The Crystal Structure of trans-Dichloro-bisethylenediamine-cobalt(III) Nitrate, [Co en_2 Cl_2]NO_3

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In the last decade, we have carried out the X-ray crystallographic determination of the structures of various *trans*-dihalogeno-bisethylenediaminemetal(III) complexes ("ethylenediamine-praseo salts") having the general formula [M en_2 X_2] Y, where M is Co or Cr, and X is Cl or Br.[1-3] It has thus been proved that the complex ion is of the centrosymmetrical configuration; namely, i) the two halogen atoms are coordinated to the central metal ion, M, definitely in the trans positions; ii) the ethylenediamine molecule is of the puckered or "gauche-type" structure, which possesses only a two-fold axis of rotation in symmetry, giving a molecular disymmetry to the ligand molecule fixed to M, while, however, iii) the two ethylenediamine molecules are constantly present in the form of an enantiomorphric pair. With the purpose of seeing if any structual changes may be brought to the complex ion in the case of the replacement of Y by the nitrate ion, an attempt has now been made to determine the crystal structure of ethylenediamine-praseo nitrate, [Co-en_2 Cl_2] NO_3. It is well-known that this compound is one of the few slightly soluble nitrates. We have been interested also in this peculiarity.

Experimental

The crystals of [Co en_2 Cl_2] NO_3 were obtained by slowly adding a dilute solution of nitric acid to an aqueous solution of [Co en_2 Cl_2] Cl·HCl·$2H_2O$. These crystals are green scale-like tablets and are slightly soluble in water. They belong to the monoclinic system, and the unit cell dimensions were found to be:

$$a=6.33\text{Å},\quad b=9.25\text{Å},\quad c=10.62\text{ Å},\quad \beta=114.5$$

The space group was determined to be $P2_1/c$ from the systematic extinctions. The unit cell contains two formula units ($\rho_{\text{obs}}=1.75$ and $\rho_{\text{calcd}}=1.72\text{ g. cm}^{-3}$). Ni*Kα* radiation (1.659 Å) was used, and a multiple film technique was employed in taking Weissenberg photographs about the principal axes. All intensities were measured visually by comparison with a standard scale. The usual correction factors were applied to the observed intensities, and a set of relative $|F_o|$ values was obtained.

Determination of the Structure

In the determination of the structure, ($h\,0\,l$) and ($0\,k\,l$) reflections on the Weissenberg photographs were used. As the unit cell contains two formula units, the cobalt atoms and the nitrogen atoms of the nitrate ions must occupy two among the four sets of two-fold special positions, all having point symmetry $\bar{1}$; the cobalt atoms may therefore be placed arbitrarily at the sets of (0 0 0) and (0 1/2 1/2). On the other hand, the nitrate ions are to be located centrosymmetrically on one of the other three sets; in short, a nitrate ion should be in some disordered arrangement, the central nitrogen atom lying on or around the special position referred to above, since the ion has no center of symmetry in its well-known, normal form. Similar disordered structures of the nitrate ion were found in the crystals of bis(glutaronitrilo) and bis(adiponitrilo)copper-(I) nitrates and in bis(dimethylglyoximato)-diamminecobalt(III) nitrate.[4-6]

The Patterson projections, $P(UW)$ and $P(VW)$, gave fairly simple patterns, and the approximate position of the chlorine atom could be derived without any trouble. Then, on the basis of the coordinates of cobalt and chlorine atoms only, the structure amplitudes were calculated; in turn, these were found rather consistent with the observed values. Consequently, the signs of all but weak reflections were assumed to be available. From the first Fourier projections, $\rho(XZ)$ and $\rho(YZ)$, we could obtain the approximate position of the ethylenediamine molecule, but not that of the nitrate ion. At this stage, our attempt to pack together the complex cations and nitrate anions, with a view of the $\rho(YZ)$, led us to

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[1] A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, **25**, 331 (1952).

[2] S. Ooi, Y. Komiyama, Y. Saito and H. Kuroya, ibid., **32**, 263 (1959).

[3] S. Ooi, Y. Komiyama and H. Kuroya, ibid., **33**, 354 (1960).

[4] Y. Kinoshita, I. Matsubara and Y. Saito, ibid., **32**, 1216 (1959).

[5] Y. Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, ibid., **32**, 1221 (1959).

[6] K. S. Viswanathan and N. R. Kunchur, *Acta Cryst.*, **14**, 675 (1961).

the deduction that the center of the nitrate ion lies close to $(0\,1/2\,0)$.

Fourier refinements were made as usual. In the case of the a-axis projection, residual electron density due to other components than the complex ion gave a diffuse peak around $(X\,1/2\,0)$. On the other hand, in the case of the b-axis projection, the residual electron density showed up as a peak around $(0\,Y\,0)$; however, because of the overlapping of the nitrate ion with the complex ion, the exact coordinates of the nitrate ion could not be elucidated from the Fourier peak.

Taking account of the shape of peak around $(X\,1/2\,0)$ in the a-axis projection, a model of the disordered structure of the nitrate ion was presented; in this model the ion occupies two different positions in the neighborhood of $(0\,1/2\,0)$, each of them having a weight of one-half, as shown in Figs. 1, 2 and 3; in these figures, the positions of the two nitrate ions of different orientations are indicated by the dotted and full lines, being related by $\bar{1}$ to one another. Thus, the nitrate ion may take up one of these positions in an asymmetric unit, while the equivalent or the opposite position in any other asymmetric unit may be assumed with quite equal probability; the probability of finding one orientation of the nitrate ion in an asymmetric unit is equal to that of finding another. No unreasonable interatomic distances have been detected in this structure. Possibly, there might be another plausible model which could account for the peak mentioned above. However, no further study was attempted, since the object of the present work was mainly to study the stereochemical configuration of the complex ion.

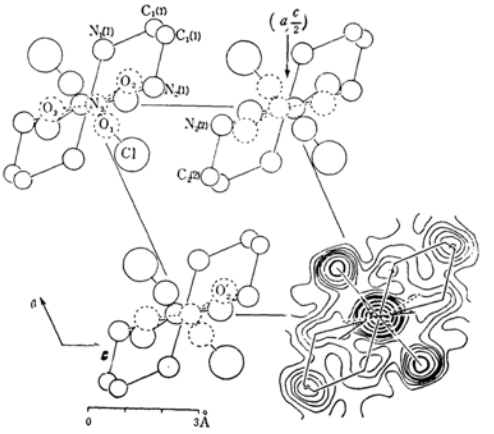

Fig. 1. Structure and electron density projected along b-axis. Contours are drawn at intervals of 2 and 10 e. Å^{-2}, starting at two and twenty electron levels for thin and thick lines, respectively.

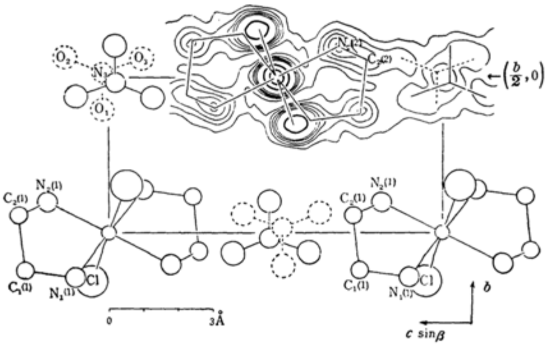

Fig. 2. Structure and electron density projected along a-axis. Contours are drawn in the same manner as Fig. 1.

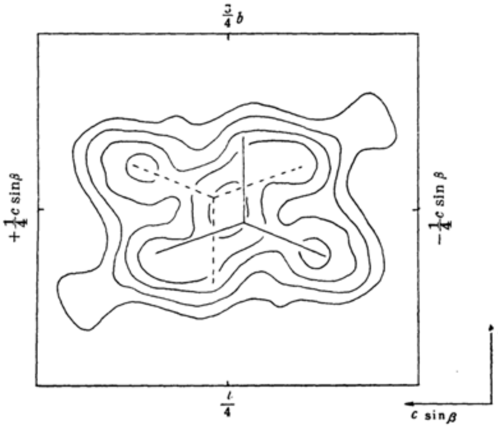

Fig. 3. Residual electron density due to a disordered structure of the nitrate ion projected along a-axis. Contours are drawn at intervals of 1 e. Å^{-2}, starting at two electron level.

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Co	0	0	0
Cl	−0.235	−0.149	0.052
N_1	0.260	−0.133	0.100
N_2	0.083	0.096	0.183
C_1	0.358	−0.112	0.250
C_2	0.322	0.055	0.270
N_3	0.000	0.508	0.017
O_1	−0.100	0.399	0.021
O_2	0.110	0.563	0.129
O_3	−0.023	0.562	−0.096

The atomic coordinates are given in Table I; they gave reliability indices of 0.157 and 0.148 for $(0\,k\,l)$ and $(h\,0\,l)$ respectively, with the exception of the $(1\,0\,0)$ reflection, which would be influenced critically by, for instance, extinction effect. Isotropic temperature factors, 4.0 Å^2 for $(0\,k\,l)$ and 3.5 Å^2 for $(h\,0\,l)$, were used in usual manner.

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	70.8	78.0	2	0	$\overline{12}$	11.6	13.2	0	9	1	6.4	5.2	0	8	5	4.4	−4.8
0	0	4	54.0	54.0	3	0	$\bar{2}$	26.4	40.0	0	10	1	4.4	−4.0	0	9	5	5.6	4.8
0	0	6	< 1.8	6.4	3	0	$\bar{4}$	55.6	52.8	0	1	2	30.8	−33.6	0	1	6	10.0	−10.4
0	0	8	6.0	10.8	3	0	$\bar{6}$	43.6	37.2	0	2	2	20.0	27.2	0	2	6	18.8	24.4
0	0	10	< 2.1	2.0	3	0	$\bar{8}$	47.6	42.0	0	3	2	10.8	−6.0	0	3	6	< 1.9	2.0
1	0	0	70.8	103.2	3	0	$\overline{10}$	9.2	10.8	0	4	2	21.2	19.6	0	4	6	25.6	28.8
1	0	2	70.4	72.8	3	0	$\overline{12}$	5.2	6.4	0	5	2	25.6	23.2	0	5	6	10.0	11.6
1	0	4	41.6	50.0	4	0	$\bar{2}$	71.2	74.0	0	6	2	53.2	44.0	0	6	6	8.4	8.8
1	0	6	57.6	62.8	4	0	$\bar{4}$	25.2	23.6	0	7	2	5.2	−6.0	0	7	6	8.4	−7.6
1	0	8	14.0	20.0	4	0	$\bar{6}$	9.2	10.4	0	8	2	24.4	20.0	0	8	6	4.4	7.2
1	0	10	12.4	13.2	4	0	$\bar{8}$	4.8	2.8	0	9	2	13.2	−10.4	0	9	6	7.2	−6.4
2	0	0	16.4	−0.4	4	0	$\overline{10}$	< 2.4	1.2	0	10	2	> 1.8	1.2	0	1	7	3.2	5.2
2	0	2	8.0	3.6	4	0	$\overline{12}$	< 1.5	4.0	0	1	3	30.4	30.0	0	2	7	< 2.1	−2.8
2	0	4	30.8	36.0	5	0	$\bar{2}$	30.4	27.6	0	2	3	49.6	−55.2	0	3	7	23.6	27.2
2	0	6	29.2	36.0	5	0	$\bar{4}$	4.0	4.4	0	3	3	17.2	18.8	0	4	7	7.2	6.8
2	0	8	19.6	21.0	5	0	$\bar{6}$	4.4	−3.6	0	4	3	8.8	6.0	0	5	7	10.4	13.2
3	0	0	38.4	47.6	5	0	$\bar{8}$	2.0	−4.8	0	5	3	34.4	28.0	0	6	7	< 1.9	1.6
3	0	2	13.2	−7.6	5	0	$\overline{10}$	1.2	5.6	0	6	3	14.0	8.8	0	7	7	< 2.1	0.1
3	0	4	16.0	17.6	6	0	$\bar{2}$	8.8	−4.8	0	7	3	27.2	18.8	0	8	7	9.2	−6.8
3	0	6	5.2	−5.2	6	0	$\bar{4}$	8.0	10.8	0	8	3	16.0	−12.4	0	1	8	2.8	−1.2
3	0	8	7.2	8.4	6	0	$\bar{6}$	5.6	7.6	0	9	3	1.6	−1.2	0	2	8	20.0	22.8
4	0	0	42.4	39.2	6	0	$\bar{8}$	20.4	20.4	0	10	3	< 1.6	0.1	0	3	8	4.4	2.4
4	0	2	32.0	30.0	6	0	$\overline{10}$	14.0	12.4	0	1	4	40.0	−38.0	0	4	8	18.8	20.0
4	0	4	4.8	6.8	7	0	$\bar{2}$	7.2	9.2	0	2	4	31.2	36.4	0	5	8	3.2	3.2
4	0	6	< 1.8	2.4	7	0	$\bar{4}$	14.0	13.6	0	3	4	18.8	−14.4	0	6	8	4.0	1.2
5	0	0	15.6	13.6	7	0	$\bar{6}$	20.4	18.4	0	4	4	20.8	22.4	0	7	8	4.0	3.2
5	0	2	26.8	21.2	7	0	$\bar{8}$	23.2	19.6	0	5	4	33.2	29.6	0	1	9	4.0	−2.8
5	0	4	22.0	18.0	0	2	0	91.2	90.4	0	6	4	22.4	20.8	0	2	9	2.4	−4.4
6	0	0	< 2.1	0.4	0	4	0	45.2	−30.8	0	7	4	6.8	0.8	0	3	9	12.4	15.2
6	0	2	4.4	3.2	0	6	0	24.8	23.6	0	8	4	10.8	15.2	0	4	9	< 2.2	1.2
1	0	$\bar{2}$	88.8	86.8	0	8	0	25.2	20.0	0	9	4	9.6	−8.0	0	5	9	6.8	8.4
1	0	$\bar{4}$	13.6	−14.4	0	10	0	< 1.9	0.2	0	10	4	6.4	7.2	0	6	9	2.0	5.2
1	0	$\bar{6}$	< 1.6	2.0	0	1	1	54.4	58.0	0	1	5	18.4	23.6	0	1	10	< 2.1	−0.8
1	0	$\bar{8}$	< 2.1	0.0	0	2	1	20.4	−18.4	0	2	5	40.8	−42.8	0	2	10	10.4	11.2
1	0	$\overline{10}$	9.6	14.4	0	3	1	42.8	−30.8	0	3	5	23.6	28.8	0	3	10	2.4	−3.2
2	0	$\bar{2}$	28.4	39.2	0	4	1	31.6	24.4	0	4	5	9.6	8.8	0	4	10	11.6	12.4
2	0	$\bar{4}$	4.8	−1.2	0	5	1	22.0	21.2	0	5	5	12.0	13.2	0	5	10	2.8	−3.6
2	0	$\bar{6}$	50.0	48.8	0	6	1	23.2	18.8	0	6	5	22.0	20.0	0	1	11	4.8	6.0
2	0	$\bar{8}$	26.8	24.8	0	7	1	50.0	40.4	0	7	5	1.6	2.0	0	2	11	2.0	2.8
2	0	$\overline{10}$	25.2	27.2	0	8	1	6.4	−5.2										

Results

The geometry of the complex ion herein determined is not significantly different from those reported before. The cobalt atom is surrounded by the four nitrogen atoms of the two ethylenediamine molecules and the two chlorine atoms at the trans-position, forming an octahedral configuration elongated in the Cl–Co–Cl direction. The two ethylenediamine molecules are of the gauche type and are enantiomorphous with one another. The ion has the approximate symmetry of C_{2h}, the two-fold axis of which passes through the central metal atom and bisects the C–C bonds of the ethylenediamine molecules coordinated.

The interatomic distances and bond angles are listed in Table III. The bond length of Co–Cl, 2.26 Å, is a little shorter than the value, 2.33 Å, found in $[Co\,en_2\,Cl_2]\,Cl\cdot HCl\cdot 2H_2O$[1] and $[Co(NH_3)_3H_2O\,Cl_2]\,Cl$,[7] but it ts comparable to that of 2.27 Å in $[Co(NH_3)_5Cl]\,Cl_2$[8] and that of 2.29 Å in $[Co\,pn_2\,Cl_2]\,Cl\cdot HCl\cdot 2H_2O$.[9] The nitrate ion appears to deviate

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7) Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, 25, 328 (1952).

8) Y. Komiyama, Y. Shigeta and H. Kuroya, Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

9) Y. Saito and H. Iwasaki, This Bulletin, 35, 1131 (1962).

TABLE III. INTERATOMIC DISTANCES AND BOND ANGLES

$\mathrm{Co{-}Cl}$	2.26 Å
$\mathrm{Co{-}N_1}$	1.99 Å
$\mathrm{Co{-}N_2}$	2.00 Å
$\mathrm{N_1{-}C_1}$	1.46 Å
$\mathrm{N_2{-}C_2}$	1.46 Å
$\mathrm{C_1{-}C_2}$	1.59 Å
$\mathrm{N_3{-}O_1}$	1.20 Å
$\mathrm{N_3{-}O_2}$	1.21 Å
$\mathrm{N_3{-}O_3}$	1.25 Å
$\mathrm{O_1 \cdots N_1}$ (1)	2.77 Å
$\mathrm{O_2 \cdots N_1}$ (1)	3.02 Å
$\mathrm{O_2 \cdots N_2}$ (2)	2.76 Å
$\mathrm{O_3 \cdots N_2}$ (2)	3.07 Å
$\mathrm{O_2 \cdots C_2}$ (2)	3.33 Å
$\mathrm{O_2' \cdots C_2}$ (2)	3.30 Å
$\mathrm{Co{-}N_1{-}C_1}$	112.0°
$\mathrm{Co{-}N_2{-}C_2}$	106.7°
$\mathrm{N_1{-}C_1{-}C_2}$	104.8°
$\mathrm{N_2{-}C_2{-}C_1}$	109.7°
$\mathrm{N_1{-}Co{-}N_2}$	85.6°
$\mathrm{O_1{-}N_3{-}O_2}$	114.6°
$\mathrm{O_2{-}N_3{-}O_3}$	124.3°
$\mathrm{O_1{-}N_3{-}O_3}$	121.0°

from D_{3h} symmetry, but our measurements are not accurate enough for the shape of the ion to be discussed in detail. The short distances, 2.77, 2.76, 3.02 and 3.07 Å, between the oxygen atoms of the nitrate ion and the nitrogen atoms of the ethylenediamine molecules may be indicative of the presence of hydrogen bonds of the $\mathrm{N{-}H \cdots O}$ type between them.

Recently, a new type of coordination of the ethylenediamine molecule was reported on the crystal of [Hg en $\mathrm{Cl_2}$],[10] where the ethylenediamine molecule is coordinatively bound to two different Hg atoms with its $-\mathrm{NH_2}$ radicals in the trans form, thereby forming a $(-\mathrm{Hg}-\mathrm{en}-)_\infty$ chain, to which the insolubility of this compound in water and alcohol could more or less be attributed. However, as is evident from the findings presented above, no remarkable structual peculiarity to which the slight solubility of the ethylenediamine-praseo nitrate would be even partially due, was found in the present work.

Summary

The crystal structure of *trans*-[Co en$_2$ Cl$_2$]·NO$_3$ has been determined by means of X-ray analysis. The space group is $P2_1/c$ with two formula units in a cell of the dimensions of $a=6.33$ Å, $b=9.25$ Å, $c=10.62$ Å, and $\beta=114.5°$. The crystal is composed of $[\mathrm{Co\,en_2\,Cl_2}]^+$ and $\mathrm{NO_3}^-$. The geometry of the complex ion herein determined is not significantly different from those reported before. It has been proposed that the nitrate ion is in a disordered arrangement.

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[10] K. Brodersen, *Z. anorg. u. allgem. Chem.*, **298**, 142 (1959).