-129
8	248	296	-171
10	64	68	55
11	111	126	-2
12	61	50	-128
7		K	3
0	233	207	-89
1	575	531	87
2	106	135	55
3	399	415	-96
4	55	50	-56
5	155	146	88
7	207	267	-99
8	71	90	-44
9	264	290	82
8		K	3
1	190	149	-21
3	191	172	156
8	103	122	34
9	78	59	-108
10	96	99	-148
9		K	3
0	313	301	-89
1	203	177	-69
2	152	167	74
3	206	194	115
5	123	147	-94
6	157	180	95
7	162	192	86
8	173	202	-87
9	160	186	-91
10		K	3
1	111	119	77
3	136	139	173
5	73	111	-48
11		K	3
0	366	318	89
2	354	296	-84
4	203	183	94
0		K	4
1	74	87	-89
2	656	618	179
3	143	115	-89
4	557	559	0
6	319	279	179
8	270	260	0
9	103	115	89
10	298	286	179
11	138	111	-89
12	147	162	0
13	68	75	89
1		K	4
0	61	0	179
1	132	119	59
2	206	167	-1
3	149	140	-140
4	231	195	-132
5	148	145	137
6	222	218	18
7	161	131	-42
8	89	89	123
9	115	82	99
10	99	91	-87
11	151	147	-121
12	117	112	155
13	82	96	67
2		K	4
0	438	465	179
1	290	232	24
2	339	292	36
4	164	168	-166
5	372	370	-11
6	213	257	-28
7	284	266	177
8	212	211	-168
9	193	208	2
10	148	189	-16
11	141	133	-170
12	145	142	-179
13	64	73	5
3		K	4
0	73	81	179
1	48	23	-45
3	205	222	-2
4	118	120	-87
6	108	106	110
10	118	151	89
11	136	111	3
12	139	122	-82
4		K	4
0	86	102	179
1	431	473	178
3	371	392	8
5	416	406	-174
6	111	87	-27
7	263	281	0
8	171	180	106
9	264	271	-175
11	237	222	3
5		K	4
0	158	137	179
1	160	204	-37
2	136	127	-89
3	285	297	135
4	68	78	8
6	103	126	-156
8	101	84	90
9	48	57	35
10	96	105	-69
11	106	78	143
12	61	85	52
6		K	4
0	343	304	0
1	283	284	-31
2	347	351	-157
3	200	213	151
4	240	267	10
5	155	168	-13
6	89	122	150
7	71	101	-172
8	108	150	-38
9	124	114	20
10	179	176	175
11	106	70	-165
7		K	4
1	71	61	130
2	89	103	-38
3	89	104	-166
6	121	115	54
7	106	109	-36
9	133	115	155
8		K	4
0	264	256	179
1	146	104	36
2	229	223	17
3	71	109	156
4	297	276	-169
5	96	110	-51
6	313	314	-2
7	84	65	157
8	231	222	-179
9		K	4
0	162	174	0
1	48	64	24
2	82	109	-175
3	104	99	-25
4	45	45	-109
5	86	105	-146
6	78	47	125
7	129	118	66
8	92	81	-14
10		K	4
0	86	81	0
1	141	137	-177
2	156	111	-150
3	180	149	4
4	164	131	11
5	217	189	-177
6	84	90	161
11		K	4
0	80	105	179
0		K	5
2	167	90	179
3	89	57	89
5	67	68	-89
6	87	63	179
7	76	63	89
9	73	73	-89
10	145	138	179
12	73	47	0
1		K	5
0	180	217	-89
1	505	560	-89
2	267	228	120
3	180	194	75
4	183	181	-76
5	125	150	-107
6	51	81	61
7	214	175	112
8	142	117	-105
9	318	295	-79
10	127	120	68
11	226	191	98
2		K	5
0	226	247	89
1	211	210	37
2	184	192	-121
3	78	77	176
5	70	84	113
6	156	171	-10
7	142	122	-94
8	131	120	136
9	136	146	35
10	114	116	-38
11	131	143	-158
3		K	5
0	328	362	89
1	144	160	97
2	256	273	-110
3	127	122	-36
4	290	305	74
5	153	160	148
6	192	237	-97
7	108	84	-66
8	260	277	91
9	87	120	54
10	273	247	-94
11	81	76	-96
4		K	5
0	151	155	-89
1	55	75	-146
2	240	260	22
3	120	113	109
4	102	146	-174
6	108	90	179
7	131	138	-53
8	155	143	-25
9	106	107	159
10	110	99	66
11	95	87	6
5		K	5
0	246	227	-89
1	159	182	81
2	229	232	84
3	147	124	-70
4	283	296	-82
5	186	191	109
6	131	162	95
7	104	129	-96
8	110	141	-89
9	87	95	75
10	172	153	95
6		K	5
1	169	160	-102
2	70	109	-168
3	108	124	53
4	108	137	59
5	92	80	-22
6	73	93	-107
7	120	118	166
8	14	42	141
10	60	87	174
7		K	5
0	92	114	89
1	223	209	-86
2	76	78	-115
3	239	243	95
5	302	313	-96
6	47	43	-21
7	181	175	79
9	99	108	-110
8		K	5
4	67	85	-118
5	151	121	118
6	151	143	32
7	120	83	-84
9		K	5
0	79	79	89
1	89	87	71
2	89	108	-119
3	144	124	-90
4	173	159	76
5	198	207	103
6	125	124	-90
10		K	5
3	55	56	78
4	99	85	-95

[a] The numbers in the four columns are *k* index, F_o, F_c, and phase angle.

TABLE III
INTRAMOLECULAR BOND LENGTHS AND NONBONDED DISTANCES (Å)[a]

Co–N(1)	1.93	N(4)···N(6)	2.71
Co–N(2)	1.90	N(1)···O(4)	2.90
Co–N(3)	1.92	N(1)···O(6)	2.95
Co–N(4)	1.97	N(2)···O(1)	3.24
Co–N(5)	1.94	N(3)···O(2)	3.24
Co–N(6)	1.97	N(4)···O(3)	2.86
N(1)–O(1)	1.22	N(4)···O(5)	3.00
N(1)–O(2)	1.22	N(5)···O(2)	2.71
N(2)–O(3)	1.26	N(5)···O(4)	3.11
N(2)–O(4)	1.25	N(5)···O(5)	2.80
N(3)–O(5)	1.26	N(6)···O(1)	2.79
N(3)–O(6)	1.22	N(6)···O(3)	2.99
N(1)···N(2)	2.71	N(6)···O(6)	2.91
N(1)···N(3)	2.70	O(1)···O(2)	2.11
N(1)···N(5)	2.75	O(3)···O(4)	2.12
N(1)···N(6)	2.81	O(5)···O(6)	2.14
N(2)···N(4)	2.76	O(2)···O(4)	3.29
N(2)···N(5)	2.77	Co···O(1)	2.76
N(2)···N(6)	2.72	Co···O(2)	2.75
N(3)···N(4)	2.76	Co···O(3)	2.77
N(3)···N(5)	2.72	Co···O(4)	2.80
N(3)···N(6)	2.73	Co···O(5)	2.77
N(4)···N(5)	2.78	Co···O(6)	2.79

[a] Bond lengths are not corrected for thermal motion; estimated standard deviations are 0.01 Å for all Co–N bonds and 0.02 Å for all N–O bonds.

TABLE IV
BOND ANGLES (DEG)[a]

N(1)-Co-N(4)	179	N(3)-Co-N(6)	89
N(2)-Co-N(3)	178	N(4)-Co-N(5)	91
N(5)-Co-N(6)	177	N(4)-Co-N(6)	87
N(1)-Co-N(2)	90	O(1)-N(1)-O(2)	119
N(1)-Co-N(3)	89	O(3)-N(2)-O(4)	114
N(1)-Co-N(5)	90	O(5)-N(3)-O(6)	118
N(1)-Co-N(6)	92	O(1)-N(1)-Co	121
N(2)-Co-N(4)	91	O(2)-N(1)-Co	120
N(2)-Co-N(5)	92	O(3)-N(2)-Co	121
N(2)-Co-N(6)	90	O(4)-N(2)-Co	125
N(3)-Co-N(4)	90	O(5)-N(3)-Co	119
N(3)-Co-N(5)	89	O(6)-N(3)-Co	123

[a] The estimated standard deviations are 1° for all angles involving the cobalt atom and 2° for the ONO angles.

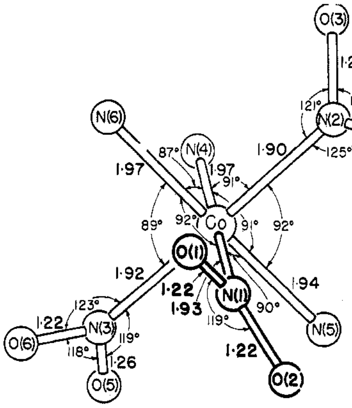

Figure 2. Bond lengths and bond angles.

TABLE V
INTERMOLECULAR NONBONDED DISTANCES

From atom in asym unit	To atom	In position[a]	Distance, Å
N(4)	O(3)	2	3.05
N(4)	O(1)	5	3.11
N(4)	O(6)	5	3.13
N(4)	O(2)	6	3.16
N(4)	O(4)	6	3.16
N(3)	O(1)	5	3.02
N(5)	O(5)	1	3.06
N(5)	O(1)	6	3.16
N(5)	O(4)	6	3.22
N(6)	O(4)	7	3.14
N(6)	O(3)	2	2.95
N(6)	O(2)	3	3.00
N(6)	O(5)	4	3.10
O(1)	O(5)	4	2.96
O(1)	O(6)	4	3.28
O(2)	O(5)	1	3.07

[a] Position: (1) $-x + {}^1/_2, -y + 1, z + {}^1/_2$; (2) $-x + {}^1/_2, -y, z - {}^1/_2$; (3) $-x + 1, y - {}^1/_2, -z + {}^1/_2$; (4) $x + {}^1/_2, -y + {}^1/_2, -z$; (5) $x - {}^1/_2, -y + {}^1/_2, -z$; (6) $x - {}^1/_2, -y + {}^1/_2, -z + 1$; (7) $x, y, z - 1$.

TABLE VI

LEAST-SQUARES PLANE PARAMETERS[a]

						Direction cosines of normal to plane	Origin to plane distance, Å
Plane atoms	Co	N(1)	N(4)	O(1)	O(2)	0.155, −542, 0.826	0.41
Dev, Å	0.01	−0.01	−0.01	0.00	0.00		
Plane atoms	Co	N(2)	N(3)	O(5)	O(6)	0.470, 0.718, 0.514	4.47
Dev, Å	−0.01	0.01	−0.02	0.01	0.01		
Plane atoms	Co	N(2)	N(3)	O(3)	O(4)	0.826, −0.269, 0.495	1.04
Dev, Å	−0.02	0.01	0.01	0.00	0.00		
Plane atoms	Co	N(1)	N(2)	N(3)	N(4)	−0.385, 0.624, 0.680	1.72
Dev, Å	0.02	0.00	−0.01	−0.01	0.00		
Plane atoms	Co	N(2)	N(3)	N(5)	N(6)	0.906, 0.411, 0.098	4.25
Dev, Å	0.01	0.03	0.03	−0.03	−0.03		
Plane atoms	Co	N(1)	N(4)	N(5)	N(6)	0.216, −0.645, 0.733	0.14
Dev, Å	0.02	0.00	0.00	−0.01	−0.01		

[a] The equation of the plane is of the form $Ax + By + Cz + D = 0$ where A, B, and C are the direction cosines referred to the real crystallographic axes and D is the perpendicular distance to the origin.

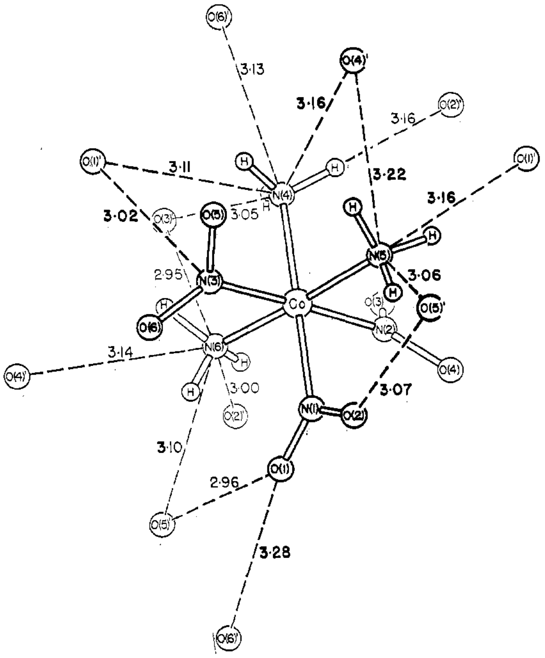

Figure 3.—Intermolecular nonbonded distances.

TABLE VII

BOND LENGTHS, ANGLES, AND NONBONDED SEPARATIONS INVOLVING HYDROGEN ATOMS[a]

Atoms	Length, Å	Atoms	Angle, deg
N(4)–H(14)	1.0	Co–N(4)–H(14)	118
N(4)–H(24)	0.9	Co–N(4)–H(24)	113
N(4)–H(34)	1.0	Co–N(4)–H(34)	110
N(5)–H(15)	1.0	Co–N(5)–H(15)	112
N(5)–H(25)	1.0	Co–N(5)–H(25)	110
N(5)–H(35)	1.0	Co–N(5)–H(35)	111
N(6)–H(16)	1.0	Co–N(6)–H(16)	113
N(6)–H(26)	0.9	Co–N(6)–H(26)	108
N(6)–H(36)	1.0	Co–N(6)–H(36)	109

Hydrogen atom in asym unit	To atom	In position[b]	Distance, Å
H(24)	O(1)	5	2.4
H(15)	O(1)	6	2.2
H(36)	O(2)	3	2.1
H(34)	O(2)	6	2.2
H(35)	O(5)	1	2.2
H(26)	O(5)	4	2.4
H(24)	O(6)	5	2.6
H(14)	O(3)	2	2.3
H(16)	O(3)	2	2.3
H(25)	O(4)	6	2.5

[a] The approximate error in the bond lengths is 0.1 Å and in the bond angles is 5°. [b] See Table V.

ammonia nitrogen distances are illustrated in Figure 3. Parameters for various least-squares planes are given in Table VI. Interatomic distances and bond angles involving hydrogen atoms are given in Table VII. The thermal vibration ellipsoids are illustrated in Figure 4. (Subsequent refinement of the structure using the 740 original molybdenum-radiation data yielded a final $R = 0.107$, with positional parameters within one standard deviation of those given in Table I. A full list of these data is available from the authors on request.

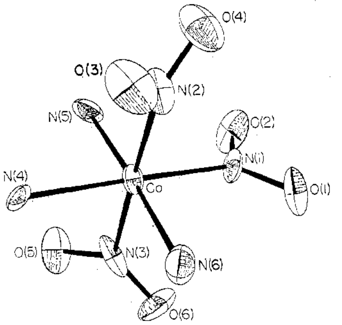

Figure 4.—Thermal vibration ellipsoids; a projection down *y*.

Discussion of the Structure

The bond lengths are similar to those found in related compounds; the average Co–NH$_3$ length of 1.96 Å compares with the average values of 1.96 and 1.95 Å found in $Co_2(NH_3)_{10}O_2^{4+}$[11] and $Co_2(NH_3)_{10}O_2^{5+}$,[12] respectively. The average Co–NO$_2$ length of 1.92 Å can be compared with the rather imprecise values of 1.96 and 1.97 Å found in $Co(NO_2)_4(NH_3)_2^-$.[13,14] Although the difference between the average Co–NH$_3$ and Co–NO$_2$ bond lengths in $Co(NO_2)_3(NH_3)_3$ is barely significant, the pattern of shorter Co–NO$_2$ and longer Co–NH$_3$ seems chemically reasonable. The average N–O bond length of 1.24 Å can be compared with the range of values from 1.21 to 1.26 Å found in $Co(NO_2)_4(NH_3)_2^-$.[13,14] The difference between the average N–O bond length in the trans pair of NO$_2$ groups and that in the unique NO$_2$ is not significant.

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(11) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

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

(13) Y. Komiyama, *Bull. Chem. Soc. Jap.*, **30**, 13 (1957).

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The six nitrogens are bonded to the cobalt in the expected octahedral arrangement; the angular distortions from ideality do not seem to follow any particular pattern. The molecule is the meridial (mer) isomer,[15] as previously reported by Tanito, *et al.*[2] All intramolecular nonbonded separations are normal, ranging upward from 2.70 Å (Table III, Figure 1). Nitro group O(1)–N(1)–O(2) is twisted 80° from the plane of N(1)–Co–N(3)–N(2)–N(4), while nitro group O(3)–N(2)–O(4) is twisted 34° and nitro group O(5)–N(3)–O(6) is twisted 52° from this plane. The planes of nitro groups O(3)–N(2)–O(4) and O(5)–N(3)–O(6) thus make an angle of 86° with each other.

The molecules are involved in a complicated three-dimensional network of hydrogen bonds, with intermolecular ammine N to nitro O distances ranging between 2.95 and 3.16 Å (Figure 3, Table V). There are also several O···O and nitro N···O contacts of about 3 Å, which share in making it a very closely packed and compact structure.

Comments on the Two Incorrect Methods

It is of interest (and rather sobering!) to find that two incorrect structures could have seemingly correct bond lengths and angles, reasonable looking Fourier maps, and relatively low values for *R*. In fact, consideration of nonbonded distances between atoms shows immediately that the structures must be incorrect in spite of apparently satisfactory bond lengths and angles[2] or a reasonably low *R*.[3]

The Tanito model gives rise to impossibly short intramolecular ammonia N···O separations of 2.20 and 2.09 Å, while there are four other intramolecular contacts about 0.3 Å shorter than is usual.[16] The relatively short intermolecular ammonia N···nitro O separations of 2.74 and 2.78 Å and especially an O···O separation of 2.76 Å mentioned in ref 2 hint that the structure may be incorrect. (A three-dimensional Fourier map, using the new observed data, and phased on the Tanito model, shows a number of spurious peaks and deep negative "holes" as well as ghost peaks in what eventually proved to be the correct positions for the oxygen atoms. *R* for this calculation was 0.35.)

In the Baines model,[3] an intermolecular O···O separation of 2.44 Å shows conclusively that the model was incorrect and this conclusion is confirmed by two impossibly short intramolecular nonbonded N···O and O···O separations of 2.53 and 2.09 Å, respectively, and the generally rather poor bond lengths and angles.

Recent work[17] confirms the existence of the two isomers of $Co(NO_2)_3(NH_3)_3$ and in fact the assignment of the mer stereochemistry to the product prepared by the method of Jorgensen[18] was made on the basis of the structure determination by Tanito, *et al.*[2] Fortunately, the redetermination shows that this was indeed the mer isomer.

Acknowledgments. We are grateful to the South African Council for Scientific and Industrial Research for a grant to cover running expenses and for the use of their computational facilities and to the Chemistry Department of California Institute of Technology for a grant to cover the cost of the final refinement. M. L. wishes to thank the faculty of the Chemistry Department of San Fernando Valley State College and especially Dr. R. E. Marsh of the California Institute of Technology for their generosity and hospitality during his stay in Los Angeles, Calif., in 1970. The diagrams were prepared by Miss Lillian Casler.

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[18] S. M. Jorgensen, *Z. Anorg. Allg. Chem.*, **17**, 475 (1898).

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The Crystal and Molecular Structure of Tris(ethylenediamine)cobalt(III) Di-μ-chloro-bis(trichlorocuprate(II)) Dichloride Dihydrate, $[Co(N_2C_2H_8)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$

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Received August 19, 1970

The crystal and molecular structure of tris(ethylenediamine)cobalt(III) di-μ-chloro-bis(trichlorocuprate(II)) dichloride dihydrate, $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group D_{2h}^{15}-*Pbca* of the orthorhombic system with four molecules in a cell of dimensions $a = 13.560$ (9), $b = 14.569$ (9), and $c = 17.885$ (12) Å. The observed and calculated densities are 1.86 and 1.862 g cm^{-3}, respectively. Least-squares refinement of the structure has yielded a final value of the conventional *R* factor (on *F*) of 0.065 for 1275 independent reflections having $F^2 > 3\sigma(F^2)$. The $Cu_2Cl_8^{4-}$ anion consists of two distorted trigonal bipyramids sharing a common edge, the bridging Cu–Cl distances being 2.325 (5) and 2.703 (5) Å while the Cu–Cu separation is 3.722 (5) Å. The $Co(en)_3^{3+}$ cation is found to have the relatively high energy configuration $\Delta(\lambda\delta\delta)$ ($\equiv\Lambda(\delta\lambda\lambda)$) as a result of intermolecular interactions within the crystal.

Introduction

A complex of formulation $Co(en)_3CuCl_5(H_2O)$ (where en = ethylenediamine, $NH_2CH_2CH_2NH_2$) was first reported by Kurnakow[1] in 1898, and it has long been assumed that the anionic moiety consisted of either the trigonal-bipyramidal $CuCl_5^{3-}$ ion, as found[2] in [Cr-

[1] N. S. Kurnakow, *Z. Anorg. Chem.*, **17**, 225 (1898).

[2] (a) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968); (b) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Jap.*, **34**, 295 (1961).