*The Crystal Structure of trans-Dichloro-bis-l-propylenediamine Cobalt(III) Chloride Hydrochloride Dihydrate and the Absolute Configuration of the Complex Ion, [Co l-pn$_2$Cl$_2$]$^{+}$**

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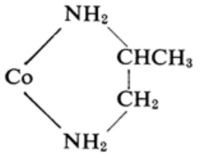
During the past several years the crystal structures of various cobalt-ethylenediamine complexes have been determined by one of the present authors (Y. S.), Kuroya et al.[1-4] and Becker et al.[5] The puckered form of the cobalt-ethylenediamine ring has thus been established. In connection with this, the present investigation was initiated in order to determine the configuration of the cobalt-propylenediamine ring;



with special interest in the orientation of the substituted methyl group. Corey and Bailar[6] have recently discussed the geometry of various metal-chelate rings. Their conclusion for the metal-propylenediamine ring agrees quite well with the results obtained here. The absolute configuration of the complex ion [Co l-pn$_2$Cl$_2$]$^+$ has also been determined by the usual absorption edge technique.

Experimental

Crystals of [Co l-pn$_2$Cl$_2$]Cl.HCl.2H$_2$O were prepared by the method of Werner and Fröhlich[7]**. They are well-developed dark green tablets, showing predominant (100) faces. In polarized light, they exhibit a marked dichroism similar to that observed for [Co en$_2$Cl$_2$]Cl.HCl.2H$_2$O. This fact suggest that the structure is closely related to those of the ethylenediamine-analogues.

As the crystals of [Co l-pn$_2$Cl$_2$]Cl.HCl.2H$_2$O decompose gradually when exposed to air, special precautions had to be taken to preserve the crystals. It was found that adequate protection was afforded by a thin layer of grease. Specimens treated with grease were preserved intact for several weeks.

From measurements made by using an X-ray diffractometer with Cu$K\alpha$ radiation (λ=1.5418 Å), the unit cell is found to be monoclinic, with

$$a=22.092\pm0.004\,\text{Å}$$
$$b=8.406\pm0.002\,\text{Å}$$
$$c=9.373\pm0.004\,\text{Å}$$
and $$\beta=99°39'\pm7'$$

The cell contains four formula units of [Co l-pn$_2$Cl$_2$]Cl.HCl.2H$_2$O (density, calculated 1.494 g./cc.; found 1.495 g./cc. at 26°C). The space group was found to be $C2/m$, Cm or $C2$ from Weissenberg photographs taken with Fe$K\alpha$ radiation. The former two space group estimates can be excluded since it is certain that the compound is optically active and cannot have a center or a plane of symmetry in the arrangement in the crystals.

The structure determination was based on analysis of the ($h0l$) and ($hk0$) reflections, which could be carried out in quite a straightforward fashion.

Intensity data for the ($h0l$) and ($hk0$) reflections were recorded on zero level Weissenberg films about the b- and c-axes by the multiple-film technique. Fe$K\alpha$ radiation was used (λ=1.937 Å). The intensities of the reflections were measured by visual comparison with an intensity scale. They were corrected for absorption, Lorentz and polarization factors. Observed structure amplitudes were brought to an absolute scale afterwards by scaling them against the calculated values, the maximum $\sin\theta/\lambda$ observed being 0.514.

Patterson functions could be solved without difficulty by comparison with those of the ethylenediamine-analogues, yielding approximate positions not only for the heavy atoms but also for lighter atoms. Thus, Fourier syntheses of the electron density projections along [001] and [010] could be computed.

Fourier refinements were repeated as usual. Final projections of the electron density along [010] and [001] are shown in Figs. 1 and 2 respectively. They can be interpreted in terms of Figs. 3 and 4 respectively. The final set of parameter values is

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* Part of this paper is taken from the paper of the same title by the same authors, from "Advances in the Chemistry of the Coordination Compounds", © Stanley Kirschner, 1961, and published by the Macmillan Company, New York.

** Optically active propylenediamine was kindly prepared by Prof. H. Kuroya of Osaka City University, to whom the authors' thanks are due.

[1] A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, **25**, 331 (1953).

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

[3] K. Nakatsu, Y. Saito and H. Kuroya, ibid., **29**, 428 (1956).

[4] K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, ibid., **30**, 158 (1958).

[5] K. A. Becker, G. Grosse and K. Plieth, *Z. Krist.*, **112**, 375 (1959).

[6] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[7] A. Werner and A. Fröhlich, *Ber.*, **40**, 2228 (1907).

TABLE I. ATOMIC PARAMETERS

		x	y	z	$B(\text{Å}^2)$
Co		0.250	0	0.250	3.4
Cl	(1)	0.392	0.365	0.171	3.2
	(2)	0.109	0.681	0.327	3.2
	(3)	0.267	0.022	0.017	3.0
	(4)	0.232	−0.022	0.483	3.0
N	(1)	0.268	−0.232	0.251	3.2
	(2)	0.338	0.036	0.320	3.2
	(1′)	0.231	0.235	0.255	3.2
	(2′)	0.164	−0.039	0.175	3.2
C	(1)	0.334	−0.250	0.261	6.0
	(2)	0.365	−0.119	0.355	6.0
	(3)	0.434	−0.117	0.345	6.0
	(1′)	0.168	0.246	0.167	6.0
	(2′)	0.136	0.109	0.211	6.0
	(3′)	0.067	0.117	0.154	6.0
O	(1)	0.441	0.488	0.473	3.4
	(2)	0.059	0.509	0.029	3.4

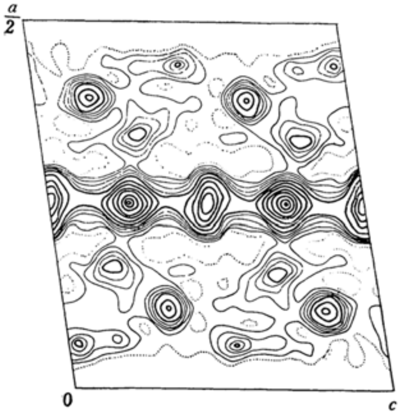
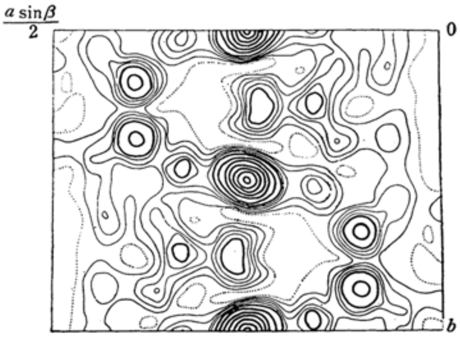


Fig. 1. Electron-density projection along [010]. Contours are drawn at intervals of $2e.\,\text{A}^{-2}$. Contours above $10e.\,\text{A}^{-2}$ are drawn at $5e.\,\text{A}^{-2}$ with thick lines. Zero contours are broken.



Electron density projection

Fig. 2. Electron-density projection along [001]. Contours are drawn at intervals of $2e.\,\text{A}^{-2}$. Thick contours are at intervals of $10e.\,\text{A}^{-2}$. Zero contours are broken.

listed in Table I. This gives the reliability index $R=\sum\big|\,|F_o| - |F_c|\,\big|/\sum|F_o|$ of 0.14 and 0.15 for ($h0l$) and ($hk0$) respectively, non-observed reflections being excluded. The contributions of hydrogen atoms were neglected. The agreement between the observed and calculated structure factors is shown in Table II.

Calculation of the structure factors as well as of the electron density projections was carried out with a PC-1 parametron computer in the Faculty of Science of this University. In the calculation of the structure factors, the atomic scattering factors were taken from the paper of Vand, Eiland and Pepinsky[8]. Different isotropic temperature factors were applied for each atoms; these are listed in the last column of Table I.

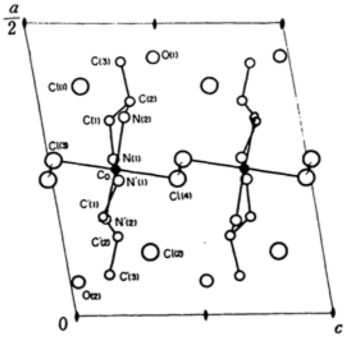


Fig. 3. Projection of the atomic arrangement on (010).

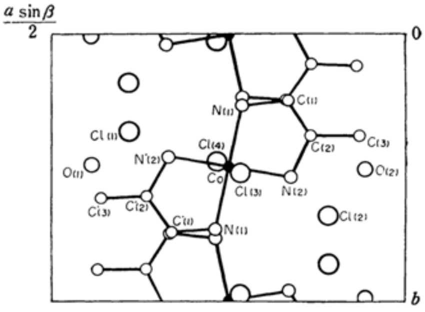


Fig. 4. Projection of the atomic arrangement on (001).

Determination of the Absolute Configuration

The absolute configuration of l-propylenediamine has been chemically related to D-alanine by modification of COOH in the latter to CH_2NH_2 of the former[9]. Since the absolute configuration of D-alanine is already known, l-propylenediamine must possess the absolute configuration shown by I:

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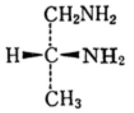
[8] V. Vand, P. F. Eiland and R. Pepinsky, *Acta Cryst.*, **10**, 303 (1957).

[9] H. Reihlen, E. Weinbrenner and G. V. Hessling, *Ann.*, **494**, 143 (1932).

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

h 0 *l*	$\lvert F_o\rvert/4$	$F_c/4$	*h* 0 *l*	$\lvert F_o\rvert/4$	$F_c/4$	*h* 0 *l*	$\lvert F_o\rvert/4$	$F_c/4$	*h k* 0	$\lvert F_o\rvert/4$	$\lvert F_c\rvert/4$
0 0 1	2.2	+0.5	8	11.0	−8.5	4	17.0	−17.3	19	7.2	7.8
2	33.0	−33.2	9	2.6	+0.9	5	0	−1.5	21	1.1	1.3
3	3.4	−1.7	8 0 0	35.0	+34.5	6	4.8	−6.5	0 2 0	44.0	43.8
4	35.0	+35.3	1	3.5	−1.9	7	3.1	−1.7	2	36.5	28.6
5	0	+0.8	2	40.5	−43.0	8	6.7	−5.9	4	39.7	40.0
6	15.4	+17.1	3	0	+1.7	16 0 0	8.0	+8.8	6	23.4	28.8
7	0	+0.1	4	23.3	+26.3	1	4.6	−0.3	8	12.4	9.7
8	14.4	+7.9	5	2.9	+2.1	2	14.0	−14.0	10	25.1	32.2
9	1.5	−0.9	6	10.6	−10.1	3	0	−2.5	12	14.1	15.9
2 0 0	58.8	−59.3	7	0	−1.7	4	7.4	+9.3	14	7.3	3.6
1	0	−1.2	8	2.0	−2.2	5	0	−1.0	16	7.0	9.8
2	14.1	+14.5	$\bar{8}$ 0 1	0.6	−2.0	$\overline{16}$ 0 1	0	−0.2	18	5.5	5.0
3	1.1	+1.4	2	3.7	+2.2	2	4.5	+4.9	20	2.3	3.3
4	41.0	−41.2	3	3.4	+4.5	3	4.5	+0.3	1 3 0	13.3	4.5
5	0	+0.3	4	9.0	+6.4	4	4.2	+2.9	3	13.3	14.7
6	6.1	+7.9	5	0	−1.4	5	0	+2.3	5	13.0	13.4
7	2.2	−2.2	6	7.5	+7.2	6	6.3	−1.7	7	5.3	6.0
8	8.5	−11.2	7	0	+0.1	7	3.0	−1.9	9	2.2	5.4
9	2.2	+1.5	8	16.8	+18.3	18 0 0	9.2	+12.3	11	2.3	4.2
$\bar{2}$ 0 1	1.1	−0.3	9	1.4	+0.7	1	1.7	+1.2	13	7.7	8.6
2	23.8	+23.7	10 0 0	32.3	−30.9	2	3.6	−4.3	15	11.0	13.8
3	2.3	−0.2	1	6.3	−0.9	3	0	−0.4	17	5.6	7.2
4	34.3	−34.5	2	16.4	+18.3	4	0	+0.3	19	1.5	0.5
5	0	−0.3	3	3.5	+2.0	$\overline{18}$ 0 1	0	+1.2	0 4 0	33.9	34.3
6	9.1	+9.2	4	21.2	−26.2	2	8.8	+7.3	2	43.7	37.1
7	1.4	+0.8	5	3.6	−2.7	3	5.0	−1.4	4	40.5	40.7
8	19.2	−18.7	6	15.9	+16.2	4	9.8	+8.9	6	16.8	18.1
9	0	−0.7	7	0	−0.7	5	0	−2.1	8	9.7	9.5
4 0 0	12.0	+13.2	$\overline{10}$ 0 1	2.7	+1.2	6	8.1	+12.8	10	26.2	27.5
1	1.2	+1.2	2	11.3	−17.4	20 0 0	4.9	+3.1	12	18.2	17.8
2	19.2	+21.8	3	5.7	−4.8	1	0	+0.4	14	7.9	6.1
3	0	+2.3	4	22.0	−22.1	2	7.8	−7.3	16	2.3	4.7
4	21.1	+22.4	5	3.5	+2.7	$\overline{20}$ 0 1	0	+0.9	18	4.6	3.7
5	0	−3.8	6	2.9	+0.8	2	8.3	−11.2	1 5 0	5.8	7.4
6	19.8	−20.8	7	2.0	−0.0	3	4.0	+0.9	3	2.8	4.5
7	0	+2.2	8	26.1	−25.3	4	5.2	+8.1	5	9.5	12.8
8	16.8	+16.2	9	0	−0.7	5	0	−0.6	7	1.9	4.1
9	0	−0.4	12 0 0	18.0	+17.9	22 0 0	6.1	−6.2	9	7.3	10.3
$\bar{4}$ 0 1	0	−0.0	1	4.9	+2.3	$\overline{22}$ 0 1	0	−1.2	11	7.5	7.9
2	8.8	+12.1	2	4.6	+2.2	2	7.1	+7.8	13	9.2	11.9
3	0	−1.2	3	0	−2.1	3	0	−0.9	15	4.4	3.5
4	65.5	+67.5	4	1.9	−1.6				17	2.4	2.8
5	2.2	+1.2	5	1.4	+0.8	*h k* 0	$\lvert F_o\rvert/4$	$\lvert F_c\rvert/4$	0 6 0	24.8	24.0
6	15.9	−15.6	6	9.3	−7.5	2 0 0	58.8	59.3	2	17.9	9.8
7	0	−0.6	7	0	−1.4	4	11.3	13.2	4	10.2	11.8
8	26.7	+25.1	$\overline{12}$ 0 1	0	+2.4	6	56.7	56.4	6	20.1	19.6
9	0	−0.2	2	32.3	−29.7	8	46.8	34.5	8	15.2	13.7
6 0 0	56.7	−56.4	3	5.5	−1.5	10	32.4	30.9	10	5.9	8.3
1	0	+1.0	4	24.3	+31.1	12	20.4	17.9	12	6.5	5.0
2	10.8	−13.2	5	0	−0.6	14	18.4	19.0	14	8.3	10.8
3	3.8	−4.4	6	3.3	−6.7	16	8.3	8.8	1 7 0	4.8	9.3
4	13.6	−16.5	7	2.3	+2.1	18	8.7	12.3	3	9.0	8.7
5	0	+2.1	8	5.5	+5.1	20	4.4	3.1	5	4.2	4.8
6	2.9	−0.2	14 0 0	15.7	−19.0	22	4.8	6.2	7	3.2	4.6
7	0	−0.1	1	4.7	−0.2	1 1 0	10.0	5.8	9	3.4	6.3
8	13.5	−13.4	2	21.3	+17.2	3	9.1	3.2	11	5.1	7.1
$\bar{6}$ 0 1	0	+0.3	3	0	−1.0	5	22.1	23.6	0 8 0	17.9	14.3
2	11.8	−13.1	4	3.6	+4.9	7	2.4	3.7	2	13.6	8.6
3	2.6	+2.3	5	0	+1.0	9	16.7	16.4	4	10.9	9.4
4	43.1	−42.3	6	3.7	+4.3	11	11.5	8.6	6	11.1	10.1
5	0	−0.8	$\overline{14}$ 0 1	3.1	−3.0	13	11.4	14.3	8	8.1	5.3
6	2.6	−0.8	2	16.1	+18.4	15	6.2	5.8			
7	1.0	−0.3	3	4.4	+2.8	17	2.6	2.8			


$$\begin{array}{c} CH_2NH_2 \\ H\text{—}C\text{—}NH_2 \\ CH_3 \end{array}$$
(I)

On the basis of the principles of stereochemical analysis developed by Corey and Bailar, it is possible to correlate the absolute configurations of various complex ions, for instance, those of L-[Co en$_3$]$^{3+}$, L-[Co *l*-pn$_3$]$^{3+}$ and *l*-pn. The result of the assignment of the absolute configuration of L-[Co en$_3$]$^{3+}$ based on that of *l*-propylenediamine agrees with the absolute configuration found for L-[Co en$_3$]$^{3+}$ by X-ray analysis[10]. Nevertheless, it was thought worthwhile to check the absolute configuration of the *l*-propylenediamine molecule, since so much stereo-specificity depends upon this chemical assignment of *l*-propylenediamine, and also, this will add support to our previous findings on the absolute configuration of L-[Co en$_3$]$^{3+}$.

The absorption edge of the K electrons of cobalt is 1.608 Å. Since Cu$K\alpha$ radiation (λ= 1.542 Å) has a wavelength a little shorter than the absorption edge of cobalt, it can excite the K electrons, and it was found that $\Delta f' = -2.2$ and $\Delta f'' = 3.9$[11]. Corrections for chlorine atoms due to the anomalous dispersion caused by K-electrons were also taken into account. They were: $\Delta f' = +0.2$ and $\Delta f'' = +0.7$ (calculated from the Table in James' book[12]).

Intensities were calculated for the structure model which corresponds to the *l*-configuration shown by I. In Table III experimental and calculated relations between I_{hkl} and $I_{h\bar{k}l}$ are compared, the latter being equal to $I_{\overline{hkl}}$ by symmetry. Visual estimations of the last column have been made, on a series of oscillation photographs taken around the b-axis, by several people independently. It is seen that the configuration is in agreement with the chemical convention.

TABLE III. DETERMINATION OF THE ABSOLUTE CONFIGURATION

	Calculated		Observed		
h k l	I_{hkl}	$I_{h\bar{k}l}$	I_{hkl}		$I_{h\bar{k}l}$
5 1 1	1240	1550		<	
3 1 3	524	669		<	
7 1 3	309	163		>	
1 1 5	1065	981		>	
11 1 5	361	460		<	
5 1 $\bar{3}$	243	303		<	
15 1 $\bar{1}$	124	81		>	
13 1 $\bar{3}$	913	1054		<	
7 1 $\bar{5}$	470	369		>	
13 1 $\bar{7}$	416	510		<	

Description of the Structure and Discussion

The determined structure seems most easily understood with the aid of the projection upon (010) shwon in Fig. 3. The interatomic distances and bond angles are given in Table IV.

The estimated errors of interatomic distances are; ± 0.01 Å for Co–Cl, ±0.04 Å for O–Cl, N–Cl, and Co–N, and ±0.06 Å for other interatomic distances between lighter atoms.

The structure is essentially ionic and consists of the complexes, [Co *l*-pn$_2$Cl$_2$]$^+$ and [H$_2$O. H. H$_2$O]$^+$ and the Cl$^-$ ion. Figure 5 shows a perspective drawing of the [Co *l*-pn$_2$Cl$_2$]$^+$ ion. Two chlorine atoms are coordinated, at a distance of 2.29 Å, to a cobalt atom in trans positions. A line joining them is approximately perpendicular to the plane in which the four nitrogen atoms of the two propylenediamine molecules were found to lie. Within the range of experimental error, these ligand atoms (4N and 2Cl) form a distorted octahedron around a cobalt atom. The bond length found for Co–Cl agrees with those found in [Co en$_2$Cl$_2$]·Cl.HCl.2H$_2$O[1] and [Co(NH$_3$)$_3$H$_2$OCl$_2$]Cl[13]. However, it is significantly longer than the value of 2.22 Å found in the crystals of anhydrous [Co en$_2$Cl$_2$]Cl[5]*. The chelating molecule assumes a gauche configuration with an azimuthal angle of 55° between the planes determined by the C–C and C–N bonds. The azimuthal angles between the planes determined by the C–C and C–N bonds and that determined by the Co–N and C–N bonds are, on the average, 38°. Consequently, the configuration of the five membered cobalt propylenediamine ring can be assigned as gauche-gauche-gauche with respect to the N–C, C–C and C–N bonds.

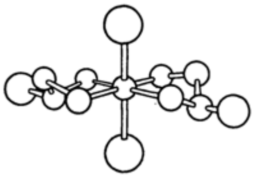


Fig. 5. A perspective drawing of the complex ion [Co *l*-pn$_2$Cl$_2$]$^+$.

The shape and size of this five-membered ring agree well with those of the cobalt-ethylenediamine rings found in [Co en$_2$Cl$_2$]$^+$, and [Co

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[10] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, This Bulletin, 30, 795 (1957).

[11] C. H. Dauben and C. F. Templeton, *Acta Cryst.*, 8, 841 (1955).

[12] R. W. James, "The Optical Principles of the Diffraction of X-Rays", G. Bell and Sons Ltd., London (1958), p. 608.

* This big difference might have some relation to the difference in stability between [Co en$_2$Cl$_2$]Cl.HCl.2H$_2$O and [Co en$_2$Cl$_2$]Cl.

[13] Y. Komiyama, Y. Saito and H. Kuroya, This Bulletin, 25, 328 (1952).

TABLE IV. INTERATOMIC DISTANCES AND BOND ANGLES

Co	Cl(3)	2.29 Å	O(1)	O(1)	2.57 A
	Cl(4)	2.29	O(2)	O(2)	2.57
	N (1)	1.99			
	N (2)	1.97	O(1)	Cl(1)	3.04
	N′(1)	2.02		Cl(2)	3.48
	N′(2)	1.94			
			O(2)	Cl(1)	3.78
N(1)	C(1)	1.46		Cl(2)	3.17
N(2)	C(2)	1.45			
C(1)	C(2)	1.50	C (3)	C (3)	3.76
C(2)	C(3)	1.51	C′(3)	C′(3)	3.77
N′(1)	C′(1)	1.49	∠CoN(1)C(1)		107.4°
N′(2)	C′(2)	1.46	∠N(1)C(1)C(2)		108.3°
C′(1)	C′(2)	1.45	∠C(1)C(2)N(2)		113.4°
C′(2)	C′(3)	1.53	∠C(2)N(2)Co		106.5°
			∠C(1)C(2)C(3)		111.0°
N (2)	Cl(1)	3.40	∠N(2)C(2)C(3)		112.3°
	Cl(2)	3.54	∠N(1)CoN(2)		87.9°
N′(2)	Cl(1)	3.37			
	Cl(2)	3.10	∠CoN′(1)C′(1)		103.1°
			∠N′(1)C′(1)C′(2)		104.3°
N (1)	Cl(3)	3.31	∠C′(1)C′(2)N′(2)		111.5°
N′(1)	Cl(4)	3.19	∠C′(2)N′(2)Co		101.5°
			∠C′(1)C′(2)C′(3)		111.7°
C (3)	O(1)	3.53	∠N′(2)C′(2)C′(3)		113.1°
C′(3)	O(2)	3.49	∠N′(1)CoN′(2)		88.8°

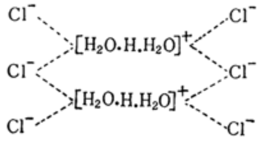
en$_3$]$^{3+}$. The same type of puckered rings is also found in other metal-ethylenediamine complexes, such as [Cr en$_2$Cl$_2$]$^{+}$ 14), [Ni en$_3$]$^{2+}$ 15) and [Cu en$_2$]$^{2+}$ 16).

The presence of a substituted methyl group on the carbon of the ethylenediamine molecule does not disturb the essential features of the five-membered ring.

The complex ion possesses approximate two-fold symmetry around the Cl–Co–Cl bond. Therefore, this complex ion assumes the *kk* form; that is, the two cobalt propylenediamine rings take the same configuration. The complex ions [Co en$_2$Cl$_2$]$^{+}$ and [Co *dl*-pn$_2$Cl$_2$]$^{+}$ 17), however, are found to take the *kk′* configuration; namely, two kinds of ligand molecules, the one being the mirror image of the other, are coordinated to the central atom in such a way that one is related by the operation of a center of symmetry to the other. According to Corey and Bailar, the *kk* form is intrinsically more stable than the *kk′* form. The reason why the *kk′* form often occurs in crystals of various complex compounds may be that the *kk′* form is favored by specific intermolecular forces in the solid state.

Since the five-membered ring is puckered, there are two possibilities of the orientation of the C–CH$_3$ group, namely, axial and equatorial types with respect to the Cl–Co–Cl bond. It was found that the bond is equatorial in the complex ion [Co *l*-pn$_2$Cl$_2$]$^{+}$, in agreement with the conclusion of Corey and Bailar that the equatorial orientation is of a lower energy than the axial one.

Since the structure is closely related to that of the en-analogue, a similar consideration of the arrangement of chlorine ions around the two water molecules leads us to locate a proton midway between the water molecules. The O–O distances were found to be 2.57 Å. A molecule of H$_2$O possesses two Cl$^-$ ions as the nearest neighbor anions, the Cl$^-$···O distance being shown in Table II. Thus, every [H$_2$O.H.H$_2$O]$^{+}$ group is surrounded by four Cl$^-$ ions. The complexes [H$_2$O.H.H$_2$O]$^{+}$ form a chain of the composition:



this chain runs parallel to the c-axis.

Such complexes have been found in crystals of Co-en analogues1,2) and in a Cr-en analogue14)

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14) S. Ooi, Y. Komiyama and H. Kuroya, ibid., 33, 354 (1960).

15) L. N. Swink and M. Atoji, *Acta Cryst.*, 13, 639 (1960).

16) Private communication from Dr. Y. Komiyama.

17) Y. Komiyama and Y. Saito, to be published.

with an average O–O distance of 2.60 Å. The existence of the complex $[H_2O.H.H_2O]^+$ was suggested by Huggins[18] and was indeed verified by our investigations of these coordination compounds.

As in the case of the en-analogues, the complex ions form a layer parallel to the plane (100). The Cl–Co–Cl bond is inclined to the plane (010) at an angle of 5°, and the projection of this direction upon (010) makes an angle of 9.5°C with the c-axis.

In the case of the en-analogues, these angles are 14.5° and 10°. The closest distance of approach between the complex ions in the layer was found to be about 3.19 Å, between the coordinated Cl atom of one complex ion and the N atom of the adjacent. Thus, the complex ions are held together in layers by these Cl···N bonds. One complex $[Co\ l\text{-}pn_2Cl_2]^+$ ion has four nearest Cl^- ions. The closest approach of a complex ion and Cl^- ion is between N′(2) and Cl(2), the Cl···N distance being 3.10 Å. Other $Cl^-\cdots N$ distances are 3.37, 3.40 and 3.54 Å. These values may be compared with those found in crystals of the en-analogues.

Between the layers of the complex $[Co\ l\text{-}pn_2Cl_2]^+$ ions are arranged the complexes $[H_2O\cdot H\cdot H_2O]^+$ and Cl^- ions. These general features of the structure are quite similar to those of the ethylenediamine analogues. This fact can be more easily seen if an alternative a-axis is taken along one of the face diagonals. Then the propylenediamine ligands lie approximately on the new (001) plane. This new unit cell is very similar to that of the en-analogues in projection. However, the packing of the chlorine ions and water molecules is different from those in the en-analogues because of the methyl groups attached to the cobalt ethylenediamine ring. Thus, there is a twofold axis of rotation midway between the water molecules instead of a center of symmetry. This situation leads to a doubling of the a-spacing in the case of the present propylenediamine analogue.

Thin tabular crystals extended on (010) appear blue when the electric vector is parallel to the c-axis, while they appear yellowish green when the light is polarized along the b-axis. Such a striking dichroism may be reasonable, since there is a large component of the Cl–Co–Cl bond along the c-axis. This dichroism is quite similar to that of the en-analogues. The dichroism of the latter crystals have been extensively measured by Yamada et al.[19]

The absolute configuration of the *l*-propylenediamine molecule is found to be given by I and to agree with the chemical convention. The absolute configuration of $[Co\ l\text{-}pn_2Cl_2]^+$ corresponds to the drawing given in Fig. 5. Accordingly, on the basis of the principles of Corey and Bailar, the absolute configuration of the complex ion $[Co\ en_3]^{3+}$ can be shown to agree with our previous results, directly obtained by X-ray techniques.

In conclusion, the stereochemical principles and the method for correlation of absolute configuration developed by Bailar et al. have been proved to be reliable and useful.

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[18] M. L. Huggins, *J. Phys. Chem.*, **40**, 723 (1936).

[19] S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, This Bulletin, **28**, 222 (1955).