The Crystal Structure of trans-Dibromo-bisethylenediamine-cobalt(III) Bromide Hydrobromide Dihydrate

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The crystal structure of the ethylenediamine-"praseo"-chloride, *trans*-[Co en_2 Cl_2] $Cl \cdot HCl \cdot 2H_2O$, was determined before by Nakahara and two of us[1]. An attempt has been made now to investigate the crystal structure of the bromine-analogue, namely, the *trans*-dibromo-bisethylenediamine cobalt(III) bromide hydrobromide dihydrate, *trans*-[Co en_2Br_2] $Br \cdot HBr \cdot 2H_2O$. This compound has almost the same properties, physical and chemical, as the corresponding chlorine-complex, and, therefore, may be expected to be isotype with the latter. However, the analysis was carried out with caution in consideration of the fact that the configuration of the chloro-dinitro-triammine-cobalt(III), $[Co(NH_3)_3(NO_2)_2Cl]$, is quite different from that of the apparently analogous bromo-compound, $[Co(NH_3)_3(NO_2)_2Br]$[2),3)].

Experimental

The crystals are well-formed dark green tablets, showing predominant (100) faces. This habit is the same as that of [Co en_2 Cl_2] $Cl \cdot HCl \cdot 2H_2O$. They are monoclinic and belong to the monoclinic holohedral class. Crystals show marked dichroism; in polarized light they appear blue when the electric vector is normal to the *b*-axis and yellowish green when this vector is parallel to the *b*-axis. From oscillation and Weissenberg photographs with Fe $K\alpha$ radiation ($\lambda=1.937$ Å) the unit cell dimension is found to be: $a=10.98$, $b=8.18$, $c=9.46$Å, $\beta=113.2°$. The space group determined from extinctions, is $P2_1/c-C_{2h}^5$.

The cell contains two formula units of [Co en_2 Br_2] $Br \cdot HBr \cdot 2H_2O$ (density calculated 2.28 $g.cm^{-3}$; found 2.21 $g.cm^{-3}$) and cobalt atoms must therefore occur on centers of symmetry.

The intensities of reflections (*h0l*), (*hk*0) were estimated by comparison with a standard scale. The exposures were taken with Fe $K\alpha$ radiation, using multiple film technique. After correction for Lorentz and polarization factors, relative F values were obtained. No correction for absorption was made.

Determination of the Structure

The structure determination is based on the analysis of the (*hk*0) and (*h0l*) reflections, which could be carried out in a rather straightforward fashion. Because of the occurrence of the cobalt atoms at symmetry centers, the Patterson functions were simple and comparison of these results with those obtained for [Co en_2Cl_2] $Cl \cdot HCl \cdot 2H_2O$ revealed that both structures were isotype. Therefore, the Patterson function could be solved without difficulty, yielding an approximate position not only for bromine atoms but for most of the lighter atoms as well. The signs of all but weak reflections could be derived on the basis of the sets of parameters thus

1) A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, 25, 331 (1952).
2) Y. Tanito, Y. Saito and H. Kuroya, ibid., 26, 420 (1953).
3) Y. Komiyama, ibid., 31, 26 (1958).

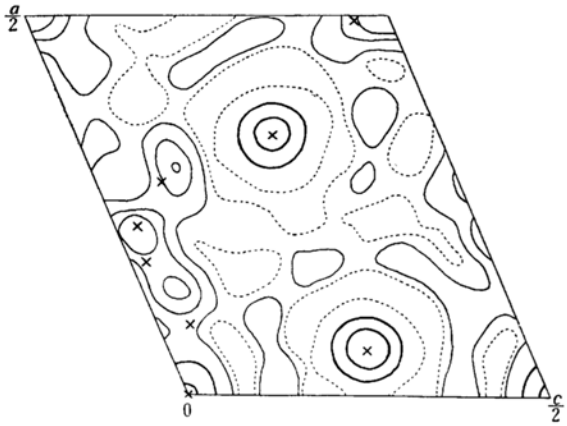

Fig. 1. Electron density projected along the *b*-axis. Contours are drawn at 4 e. Å^{-2} intervals and 20 e. A^{-2} for heavy lines of Co and Br peaks. Broken lines show zero electron level.

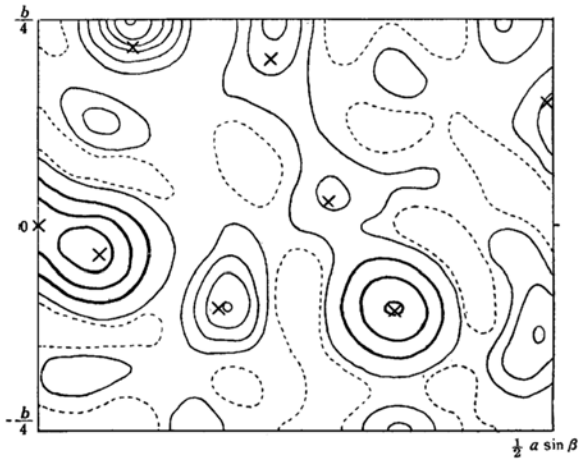

Fig. 2. Electron density projected along the *c*-axis. Contours are drawn in the same manner as Fig. 1.

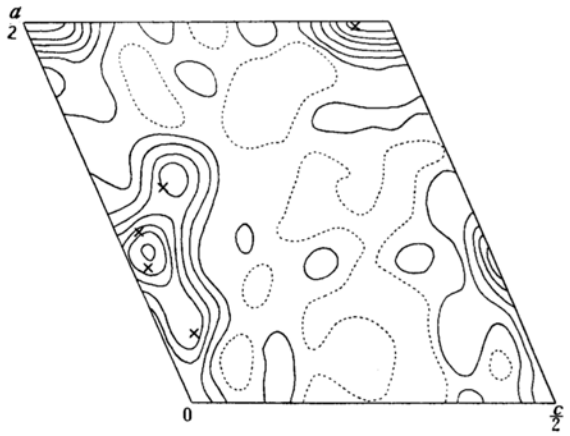

Fig. 3. Residual electron density projected along the *b*-axis, showing the positions of light atoms. Contours are drawn at 2 e. Å^{-2} intervals.

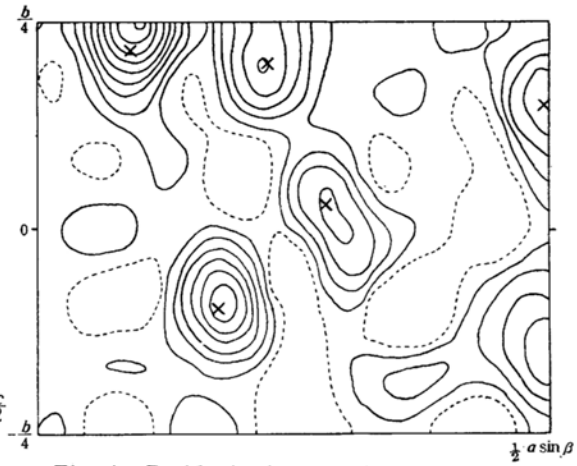

Fig. 4. Residual electron density projected along the *c*-axis, showing the positions of light atoms. Contour lines as in Fig. 3.

deduced. Then the Fourier syntheses of the electron density projected along [001] and [010] were evaluated. In the *c*-axis projection almost every atom was resolved. But it was not the case in the *b*-axis projection. The outlines of the ethylenediamine ligands did not come out clearly, probably due to the diffraction effect of heavy bromine atoms. In order to improve the situation, the contribution of the cobalt and bromine atoms was subtracted from the observed structure factors and trial of computing the residual electron density projections along the *b*-axis was made. (The result is given in Fig. 3).

Fourier refinements were repeated as usual. Final projections shown in Fig. 1—Fig. 4 lead to the structure illustrated in Fig. 5 and Fig. 6. Parameter values are listed in Table I. The parameter of the oxygen atom is less reliable because of poor resolution of the projection. The parameters listed in Table I gave the reliability index $R=\Sigma||F_o|-|F_c||/\Sigma|F_c|$ of 0.133 and 0.130 for (*h*0*l*) and (*hk*0) respectively. Calculated and observed structure amplitudes are given in Table II. In the calculation of structure factors,

TABLE I
FINAL ATOMIC COORDINATES

	x/*a*	*y*/*b*	*z*/*c*
Co	0	0	0
Br(1)	0.060	−0.037	0.275
Br(2)	0.344	−0.397	0.269
N(1)	0.092	0.216	0.045
N(2)	0.175	−0.099	0.024
C(1)	0.225	0.201	0.032
C(2)	0.281	0.029	0.091
O	0.494	0.150	0.452

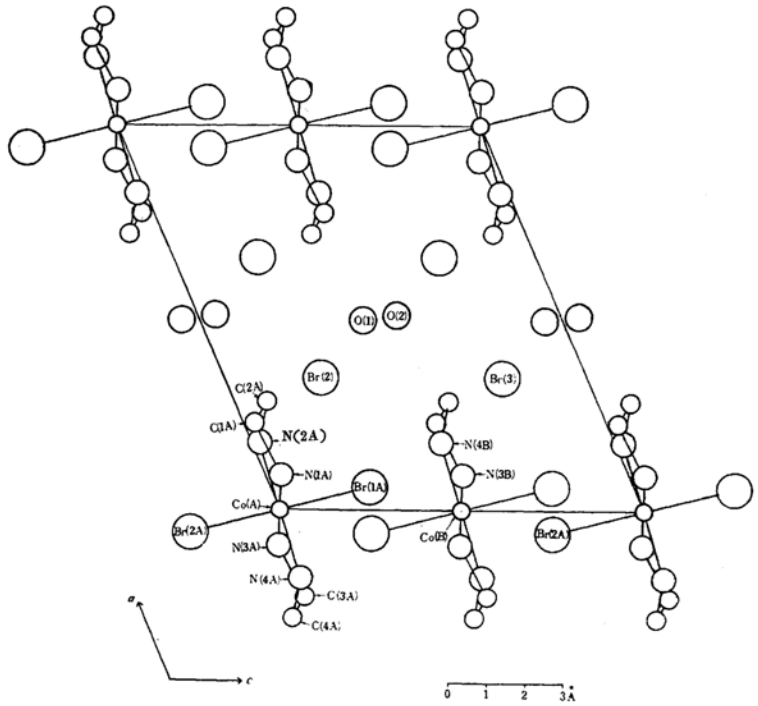

Fig. 5. Projection of the structure upon a plane normal to the *b*-axis.

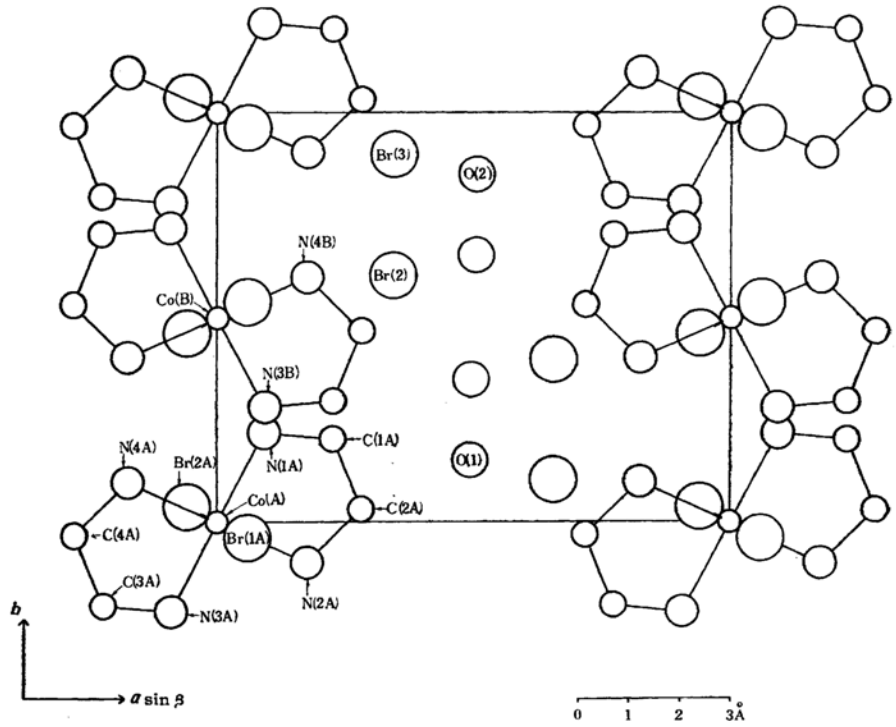

Fig. 6. Projection of the structure upon a plane normal to the *c*-axis.

Table II
Observed and calculated structure amplitudes

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
100	101	106	410	40	53	002	82	−104	502	66	59
200	82	82	420	32	24	004	236	226	50$\bar{2}$	86	67
300	233	158	430	88	104	006	75	−74	504	<16	−9
400	<12	−6	440	70	74	008	81	63	50$\bar{4}$	10	16
500	35	−34	450	53	51				506	54	55
600	75	60	460	60	73	102	<9	13	50$\bar{6}$	50	58
700	127	−115	470	28	22	10$\bar{2}$	12	5	50$\bar{8}$	23	26
800	41	−36				104	<14	−18			
900	<14	6	510	65	−54	10$\bar{4}$	153	158	602	47	38
1000	55	−60	520	<12	11	106	54	68	60$\bar{2}$	24	−18
			530	16	−30	10$\bar{6}$	32	−23	604	<14	7
020	163	169	540	14	22	108	26	−44	60$\bar{4}$	112	119
040	16	6	550	53	63	10$\bar{8}$	116	96	60$\bar{6}$	41	−46
060	<14	−9	560	23	17				60$\bar{8}$	120	118
080	25	28	570	99	103	202	<11	−9			
						20$\bar{2}$	12	15	702	145	142
110	51	54	610	33	38	204	58	40	70$\bar{2}$	134	114
120	122	115	620	22	13	20$\bar{4}$	89	83	704	96	−96
130	135	129	630	63	71	206	<17	−6	70$\bar{4}$	50	−67
140	150	146	640	64	−78	20$\bar{6}$	32	39	70$\bar{6}$	38	43
150	13	13	650	48	47	20$\bar{8}$	42	23	70$\bar{8}$	43	38
160	54	51	660	27	−24						
170	28	13				302	97	−93	802	83	69
180	<8	−11	710	70	49	30$\bar{2}$	206	−203	80$\bar{2}$	132	112
			720	17	−25	304	56	59	80$\bar{4}$	70	−60
210	65	−60	730	74	56	30$\bar{4}$	167	187	80$\bar{6}$	99	83
220	84	86	740	35	42	306	<15	7	80$\bar{8}$	63	−54
230	10	−14	750	40	29	30$\bar{6}$	106	−122			
240	88	88				30$\bar{8}$	168	140	902	33	30
250	57	53	810	17	−20				90$\bar{2}$	21	14
260	56	61	820	44	−39	402	134	135	90$\bar{4}$	20	19
270	91	95	830	62	−60	40$\bar{2}$	70	82	90$\bar{6}$	<14	3
280	<7	4	840	13	−15	404	72	−85	90$\bar{8}$	20	37
			850	10	10	40$\bar{4}$	65	71			
310	34	30				406	145	123	100$\bar{2}$	151	131
320	124	122	910	17	18	40$\bar{6}$	48	−43	100$\bar{4}$	82	−75
330	80	81	920	35	−29	40$\bar{8}$	102	79	100$\bar{6}$	104	97
340	13	4	930	<9	13						
350	49	63							110$\bar{4}$	41	−48
360	<14	−19	1010	<7	1						
370	56	51									

atomic scattering factors listed in the International Table were employed. Temperature correction of the form $\exp -B(\sin\theta/\lambda)^2$, where $B=0.9$ Å^2, was applied in the final calculation of the structure factors.

Discussion

The structure is isotype with [Co en_2 Cl_2] Cl·HCl·$2H_2O$. The principal points of stereochemical interest which emerge from this X-ray analysis are as follows.

(1) The structure is essentially ionic and consists of [Co en_2Br_2]$^+$, [H_2O···H···H_2O]$^+$ and Br^-. Since the structure is isotype with chloro-analogue, a similar consideration of the arrangement of bromine ions leads us to locate a proton midway between the two water molecules. The O···O distance is found to be 2.60 Å. The existence of the group [H_2O···H···H_2O]$^+$ was suggested by Huggins and this was indeed verified by our investigation on the structures of *trans*-dihalogeno-*iso*-ethylenediamine complexes[4].

4) M. L. Huggins, *J. Phys. Chem.*, **40**, 723 (1936).

(2) The interatomic distances are given in Table III. Co-Br distance is found to be 2.44 Å. This is 0.14 Å larger than the corresponding Co-Cl distance and the difference agrees with that in covalent bond radius of chlorine and bromine atom. Other distances agree well with those found in $[Co\ en_2\ Cl_2]Cl \cdot HCl \cdot 2H_2O$.

TABLE III

INTERATOMIC DISTANCES AND BOND ANGLES

Co—Br(1)	2.44 Å
Co—N(1)	2.00
Co—N(2)	2.01
N(1)—C(1)	1.52
N(2)—C(2)	1.51
C(1)—C(2)	1.55
Br(1A)···N(3B)	3.58
Br(2A)···N(3B)	3.46
Br(2)···N(4B)	3.58
Br(3)···N(4B)	3.37
Br(2)···O(2)	3.24
Br(3)···O(2)	3.26
O(1)···O(2)	2.60
N(1)—Co—N(2)	86.5°
Co—N(1)—C(1)	109.2°
Co—N(2)—C(2)	108.3°
N(1)—C(1)—C(2)	107.6°
N(2)—C(2)—C(1)	110.3°

(3) The dichroism of the crystal has been measured by Yamada et al. and their investigation revealed that the general features of the absorption curve are essentially the same as those obtained for $[Co\ en_2\ Cl_2]Cl \cdot HCl \cdot 2H_2O$[5]. This is quite feasible since both structures are isotype. The marked dichroism is reasonable since all the Br-Co-Br bonds are nearly parallel to the *c*-crystal axis.

5) S. Yamada et al., This Bulletin, 28, 222 (1955).

Summary

The structure of *trans*-dibromo-bisethylenediamine cobalt(III) bromide hydrobromide dihydrate has been determined by X-ray analysis.

$[Co\ en_2Br_2]Br \cdot HBr \cdot 2H_2O$ is monoclinic, $a=10.98$, $b=8.18$, $c=9.46$ Å, and $\beta=113.2°$, space group $P2_1/c$, two formula units in the cell. The structure consists of $[Co\ en_2Br_2]^+$, $[H_2O\cdots H\cdots H_2O]^+$ and Br^-, and is isotype with $[Co\ en_2Cl_2]Cl \cdot HCl \cdot 2H_2O$. The complex ion has a center of symmetry. Two enantiomorphous ethylenediamine molecules, taking "*gauche*" configration, are coordinated to a cobalt atom. A cobalt atom is surrounded in a square coplanar configuration by four nitrogen atoms at distances 2.0 Å, and on a line approximately perpendicular to the plane of nitrogen atoms are two bromine atoms at distances 2.44 Å. The marked dichroism of the crystal is explainable in terms of the characteristic features in the arrangement of the complex ions in the crystal.

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