The Crystal Structure of Potassium Tetranitro-diammine-cobaltiate (III), $K[Co(NH_3)_2(NO_2)_4]$

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Introduction

Various attempts[1] have been made to determine the configuration of a complex anion, $[Co(NH_3)_2(NO_2)_4)]^-$, because such a di-substituted complex should be capable of existing in two geometrically isomeric forms on the octahedral theory. In 1936, Wells[2] determined the crystal structure of the silver salt, $Ag[Co(NH_3)_2(NO_2)_4]$, and found that the two ammonia groups were co-ordinated to the central cobalt atom in *trans*-positions with respect to each other. On the other hand, in 1949 Kuroya and Yamasaki[3] examined very closely the oxalato-dinitrodiammine complex derived from the NH_4-salt or "Erdmann's salt". Namely they repeated fractional crystallizations and attempted to resolve each fraction into optical isomers. Finally they came to the conclusion that in the aqueous solution of the Erdmann's salt at room temperatures the *cis*- and *trans*-isomers should possibly coexist as an equilibrium mixture. It would be of interest to determine the configuration of the complex anion in the crystals of the Erdmann's salt itself, $NH_4[Co(NH_3)_2(NO_2)_4]$ and also the potassium salt. Since these two salts are isomorphous, their structures have been determined at the same time. In this paper the crystal structure of the potassium salt will be given; that of the Erdmann's salt will be treated in the next paper.

Experimental

Potassium tetranitro-diammine-cobaltiate (III) was prepared according to the method described by Jörgensen[4] and was recrystallized from water not exceeding 60°C. They belong to the orthorhombic bipyramidal class and are usually thin needles elongated along the *c*-crystal axis. Three crystal rods less than 0.2 mm. in diameter parallel to each principal axis were prepared. All the equatorial reflections were recorded by using Fe K_α radiation ($\lambda=1.937$ Å). Usual multiple film technique was employed and the intensity of reflections were visually estimated by comparison with a standard scale. The usual correction factors were applied by means of the chart given by Cochran[5]. No correction for absorption was applied. A temperature factor and a scale factor for converting the observed values of $|F_{rel}|$ approximately to the absolute scale were calculated by Wilson's method[6]. The unit cell dimensions were obtained from high order reflections of the equatorial lines of the oscillation photographs.

The results are: $a=11.38\pm0.02$ Å, $b=12.95\pm0.02$ Å and $c=6.76\pm0.01$ Å, giving the axial ratio $a:b:c=0.879:1:0.522$, in agreement with those obtained morphologically, i.e., 0.8783: 1: 0.5192. From the density 2.107 g./cc. measured by the pyknometer method at 25.0°C, it was found that the unit cell contains four formula units of $K[Co(NH_3)_2(NO_2)_4]$, the calculated value being 2.106 g./cc. The space group is D_2^4-$P\ 2_12_12_1$. All the atoms are on the general positions: x, y, z; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\bar{x}, \bar{y}, \frac{1}{2}+z$.

Determination of the Structure

Firstly the Patterson projections $P(X, Y)$ $P(Y, Z)$ and $P(X, Z)$ were evaluated.

Comparing these results with the corresponding Patterson maps of the Erdmann's salt, whose analysis has been carried out at

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[1] Y. Shibata and T. Maruki, *J. Chem. Soc. Japan*, 37, 1142 (1916); E.H. Riesenfeld and R. Klement, *Z. anorg. Chem.*, **124**, 1 (1922). W. Thomas, *J.C.S.*, 123, 617 (1923); I.E. Knaggs, *J. C. S.* **121**, 2074 (1922); B.C. Ray, *J. Indian Chem. Soc.*, 440 (1937); H. Sueda, *J. Chem. Soc. Japan*, **57**, 406 (1936); E.A. Gilinskaya, *Ser. Fiz-Mat. i Estestven. Nauk*, 3, 133 (1953).

[2] A.F. Wells, *Z. Krist.*, (A)., **95**. 74 (1936).

[3] Read at the annual meeting of Chem. Soc. Japan, (1949).

[4] S.M. Jörgensen, *Z. anorg. Chem.*, **17**, 477 (1898).

[5] W. Cochran, *J. Sci.*, *Inst.*, **25**, 253 (1949).

[6] A.J.C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

the same time, it was confirmed that these two crystals are isomorphous as expected, and moreover it was possible to identify Co–Co, K–K and K–Co vectors on each projection. Hence the positions of cobalt and potassium were fixed at once.

Preliminary Fourier projections of electron density upon the planes perpendicular to each principal axis were synthesized using observed F-values, whose sign was calculated from the parameter values of cobalt and potassium. From these projections it was possible to assign approximate parameters for nitrogen atoms which are co-ordinated nearly octahedrally around each cobalt atom. These were in good accord with the conclusion drawn from each Patterson projection. Though the Fourier prejections showed faint outlines of oxygen atoms they could not be located unequivocally. The c-crystal axis is as short as 6.76 Å, and it should be possible to obtain a clear projection of the whole structure in this direction, as any interleaving of the complex anion within this periodicity is probably ruled out. An attempt was made to determine the signs of $F(hk0)$ directly by taking the difference of the corresponding F-values observed for the ammonium and potassium salt, since both are isomorphous and the positions of potassium atoms are already known. The signs of 46 out of 120 observed reflections could be determined successfully. The projection thus obtained showed the outlines of the oxygen atoms more clearly than the previous one. A vector convergence map[7] was also made for this projection, by using the positions of cobalt atoms. Closer examination of this projection and vector convergence map enabled one to deduce the x- and y-parameters of all the atoms in the unit cell. $F(hk0)$ were then calculated. The agreement was reasonably good and enabled a start to be made with the process of refinement by means of Fourier syntheses. At this stage, all the z-parameter values of oxygen atoms were assumed using the data of interatomic distances and bond angles. Calculation of $F(0kl)$ and $F(h0l)$ values eliminated at once the possibility of the *cis*-configuration. Finally only one set of parameter values corresponding to the *trans*-configuration remained which could account for $F(0kl)$ and $F(h0l)$s. Then all the projections were refined by successive approximations as usual. The final parameters are listed in Table I. A final electron density projection along the c-crystal axis is shown in Fig. 1.

TABLE I

FINAL PARAMETERS

	x/a	y/b	z/c
Co	0.1690	0.1915	0.2500
K	0.117	0.473	0.695
NH_3(1)	0.278	0.265	0.064
NH_3(2)	0.062	0.118	0.436
N(1)	0.250	0.264	0.466
N(2)	0.056	0.305	0.234
N(3)	0.088	0.119	0.034
N(4)	0.281	0.078	0.266
O(1)	0.264	0.226	0.632
O(2)	0.293	0.350	0.442
O(3)	0.040	0.353	0.083
O(4)	−0.003	0.332	0.383
O(5)	−0.018	0.112	0.017
O(6)	0.150	0.072	−0.078
O(7)	0.257	0.005	0.376
O(8)	0.367	0.080	0.163

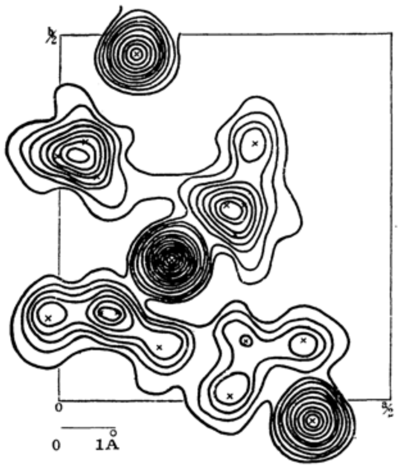

Fig. 1. Electron densities along the c-axis of K[Co(NH_3)$_2$(NO_2)$_4$]. Contours are at intervals of 2 e. A^{-2}.

The comparison of the observed structure factors with those calculated is given in Table II. The atomic scattering factors used for the calculation of the structure factors were those listed in the International Tables. A temperature factor of the form $\exp -B\left(\frac{\sin\theta}{\lambda}\right)^2$ was used, where B was given the value 2.5 Å^2. The value of B and the scale factor were estimated by plotting the values of $\log F_c/F_o$ versus $(\sin\theta)^2$ at the final stage. The reliability factor $R=\sum||F_o|-|F_c||/\sum|F_o|$ are 0.165, 0.185 and 0.235 for $(hk0)$, $(0kl)$ and $(h0l)$ respectively. The weighted mean value of R is 0.179, for which only observed reflections up to $\frac{\sin\theta}{\lambda}=0.501$ have been used.

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[7] C. A. Beevers and J. H. Robertson, *Acta Cryst.*, 3, 164 (1950).

TABLE II
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES
ORIGIN OF CO-ORDINATE IS TAKEN AT A CENTER OF SYMMETRY ON EACH PROJECTION

hkl	$F_{obs.}$	$F_{cal.}$
200	17.8	-19.8
400	1.8	3.8
600	9.0	4.5
800	4.0	7.1
1000	3.6	-4.6
020	12.3	-12.2
040	2.7	0.8
060	9.2	9.5
080	6.5	-4.4
0100	7.5	11.0
0120	—	-1.0
110	4.8	-4.9
120	19.3	-19.9
130	13.5	-13.9
140	5.5	4.7
150	13.5	-12.1
160	7.1	-7.7
170	6.3	-5.3
180	10.5	14.1
190	7.2	6.7
1100	13.0	11.3
1110	3.6	1.9
1120	6.0	-4.4
1130	5.0	-4.8
210	24.9	-24.4
220	11.1	11.0
230	—	-3.2
240	27.0	-26.4
250	1.8	0.1
260	8.2	6.0
270	18.9	-18.5
280	5.2	4.0
290	2.5	1.3
2100	4.3	-2.3
2110	12.3	-11.8
2120	2.9	-3.6
310	1.2	-0.9
320	1.5	-1.0
330	36.0	35.3
340	5.0	1.2
350	20.5	-20.2
360	14.2	13.7
370	4.2	4.6
380	10.8	7.1
390	10.9	9.4
3100	3.0	1.9
3110	10.6	-5.4
3120	6.0	5.0
410	—	-3.8
420	16.2	-19.7
430	11.8	-9.7
440	6.7	-1.7
450	3.9	1.4
460	4.9	-2.1
470	8.1	9.4
480	10.2	10.7
490	13.4	-12.6
4100	6.4	-3.9
4110	2.5	3.1
4120	4.2	4.5
510	13.2	10.9
520	16.3	15.5
530	1.5	-0.2
540	16.5	-14.9
550	11.7	11.3
560	10.3	6.1
570	2.5	-2.1
580	5.2	-5.6
590	—	0.1
5100	9.1	-8.9
5110	4.0	-1.8
610	3.2	4.2
620	12.3	-8.5
630	5.8	3.8
640	9.3	-9.6
650	8.7	9.2
660	6.6	6.8
670	3.9	3.1
680	16.5	-16.0
690	6.3	7.0
6100	5.0	5.0
6110	3.0	1.9
710	2.0	-1.7
720	2.4	-2.3
730	6.0	-1.9
740	5.8	4.3
750	4.2	3.0
760	14.9	-14.0
770	9.0	-7.8
780	2.6	-2.9
790	—	0
7100	—	0.1
810	13.5	-13.8
820	15.0	11.7
830	4.0	6.3
840	6.2	9.3
850	4.5	0.9
860	3.0	-3.3
870	6.3	-5.2
880	6.6	5.6
890	7.0	6.2
910	12.4	-11.8
920	4.0	2.1
930	—	0.5
940	1.2	-1.4
950	10.8	-9.7
960	1.9	-1.7
970	4.0	4.1
1010	12.2	12.4
1020	5.0	4.1
1030	2.1	-2.8
1040	2.0	-2.4
1050	2.7	-2.8
1060	3.7	1.8
1110	6.0	5.5
1120	7.9	8.5
1130	3.3	-3.2
1140	1.4	-1.6
002	8.8	-12.5
004	13.7	11.6
006	5.6	-9.9
011	2.0	-1.6
012	12.9	13.1
013	8.3	5.6
014	5.4	-5.5
015	2.0	1.4
016	3.8	3.7
021	15.1	-16.2
022	1.8	1.5
023	19.5	21.7
024	9.0	9.0
025	6.5	-6.0
026	8.6	-9.3
031	7.0	-14.4
032	13.0	-18.0
033	8.0	-4.5
034	—	4.7
035	—	2.2
036	—	-2.7
041	6.3	8.1
042	14.0	-16.3
043	12.6	13.7
044	—	-2.7
045	8.1	-8.8
046	2.2	2.1
051	—	-0.5
052	6.3	4.6
053	4.7	4.1
054	7.0	-7.2
055	7.4	-7.2
056	4.7	3.5
061	15.7	-15.9
062	13.5	13.5
063	16.2	16.4
064	7.3	-2.3
065	2.2	-2.6
066	2.7	4.5
071	9.0	8.8
072	6.8	-5.9
073	1.8	-4.0
074	4.3	5.4
075	4.0	4.6
081	2.9	1.9
082	21.0	21.1
083	3.1	-2.9
084	9.0	-8.0
085	2.4	-3.4
091	7.2	-5.9
092	2.5	2.1
093	4.5	6.6
094	2.7	-0.5
0101	—	0.7
0102	10.3	10.3
0103	6.7	-4.8
0104	7.0	-7.2
0111	2.3	1.1
0112	—	0.2
0113	2.9	-6.4
0121	12.2	13.0
0122	2.1	2.1
101	26.8	27.4
102	4.8	-0.1
103	7.4	5.9
104	4.2	-3.9
105	17.2	16.6
106	6.0	-7.1
201	2.2	-2.6
202	6.8	11.6
203	16.2	13.2
204	4.6	3.5
205	8.4	8.8
206	5.0	4.8
301	8.2	9.5
302	6.0	0.4
303	2.6	3.6
304	7.2	-6.0
305	—	2.0
306	1.4	-1.3
401	—	-5.3
402	23.0	-22.4
403	—	-0.2
404	8.0	-7.8
405	3.2	-0.2
406	2.6	1.1
501	1.4	0.4
502	8.6	5.6
503	20.0	-16.4
504	6.0	5.8
505	4.0	1.2
506	2.6	1.2
601	3.2	-5.4
602	15.0	-11.1
603	14.1	-13.4
604	8.0	-8.0
605	7.8	-4.6
701	17.6	-18.1
702	4.8	-4.4
703	15.2	-13.6
704	4.8	2.1
705	5.2	-5.5
801	—	-0.9
802	2.5	-2.4
803	—	2.1
804	3.6	-8.0
805	—	-1.7
901	—	-2.7
902	5.0	-1.6
903	—	-2.8
904	3.6	-2.9
1001	2.4	2.0
1002	2.6	1.1
1003	2.1	1.6
1101	11.0	9.3
1102	—	0.4

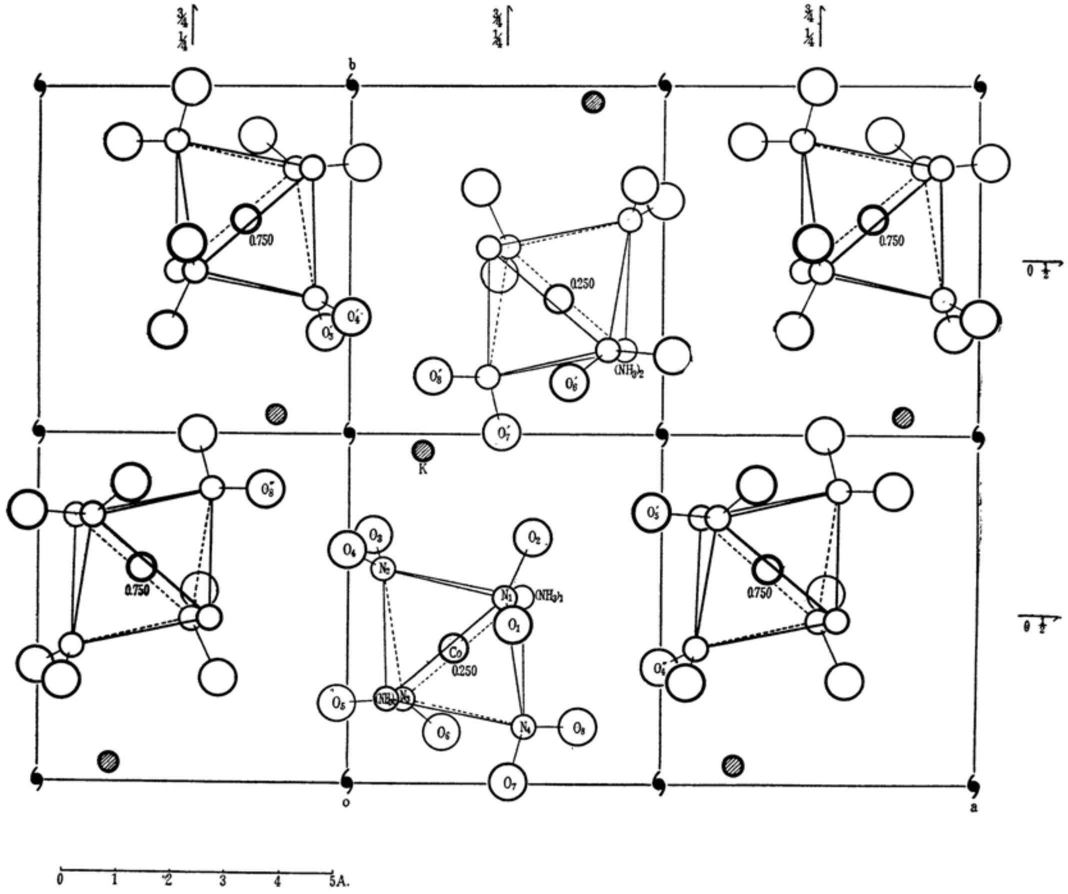

Fig. 2. Projectcion of the structure upon (001).

Description of the Structure

The structure projected upon a plane normal to the *c*-crystal axis is shown in Fig. 2, which corresponds to Fig. 1. The structure is built from potassium ions and complex anions $[Co(NH_3)_2(NO_2)_4]^-$, thus being essentially ionic.

Interatomic distances and bond angles calculated on the basis of the atomic parameters in Table I are listed in Table III. A perspective drawing of the complex anion is shown in Fig. 3.

TABLE III

INTERATOMIC DISTANCES AND INTERBOND ANGLES

Co	.....NH_3(1)	2.00 Å	K	O(2)	3.08 Å
	.....NH_3(2)	2.00 Å		O(3)	3.17 Å
	.....N(1)	1.96 Å		O(4)	3.11 Å
	.....N(2)	1.96 Å		O(3′)	2.97 Å
	.....N(3)	1.96 Å		O(4′)	3.11 Å
	.....N(4)	1.96 Å		O(7′)	3.26 Å
				O(8′)	2.79 Å
N(1)	......O(1)	1.24 Å		O(8″)	3.08 Å
	......O(2)	1.23 Å			
O(1)	O(2)	2.08 Å	(NH_3)(1)	O(1)(−)	2.97 Å
∠O(1)N(1)O(2)		115°		O(5′)	2.87 Å
N(2)	......O(3)	1.21 Å	(NH_3)(2′)	O(5′)	3.07 Å
	......O(4)	1.26 Å			
O(3)	O(4)	2.10 Å	O(1)	O(4″)	2.76 Å
∠O(3)N(2)O(4)		116°	O(2)	O(6′)	3.09 Å
			O(2)	O(7′)	2.99 Å
N(3)	......O(5)	1.22 Å	O(3)	O(7′)	3.05 Å
	......O(6)	1.20 Å	O(3)	O(8″)	2.72 Å
O(5)	O(6)	2.08 Å			
∠O(5)N(3)O(6)		118°			
N(4)	......O(7)	1.23 Å			
	......O(8)	1.20 Å			
O(7)	O(8)	2.14 Å			
∠O(7)N(4)O(8)		124°			

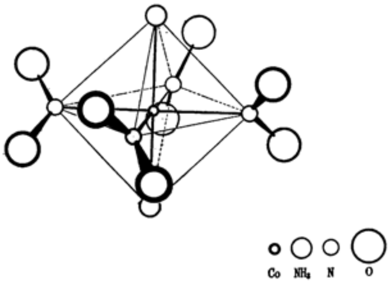

Fig. 3. A perspective drawing of a complex anion.

Two ammonia molecules are co-ordinated to a cobalt atom in *trans*-positions with respect to each other at a distance of 2.00 Å. Four nitrogen atoms of the nitro groups form a square around the cobalt atom within experimental errors, being 1.96 Å apart from it. Thus an octahedral co-ordination is completed around a cobalt atom. These interatomic distances are in good agreement with those found in the structures of various complex compounds of tervalent cobalt[8,9,10,11].

The size and shape of the nitro groups are also in agreement with our previous results.

The planes containing each nitro group are inclined at angles 58°, 56°, 42° and 86° respectively with the plane of four nitrogen atoms of the nitro groups in the same sense. Hence, the configuration of the complex anion is essentially similar to that found in crystals of the silver salt, $Ag[Co(NH_3)_2(NO_2)_4]$[2].

The distances of approach between N atom of ammonia molecule and O atom of nitro group of adjascent complex anion are found to be 2.87 Å, and 2.97 Å. They may be compared with those found in crystals of trinitrotriammine-cobalt (III). These short distances suggest hydrogen bonding between them. By these NH……O bonds the complex anions are held together, forming a network perpendicular to the *b*-crystal axis. Between these layers exist potassium ions.

A potassium ion is surrounded by eight oxygen atoms of the nitro groups with distances ranging from 2.79 Å to 3.26 Å. The co-ordination polyhedron around a potassium atom is rather distorted.

Summary

The crystal structure of potassium tetranitrodiammine-cobaltiate (III), $K[Co(NH_3)_2(NO_2)_4]$, prepared according to the method of Jörgensen, has been determined by two-dimensional Fourier method. The orthorhombic unit cell has the dimensions $a=11.38\pm0.02$ Å, $b=12.95\pm0.02$ Å and $c=6.76\pm0.01$ Å containing four formula units in it (Fe K_α, $\lambda=1.937$ Å), and the space group is D_2^4-$P2_12_12_1$. The shape and size of a complex ion was found to be similar to the one found in crystals of silver salt, $Ag[Co(NH_3)_2(NO_2)_4]$. Two ammonia molecules are co-ordinated to the central cobalt atom in *trans*-positions, with Co–N distance 2.00 Å.

The average dimensions of the nitro groups were: N–O = 1.22 Å and ∠ONO = 118°, in agreement with the results obtained for other nitro-complex compounds of cobalt. Each potassium atom is surrounded by eight oxygen atoms of the nitro-groups with distances ranging from 2.79 Å to 3.26 Å.

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