The Crystal Structure of trans-[*Cr* en_2Cl_2]*Cl·HCl·2H₂O*

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(Received September 22, 1959)

The crystal structures of the two cobalt(III)-complexes, which are of the type *trans*-[Co en_2X_2] X·HX·$2H_2O$ (X=Cl, Br)[1], were determined by Saito, Kuroya and their collaborators during the past several years[2,3]. In connection with this, it seems really interesting and important to investigate the crystal structures of the chromium(III)-analogues, which have a great resemblance to the cobalt(III)-complexes in various respects; particularly, it may be very instructive to examine what discrepancies can be found between the bond lengths M–N and M–X in these compounds, where M denotes a central metallic ion and N a nitrogen atom of the coordinated ethylenediamine molecule.

The present authors took up the *trans*-dichloro-bis-ethylenediamine-chromium(III) chloride hydrochloride dihydrate, *trans*-[Cr en_2Cl_2] Cl·HCl·$2H_2O$, in the first place, and made an attempt to analyze the crystal structure of this compound by means of X-rays. This paper is to report the results obtained.

Experimental

The crystal of [Cr en_2Cl_2]Cl·HCl·$2H_2O$ was prepared by the method of Pfeiffer et al.[4] The crystals are bluish-green tablets and show marked dichroism like the crystals of [Co en_2Cl_2]-Cl·HCl·$2H_2O$. From oscillation and Weissenberg photographs the unit cell dimensions were found to be:

$a=10.97,\quad b=7.88,\quad c=9.12\ \text{Å},\quad \beta=111.5°.$

The space group was determined to be No. 14 $P2_{1/c}$ from the systematic extinctions of reflections. The unit cell contains two formula units ($\rho_{calcd}=1.59$, $\rho_{obs}=1.54$ g./cm³). The photographs were taken with Cu$K\alpha$ radiation using multiple film technique. All intensities were estimated visually by comparison with standard scales. The usual correction factors were applied by means of a chart given by Cochran and relative $|F_o|$ values were obtained.

Structure Determination

The structure determination was carried out using ($h\,k\,0$) and ($h\,0\,l$) reflections from Weissenberg data. It was observed that the intensity of each reflection is similar to the corresponding one of the cobalt-analogue at low-angle reflections. This had been expected from the dichroism mentioned above and the crystallographic data, and the outline of the crystal structure was determined without difficulty.

At the stage of refinement, the method of successive difference syntheses was employed. The atomic coordinates obtained are shown in Table I. These parameters gave the reliability index $R=\sum||F_o|-|F_c||/\sum|F_o|$ of 0.131 and 0.121 for ($h\,k\,0$) and ($h\,0\,l$) respectively, excluding (100) reflection which could not be observed with full certainty. Calculated and observed structure factors are listed in Table II. In the calculation of structure factors, atomic scattering factors listed in the International Table (1935) were used. Overall temperature factors of the form exp $[-B(\sin\theta/\lambda)^2]$, where $B=2.7$ Å², were applied in the final calculation of structure factors. Final electron density projections on (010) and (001) are shown in Figs. 1 and 2.

TABLE I. FINAL ATOMIC COORDINATES

	x/a	y/b	z/c
Cr	0	0	0
Cl(1)	0.050	0.038	0.269
Cl(2)	0.345	0.387	0.272
N(1)	0.100	−0.235	0.042
N(2)	0.185	0.106	0.023
C(1)	0.227	−0.200	0.037
C(2)	0.288	−0.022	0.100
O	0.478	0.150	0.538

1) N. Fogel and S. D. Christian reported in *J. Am. Chem. Soc.*, **80**, 2356 (1958) that the dichloro-complex should be given a composition formula [Co en_2Cl_2]Cl·HCl·$6H_2O$ instead of [Co en_2Cl_2]·Cl·HCl·$2H_2O$. However, no other formula than the latter can give any satisfactory agreement between the measured and calculated values of density, and furthermore, between $|F_o|$ and $|F_c|$, i. e., the observed and calculated intensities of X-ray diffraction.

2) A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, **25**, 331 (1952).
3) S. Ooi, Y. Komiyama, Y. Saito and H. Kuroya, ibid., **32**, 263 (1959).
4) P. Pfeiffer et al., *Ber.*, **37**, 4255 (1904).

TABLE II. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

h k l	F_o	F_c
100	39.2	68.4
200	38.4	51.6
300	70.0	72.4
400	36.4	33.6
500	9.6	5.2
600	42.4	42.8
700	21.6	−27.6
800	4.0	−0.4
900	4.4	10.0
1000	<5.4	−9.2
1100	10.4	8.0
1200	2.4	4.4
020	75.2	72.4
040	21.2	11.6
060	9.6	12.4
080	23.2	22.8
0100	7.6	6.4
110	12.4	−19.2
120	59.2	64.4
130	64.4	−61.2
140	77.2	78.0
150	10.8	12.8
160	17.6	11.6
170	15.2	16.8
180	<5.2	0.4
190	<3.6	−2.4
210	43.6	44.8
220	52.0	49.6
230	14.0	−8.8
240	42.8	40.8
250	21.2	−20.8
260	28.0	25.2
270	28.4	−26.8
280	9.6	4.8
290	<3.6	−3.2
310	18.4	−15.2
320	76.0	76.4
330	38.4	−33.6
340	28.0	22.8
350	9.6	−9.2
360	15.2	8.8
370	20.4	−20.4
380	17.2	16.0
390	5.6	−6.4
410	5.2	−4.4
420	38.8	38.4
430	24.8	−27.6
440	37.6	37.2
450	12.4	−13.6
460	31.2	32.0
470	10.0	−8.0

h k l	F_o	F_c
480	<5.2	−2.4
490	4.8	−4.4
510	23.2	16.8
520	28.0	28.8
530	<3.6	3.6
540	11.2	14.0
550	23.2	−22.0
560	13.2	10.8
570	29.2	−28.4
580	6.0	3.6
590	10.0	−8.8
610	23.6	−12.0
620	30.8	26.4
630	27.2	−27.6
640	14.0	−22.4
650	19.2	−23.2
660	7.2	7.2
670	2.8	−3.6
680	18.4	18.8
710	38.4	−33.6
720	19.6	15.6
730	22.0	−21.2
740	28.8	28.0
750	11.2	−7.6
760	18.0	14.8
770	<3.6	−0.4
780	6.0	2.4
810	<5.2	6.4
820	<5.2	−6.0
830	19.6	18.8
840	8.8	6.0
850	18.0	−19.2
860	18.0	9.6
870	10.8	−12.0
910	9.6	−13.2
920	8.0	−9.2
930	8.4	−8.4
940	6.0	−4.0
950	<5.2	−0.4
960	<3.6	0.8
970	<3.6	0.4
1010	6.0	4.8
1020	<5.2	−5.2
1030	<5.2	−2.0
1040	20.0	15.2
1050	<3.6	−3.6
1060	10.4	7.6
1110	6.8	7.2
1120	5.6	0.8

h k l	F_o	F_c
1130	9.6	9.6
1140	<3.6	−0.8
1150	5.2	4.0
1210	3.2	−2.8
1220	<3.6	−1.6
1230	<3.6	−4.0
002	19.2	16.8
004	114.3	114.9
006	14.8	−13.3
008	28.4	26.8
0010	<4.0	−2.0
102	<4.0	0.4
10$\bar{2}$	47.2	40.8
104	<4.0	−3.6
10$\bar{4}$	96.4	96.8
106	15.6	18.8
10$\bar{6}$	<5.6	6.4
108	<5.6	−5.6
10$\bar{8}$	41.2	43.2
1010	<4.0	10.4
10$\overline{10}$	<4.0	−1.6
202	<5.6	2.4
20$\bar{2}$	19.2	23.2
204	37.6	37.2
20$\bar{4}$	51.6	54.4
206	<5.6	−7.2
20$\bar{6}$	32.0	32.8
208	8.8	10.0
20$\bar{8}$	23.2	17.6
2010	<4.0	−4.8
20$\overline{10}$	<4.0	9.2
302	44.8	−48.4
30$\bar{2}$	98.0	−96.8
304	20.8	24.0
30$\bar{4}$	74.4	69.6
306	<5.6	−4.8
30$\bar{6}$	29.6	−29.6
308	<5.6	6.8
30$\bar{8}$	48.8	50.8
30$\overline{10}$	<5.6	−2.4
402	59.6	60.4
40$\bar{2}$	44.4	46.0
404	<5.6	−4.0
40$\bar{4}$	35.2	38.0
406	29.2	42.4
40$\bar{6}$	16.8	−16.8
408	<4.0	−2.8
40$\bar{8}$	33.2	25.6
40$\overline{10}$	14.8	−14.0

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
502	10.4	12.0	$70\bar{4}$	6.8	−8.4	1002	33.6	42.0
$50\bar{2}$	32.4	35.6	706	19.6	25.2	$100\bar{2}$	46.0	46.8
504	14.0	12.0	$70\bar{6}$	16.8	14.4	1004	<4.0	−7.2
$50\bar{4}$	30.0	35.2	$70\bar{8}$	26.4	23.2	$100\bar{4}$	12.0	−16.0
506	11.2	12.8	$70\overline{10}$	<4.0	6.4	$100\bar{6}$	32.4	26.4
$50\bar{6}$	32.0	38.4				$100\bar{8}$	<5.6	−1.6
508	<4.0	6.8	802	22.8	26.4	$100\overline{10}$	9.6	6.0
$50\bar{8}$	19.2	18.0	$80\bar{2}$	35.2	35.2			
$50\overline{10}$	10.0	12.4	804	6.8	10.4	1102	6.8	8.4
			$80\bar{4}$	7.2	−15.6	$110\bar{2}$	32.8	34.4
602	25.2	22.0	806	8.0	15.6	$110\bar{4}$	<5.6	1.2
$60\bar{2}$	10.4	−11.6	$80\bar{6}$	17.6	13.3	$110\bar{6}$	36.4	34.0
604	11.2	17.2	$80\bar{8}$	11.2	−18.0	$110\bar{8}$	<4.0	−5.2
$60\bar{4}$	46.8	51.6	$80\overline{10}$	9.2	7.6			
606	18.8	17.2				$120\bar{2}$	17.6	10.0
$60\bar{6}$	6.8	−8.4	902	20.4	20.2	$120\bar{4}$	12.0	10.4
$60\bar{8}$	38.8	42.8	$90\bar{2}$	16.8	14.0	$120\bar{6}$	12.0	9.2
$60\overline{10}$	<5.6	−4.8	904	<4.0	4.4	$120\bar{8}$	6.0	5.6
			$90\bar{4}$	24.0	24.4			
702	40.4	40.8	$90\bar{6}$	9.6	8.4	$130\bar{2}$	16.0	22.8
$70\bar{2}$	38.0	38.8	$90\bar{8}$	19.6	16.8	$130\bar{4}$	<4.0	−7.2
704	14.4	−26.4	$90\overline{10}$	<4.0	−5.2	$130\bar{6}$	31.6	27.6

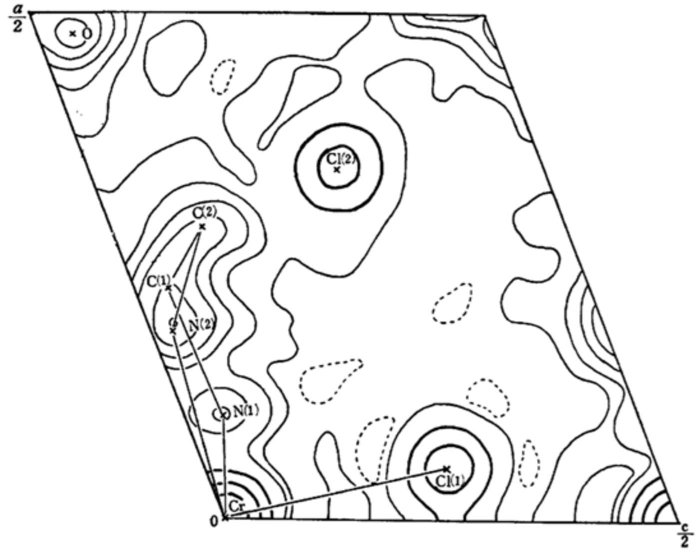

Fig. 1. Electron density projected along the *b*-axis. Contours are drawn at intervals 10 e. Å^{-2} for peaks Cr and Cl (heavy lines) of 2 e. Å^{-2} for other peaks, zero-electron level being broken.

Results

The crystal structure determined is isomorphous with [Co en_2Cl_2] Cl·HCl·$2H_2O$ and consists of the following elements: [Cr en_2Cl_2]$^+$, Cl^- and [H_2O···H···H_2O]$^+$. The configuration of the complex is as follows. Two enantiomorphous ethylenediamine molecules, taking *gauche* form, are coordinated to a chromium atom with their four nitrogen atoms. The arrangement of nitrogen atoms around the chromium atom is square coplanar. On a line approximately perpendicular to the plane are two chlorine atoms and these are coordinated to the central metal atom. The calculated bond lengths and angles are shown in Table III. The interatomic distance O···O of [H_2O···H···H_2O]$^+$ was found to be 2.56 Å.

A trial was made for the estimation of some coordinate standard deviations by

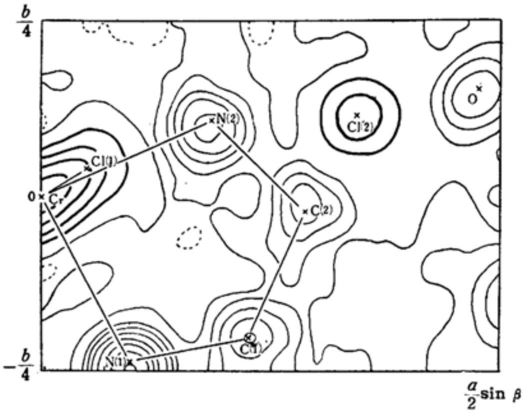

Fig. 2. Electron density projected along the *c*-axis. Contours are drawn in the same manner as Fig. 1.

TABLE III. BOND LENGTHS AND ANGLES

Cr-Cl(1)	2.33 Å
Cr-N(1)	2.11
Cr-N(2)	2.13
N(1)-C(1)	1.44
N(2)-C(2)	1.48
C(1)-C(2)	1.57
N(1)-Cr-N(2)	85.2°
Cr-N(1)-C(1)	105.8
Cr-N(2)-C(2)	108.3
N(1)-C(1)-C(2)	116.5
N(2)-C(2)-C(1)	106.8

TABLE IV. ESTIMATED COORDINATE STANDARD DEVIATIONS (VALUES IN ANGSTROM UNITS)

	Cl	N(1)	N(2)
$\sigma(X^*)$	0.013**	0.022	0.039
$\sigma(y)$	0.010	0.054	0.032
$\sigma(z)$	0.012	—***	—***

* X is the axis normal to the yz-plane.
** 0.013 was estimated from the data for $(h\,0\,l)$, 0.012 from those for $(h\,k\,0)$.
*** $\sigma(z)$ for N(1) and N(2) could not be estimated because of the required tedious calculation**** due to mutual overlaps of atomic peaks (see Fig. 1).
**** D.W.J. Cruickshank, *Acta Cryst.*, **5**, 511 (1952).

the method of Cruickshank[5], and the results are listed in Table IV. Regarding the bond lengths of chromium to nitrogen atoms, 2.11 and 2.13 Å are found for Cr–N(1) and Cr–N(2), respectively. These values are greater than the corresponding ones in the cobalt-analogue by ca. 0.1 Å. On this value, then, "significance tests"[3] were tried. At a rough approximation with $\sigma(z)$ of N(1) and N(2) ignored, the standard deviations of bond lengths $\sigma(l)$'s could be calculated from the data given in Table IV.

$$\sigma(\text{Cr–N(1)})=0.049, \quad \sigma(\text{Cr–N(2)})=0.037\text{ Å}.$$

Similar treatments on the data of cobalt-analogues gave

$$\text{N(1)}: \sigma(X)=0.068, \quad \sigma(y)=0.084\text{ Å},$$

and $\text{N(2)}: \sigma(X)=0.100, \quad \sigma(y)=0.108\text{ Å},$

from which were obtained the values:

$$\sigma(\text{Co–N(1)})=0.080, \quad \sigma(\text{Co–N(2)})=0.099\text{ Å}.$$

The values of $|l_1-l_2|/\{\sigma(l_1)^2+\sigma(l_2)^2\}^{1/2}$ were estimated to be 1.4 for Cr–N(1) and Co–N(1), and 1.2 for Cr–N(2) and Co–N(2), where l_1 and l_2 are bond lengths of Cr–N and Co–N, respectively. According to the levels given by Cruickshank, these values indicate that the difference between l_1 and l_2 is not significant.

The bond length found for Cr–Cl(1) is 2.33 Å which is the same as that found in the cobalt-analogue, and the estimated σ(Cr–Cl(1)) is 0.012 Å. The cell dimensions of cobalt-analogue are

$$a=10.68, \quad b=7.89, \quad c=9.09\text{ Å}, \quad \beta=110.4°,$$

and a is shorter than that of the present crystal by ca. 0.3 Å which is apparently beyond the experimental error while no remarkable discrepancies can be found between the values of b's, c's and β's, respectively, of the two paired coordination compounds of Cr(III) and Co(III).

Thus, it has been evidenced that the substitution of metal causes the deformation of the unit cell. It is probably not unduly bold to consider that the effect of a metal substitution takes place first of all in the nearest neighbor of the metal. However, since the accuracy is not high enough as can be seen above, the authors' opinion is that it is going too far to give a definite conclusion to this problem.

The present authors wish to express their sincere thanks to Professor Y. Saito for his kind advice and encouragement throughout this work. Part of the cost of this investigation was defrayed from the Fund for Scientific Resarch Expenditure of the Ministry of Education, to which the authors' thanks are also due.

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5) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).