

Ti ist in Form einer tetragonalen Pyramide von vier Cl-Atomen in der Basis und einem O-Atom in der Spitze umgeben. Der Winkel O-Ti-Cl(1) beträgt annähernd 102°. Wichtige Abstände des Anions sind in Tabelle 2 enthalten.

Tabelle 2. *Abstände am Anion*

Ti—Cl(1)	2,34 Å
Ti—Cl(2')	2,32
Ti—O	1,79
Cl(1)—Cl(2)	3,24

Der relativ kurze Bindungsabstand Ti—O = 1,79 Å deutet auf eine zusätzliche  $\pi\pi$ - $d\pi$ -Bindung zwischen Titan und Sauerstoff. Das grosse Tetraäthylammonium-Kation könnte verantwortlich gemacht werden für die Ausbildung der monomeren Struktur, denn nach spektroskopischen Untersuchungen (Feltz, 1967) am  $[\text{NH}_3(\text{C}_2\text{H}_5)_2\text{TiCl}_4\text{O}]$  und  $\text{Rb}_2\text{TiCl}_4\text{O}$  liegt es nahe, dass es bei diesen Verbindungen zu einer Wechselwirkung zwischen den Anionen und zur Ausbildung von Sauerstoffbrücken kommen wird, wobei sich die Koordinationszahl am Titan auf 6 erhöhen müsste.

Die schwach grünliche, stark hygroskopische Verbindung  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{VCl}_4\text{O}$  (Feltz, 1966) mit 4-wertigem Vanadin

kristallisiert in der gleichen Raumgruppe wie  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{TiCl}_4\text{O}$ . Die Gitterparameter sind:

$$a = b = 10,12 \pm 0,03 \text{ \AA}$$

$$c = 12,68 \pm 0,04$$

$$V = 1299 \text{ \AA}^3$$

$$\rho_{\text{exp}} = 1,23 \text{ g.cm}^{-3}$$

Auf Grund des Vergleiches der Intensitäten aus Weissenberg-Böhm-Aufnahmen um [110] (0.-2. Schicht) von beiden Verbindungen darf auf Isomorphie zwischen  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{TiCl}_4\text{O}$  und  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{VCl}_4\text{O}$  geschlossen werden. Danach liegen auch in der Vanadinverbindung isolierte  $\text{VCl}_4\text{O}$ -Gruppen mit tetragonal-pyramidaler Anordnung vor.

Herrn Professor Dunken danken wir für die Unterstützung bei den Untersuchungen und Herrn Dr Feltz für die Präparation der Substanzen.

#### Literatur

FELTZ, A. (1965). *Z. anorg. allg. Chem.* **334**, 242.

FELTZ, A. (1966). Persönliche Mitteilung.

FELTZ, A. (1967). *Z. Chem.* **7**, 158.

*Acta Cryst.* (1968). **B24**, 283

**A reinvestigation of the crystal structure of decammine- $\mu$ -amido-dicobalt pentanitrate\***. By WILLIAM P. SCHAEFER†, A. W. CORDES‡ and RICHARD E. MARSH, *Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

(Received 18 July 1967)

The crystal structure of  $(\text{NH}_3)_5\text{Co}(\text{NH}_2)\text{Co}(\text{NH}_3)_5(\text{NO}_3)_5$  has been reinvestigated. A satisfactory refinement has been carried out in space group  $P4_2/mnm$ , based on three-dimensional Fe  $K\alpha$  data collected on an automated diffractometer; the  $R$  index is 0.076 for 357 reflections. Although the dimensions of the cation are similar to those found earlier by Vannerberg, its orientation within the cell is different. The cation is severely strained, the Co—N(bridge) distances being 2.06 Å and the Co—N—Co angle 153°. The crystals are approximately isostructural with those of the corresponding  $\text{O}_2$ -bridged compound; they probably contain a small and variable amount of water of crystallization.

As part of a program of investigation on bridged dicobalt compounds, we have reinvestigated the crystal structure of decammine- $\mu$ -amido-dicobalt pentanitrate,



Although we find the molecular structure to be very similar to that reported in an earlier investigation (Vannerberg, 1963), the crystal structure is significantly different.

#### Experimental

Crystals of the red compound, in the form of thin needles and small prisms, were kindly furnished by Professor C. Brubaker. The analysis for cobalt was reported as 19.1%; calculated for the anhydrous nitrate, 19.2%. Pre-

liminary Weissenberg photographs of several crystals all showed tetragonal symmetry but with appreciable variations in diffraction patterns, both in regard to intensities and cell dimensions; the variations were particularly large in going from a needle-shaped crystal (for which reflections  $hk0$  with  $h+k$  odd were unobservably weak) to a prismatic crystal (for which many such reflections could be observed, although they were of low intensity). All the data on which this report is based were obtained from a needle-shaped crystal; the intensities are in good general agreement with the values reported by Vannerberg (1963).

Unit-cell dimensions were measured on a diffractometer with Fe  $K\alpha$  radiation ( $\lambda = 1.9373 \text{ \AA}$ ). Our values are  $a = 11.79$ ,  $c = 8.27 \text{ \AA}$ , both  $\pm 0.01$ ; Vannerberg reports  $a = 11.68 \pm 0.03$ ,  $c = 8.28 \pm 0.02 \text{ \AA}$ . This discrepancy is within the variation we find among different crystals.

Intensity data were collected on a Datex-automated General Electric diffractometer using  $\text{MnO}_2$ -filtered iron radiation. (Attempts were first made to collect the data with the use of copper radiation, but the crystal deteriorated extensively during the process.) The crystal was cut to an approximate cube, about 0.1 mm on an edge ( $\mu t \approx 0.3$ ). A periodic check of a standard reflection showed an ap-

\* Contribution no. 3535 from the Gates and Crellin Laboratories. This work was supported in part by Grant GP-5768 from the National Science Foundation.

† Present address: Department of Chemistry, University of California, Davis, California, U.S.A.

‡ Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A.



preciable drop-off in intensity toward the end of the collection period, the final intensity measurements being only 93% as large as the starting values. Variances  $\sigma(F_0^2)$  were assigned on the basis of counting statistics but including an additional term, equal to  $(0.02F_0^2)^2$ , to take account of crystal decomposition and other, unknown experimental errors.

Severe disorder has limited the accuracy of the refinement. The final set of parameters was derived by difference-map and least-squares calculations, starting with the positions of the cobalt atoms given by Vannerberg (1963); they

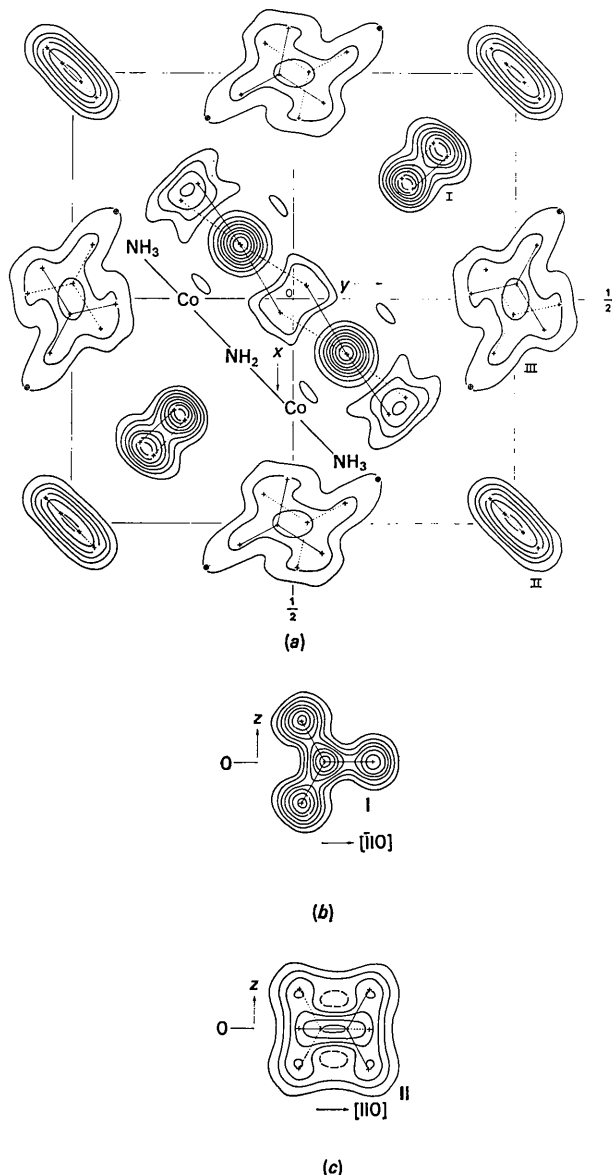


Fig. 1. Electron density maps calculated at the conclusion of the refinement. (a) The section  $z=0$ . (b) A section parallel to (110), through nitrate group I. (c) A section parallel to (110), through nitrate group II. Contours are at 1, 2, 3...  $e.\text{\AA}^{-3}$  except around the cobalt atoms, where they are at 1, 5, 10, 15...  $e.\text{\AA}^{-3}$ . Crosses indicate the final atomic positions. All heavy atoms are shown except for the nitrogen atoms N(2) and N(3), which complete the octahedra about the cobalt atoms.

are given in Table 1. Observed and calculated structure factors are given in Table 2, and sections of the electron density calculated at the conclusion of the refinement are shown in Fig. 1. All calculations were carried out on an IBM 7094 computer using the CRYRM system (Duchamp, 1964). Atomic form factors for Co, N, and O were taken from *International Tables for X-ray Crystallography* (1962), the values for cobalt having been corrected by  $-1.74$  electrons to take account of anomalous dispersion (Cromer, 1965); form factors for hydrogen were taken from Stewart, Davidson & Simpson (1965). The quantity minimized in the full-matrix least-squares calculations was  $\sum w(F_0^2 - F_c^2)^2$ , with weights  $w$  equal to  $1/\sigma^2(F_0^2)$ . The hydrogen atoms were positioned on chemical grounds with difference maps as guides. In the final least-squares calculations all the heavy-atom parameters given in Table 2 were adjusted except

Table 2. Observed structure factors, their standard deviations, and the final calculated structure factors (all  $\times 10$ )

Asterisks in the column of standard deviations indicate reflections assigned zero weight in the least-squares calculations.

H 0 0	0	H 2 1	2	H 4 2	4	H 0 4	4	H 4 5	5
0	0	2	750	4	749	0	728	4	875
2	137	3	360	5	43	2	176	5	27
4	503	4	473	6	154	4	501	6	76
6	311	5	111	7	81	5	22	7	146
8	254	6	236	8	137	6	407	8	24
10	35	7	151	9	28	7	27	9	31
		8	122	10	98	8	27	10	5
		9	25	11	2	9	10	11	5
H 1 0	1	10	272	H 5 2	5	H 1 4	4	H 5 5	5
1	567	11	272	5	324	1	102	5	37
2	791	12	838	6	117	2	617	6	189
3	415	13	24	7	92	3	274	7	27
4	115	14	132	8	40	4	326	8	170
5	131	15	83	9	23	5	272	9	6
6	440	16	4	10	223	6	172	10	325
7	100	17	4	11	74	7	243	11	4
8	114	18	4	12	165	8	146	12	151
9	184	19	4	13	124	9	129	13	131
10	163	20	4	14	110	10	144	14	132
11	127	21	4	15	91	11	307	15	10
		22	1003	H 6 2	6	H 2 4	4	H 6 5	5
		23	15	6	155	2	297	6	1031
		24	1020	7	124	3	50	7	251
		25	461	8	110	4	3	8	95
		26	385	9	91	5	341	9	186
		27	230	H 4 1	4	6	49	10	180
		28	7	4	67	7	23	11	16
		29	5	5	575	8	91	12	339
		30	6	6	138	9	96	13	279
		31	7	7	229	10	7	14	200
		32	8	8	52	11	8	15	227
		33	9	9	176	12	8	16	248
		34	10	10	115	13	9	17	248
		35	11	11	204	14	10	18	248
		36	12	12	310	15	11	19	248
		37	13	13	421	16	12	20	248
		38	14	14	272	17	13	21	248
		39	15	15	301	18	14	22	248
		40	16	16	114	19	15	23	248
		41	17	17	360	20	16	24	248
		42	18	18	189	21	17	25	248
		43	19	19	258	22	18	26	248
		44	20	20	127	23	19	27	248
		45	21	21	204	24	20	28	248
		46	22	22	473	25	21	29	248
		47	23	23	117	26	22	30	248
		48	24	24	154	27	23	31	248
		49	25	25	272	28	24	32	248
		50	26	26	301	29	25	33	248
		51	27	27	114	30	26	34	248
		52	28	28	360	31	27	35	248
		53	29	29	189	32	28	36	248
		54	30	30	258	33	29	37	248
		55	31	31	127	34	30	38	248
		56	32	32	204	35	31	39	248
		57	33	33	473	36	32	40	248
		58	34	34	117	37	33	41	248
		59	35	35	154	38	34	42	248
		60	36	36	272	39	35	43	248
		61	37	37	301	40	36	44	248
		62	38	38	114	41	37	45	248
		63	39	39	360	42	38	46	248
		64	40	40	189	43	39	47	248
		65	41	41	258	44	40	48	248
		66	42	42	127	45	41	49	248
		67	43	43	204	46	42	50	248
		68	44	44	473	47	43	51	248
		69	45	45	117	48	44	52	248
		70	46	46	154	49	45	53	248
		71	47	47	272	50	46	54	248
		72	48	48	301	51	47	55	248
		73	49	49	114	52	48	56	248
		74	50	50	360	53	49	57	248
		75	51	51	189	54	50	58	248
		76	52	52	258	55	51	59	248
		77	53	53	127	56	52	60	248
		78	54	54	204	57	53	61	248
		79	55	55	473	58	54	62	248
		80	56	56	117	59	55	63	248
		81	57	57	154	60	56	64	248
		82	58	58	272	61	57	65	248
		83	59	59	301	62	58	66	248
		84	60	60	114	63	59	67	248
		85	61	61	360	64	60	68	248
		86	62	62	189	65	61	69	248
		87	63	63	258	66	62	70	248
		88	64	64	127	67	63	71	248
		89	65	65	204	68	64	72	248
		90	66	66	473	69	65	73	248
		91	67	67	117	70	66	74	248
		92	68	68	154	71	67	75	248
		93	69	69	272	72	68	76	248
		94	70	70	301	73	69	77	248
		95	71	71	114	74	70	78	248
		96	72	72	360	75	71	79	248
		97	73	73	189	76	72	80	248
		98	74	74	258	77	73	81	248
		99	75	75	127	78	74	82	248
		100	76	76	204	79	75	83	248
		101	77	77	473	80	76	84	248
		102	78	78	117	81	77	85	248
		103	79	79	154	82	78	86	248
		104	80	80	272	83	79	87	248
		105	81	81	301	84	80	88	248
		106	82	82	114	85	81	89	248
		107	83	83	360	86	82	90	248
		108	84	84	189	87	83	91	248
		109	85	85	258	88	84	92	248
		110	86	86	127	89	85	93	248
		111	87	87	204	90	86	94	248
		112	88	88	473	91	87	95	248
		113	89	89	117	92	88	96	248
		114	90	90	154	93	89	97	248
		115	91	91	272	94	90	98	248
		116	92	92	301	95	91	99	248
		117	93	93	114	96	92	100	248
		118	94	94	360	97	93	101	248
		119	95	95	189	98	94	102	248
		120	96	96	258	99	95	103	248
		121	97	97	127	100	96	104	248
		122	98	98	204	101	97	105	248
		123	99	99	473	102	98	106	248
		124	100	100	117	103	99	107	248
		125	101	101	154	104	100	108	248
		126	102	102	272	105	101	109	248
		127	103	103	301	106	102	110	248
		128	104	104	114	107	103	111	248
		129	105	105	360	108	104	112	248
		130	106	106	189	109	105	113	248
		131	107	107	258	110	106	114	248
		132	108	108	127	111	107	115	248
		133	109	109	204	112	108	116	248
		134	110	110	473	113	109	117	248
		135	111	111	117	114	110	118	248
		136	112	112	154	115	111	119	248
		137	113	113	272	116	112	120	248
		138	114	114	301	117	113	121	248
		139	115	115	114	118	114	122	248
		140	116	116	360	119	115	123	248
		141	117	117	189	120	116	124	248
		142	118	118	258	121	117	125	248
		143	119	119	127	122	118	126	248
		144	120	120	204	123	119	127	248
		145	121	121	473	124	120	128	248
		146	122	122	117	125	121	129	248
		147	123	123	154	126	122	130	248
		148	124	124	272	127	123	131	248
		149	125	125	301	128	124	132</	

the temperature factors of nitrate group III and of the water molecule; these parameters are extensively coupled with the coordinates. The final shifts were all less than  $0.4\sigma$ . The final  $R$  index is 0.076 for 357 observed reflections of non-zero weight; the goodness of fit,  $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ , is 4.0.

The structure we find is almost identical – except for the changes in dimensions in the cation associated with replacing an  $O_2$  bridge with an  $NH_2$  bridge – with that of the  $\mu$ -peroxo compound  $(NH_3)_5Co(O_2)Co(NH_3)_5(NO_3)_5$  (Marsh & Schaefer, 1968). As in that compound, the structure we have derived is based on the space group  $P4_2/mnm$  – the highest symmetry space group consistent with the systematic absences. There seems to be no advantage in assuming a lower symmetry, as the disorder (which affects every atom in the structure except for the cobalt) would remain while the number of parameters would increase.

### Discussion

The largest difference between the structure we have found and that derived by Vannerberg (1963) is in the orientation of the  $(NH_3)_5Co(NH_2)Co(NH_3)_5^{2+}$  cation. Vannerberg assumed the polar space group  $P4_2nm$  with the cation positioned on a twofold axis parallel to  $c$  and on a mirror plane parallel to  $(1\bar{1}0)$ ; we find it to be rotated  $90^\circ$  from this orientation, lying on a mirror plane parallel to  $(001)$ . The disorder allows the cation to accommodate the diagonal mirror plane (Fig. 1).

The cation is shown in Fig. 2. It is obviously highly strained, as manifested by the extreme length of the Co–N(1) bond (about  $0.1 \text{ \AA}$  longer than the normal value for a Co–N distance) and the almost ridiculous valency angle at N(1). The strain is caused by interactions between ammonia groups N(3) in the two halves of the cation; it is partly relieved by an enlargement of the N(1)–Co–N(3) angles to  $93^\circ$ .

Nitrate group I (Fig. 1) is satisfactorily represented by two sets of isotropic, half-weight atoms, suggesting that the group is disordered between two positions related by a mirror plane parallel to  $(110)$  and separated by about  $0.45 \text{ \AA}$ ; the N–O distances are  $1.23 \text{ \AA}$  (twice) and  $1.24 \text{ \AA}$  and the O–N–O angles  $121$  and  $119^\circ$  (twice). Nitrate group II is somewhat less satisfactory: the distances are  $1.20$  (twice) and  $1.22 \text{ \AA}$  and all three angles are  $120^\circ$ , but even assuming twofold disorder we find it necessary to introduce anisotropic temperature factors for the oxygen atoms, implying very large in-plane displacements and, perhaps, additional disorder. The same situation obtains in the  $\mu$ - $O_2$  compound (Marsh & Schaefer, 1968), although there nitrate

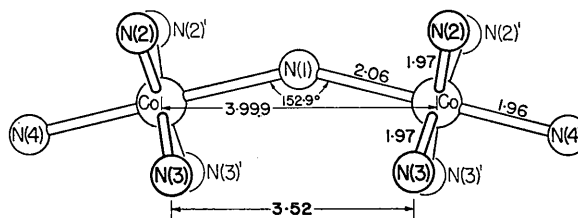


Fig. 2. A drawing of the cation, showing the more important dimensions. Standard deviations in the bond distances are about  $0.02$ – $0.03 \text{ \AA}$ .

group II was found to have one N–O bond parallel to the  $c$  axis rather than parallel to  $[110]$ .

We have represented nitrate group III by fourfold disorder of isotropic atoms, plus an additional atom (perhaps a water molecule) in one-eighth of the available sites. This is a slightly simpler representation than was proposed for the  $\mu$ - $O_2$  compound, where this nitrate group was found to have at least eightfold disorder. It is possible that the model we propose here would not have been as satisfactory had the data been of as high quality as they were for the  $\mu$ - $O_2$  compound; crystals of it did not show signs of decomposition, and three complete sets of intensity data were collected.

No analysis for water was made, since its presence was not suspected until the refinement was nearly complete. We did not have enough material to make such an analysis, and its preparation is difficult. Our results suggest that there is approximately one-quarter molecule of water per formula unit in the crystal we used; it is likely that the water content is variable, and is related to the differences in intensity and cell dimensions we find in going from one crystal to another.

We are very grateful to Professor C. Brubaker for providing the crystals.

### References

- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.  
 DUCHAMP, D. J. (1964). A.C.A. Meeting, Bozeman, Montana, paper B-14, p. 29.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 MARSH, R. E. & SCHAEFER, W. P. (1967). *Acta Cryst.* **B24**, 246.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.  
 VANNERBERG, N.-G. (1963). *Acta Chem. Scand.* **17**, 79.

*Acta Cryst.* (1968). **B24**, 286

**An X-ray study of gel-grown strontium tartrate tetrahydrate** By JOSEPH BOHANDY and JOHN C. MURPHY, *Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland, U.S.A.*

(Received 28 August 1967)

The space group ( $P2_12_12_1$ ) and unit-cell dimensions ( $a = 9.48 \pm 0.04$ ,  $b = 10.96 \pm 0.04$ ,  $c = 9.46 \pm 0.04 \text{ \AA}$ ) of gel-grown strontium tartrate have been determined by the precession method.

Recently, there has been renewed interest in the growth of crystals in silica gel (Dennis & Henisch, 1967; Henisch, Dennis & Hanoka, 1965). Using this technique, we have grown a large variety of single crystals such as the alkaline

earth tartrates and various sulfite, formate, and borate salts. Briefly, the method consists of adding an acid (tartaric acid, for example) to a sodium metasilicate solution. After the mixture has set, an appropriate solution is placed on top