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The Crystal Structure of Tris(l-propylenediamine)cobalt(III) Bromide and the Absolute Configuration of the Complex Ion, [Co l-pn$_3$]$^{3+}$ [*1]

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Crystals of L-[Co l-pn$_3$]Br$_3$ (pn: propylenediamine) were prepared and their crystal structure was completely determined by means of X-rays. They are hexagonal, with the space group $P6_3$; $a=11.08\pm0.03$, $c=8.59\pm0.02$ Å and $Z=2$. The structure is essentially ionic, consisting of complex ions and bromide anions. A complex ion has a three-fold axis of symmetry through the central cobalt atom. Five-membered Co-pn rings are puckered, and the C–C bonds in these rings are nearly parallel to the threefold axis. The methyl carbon bonds are equatorial with respect to the plane of the ring. The absolute configuration of the complex ion has been determined by using the absorption-edge technique. The L*lll*-type complex ion has been found to be laevorotatory with respect to the NaD lines. By the introduction of an asymmetric carbon atom into the ligands, the absolute configuration of a series of tris(bidentate)-complexes could be successfully correlated to the configurational series in organic compounds.

In the study of the optical properties of complex compounds, tris(bidentate)-metal complexes are most frequently taken up since they have relatively simple structures and exhibit typical optical isomerism. When three bidentate ligands are coordinated to the central atom in an octahedral fashion, it is possible for two optically active isomers, D and L, to occur (Fig. 1). Niekerk et al. have shown that a [Cr ox$_3$]$^{3-}$ ion (ox=oxalate ion) essentially possesses the structure shown in Fig. 1.1) When the chelating molecules are not planar, another kind of isomer appears. For example, when ethylenediamine molecules (usually denoted as "en") are chelated to a metal atom, they assume the "gauche" configuration, and the five-membered ring, consisting of metal and an ethylenediamine molecule, is puckered. If we denote the two possible and enantiomorphous conformations of ethylenediamine as d and l[*2] (Fig. 2), there will be eight isomers of the [M en$_3$], such as D*ddd*, L*ddl*, etc.3) Kuroya et al. found that the most stable form of the [Co en$_3$]$^{3+}$ ion has a three-fold symmetry and takes either the D*ddd* or the L*lll* form,[*3], 3-5) forms which correspond to the "lel" type according to Corey and Bailar's notation.2) The determination of the absolute configuration proved that the D-type complex is dextrorotatory with respect to the NaD lines.4)

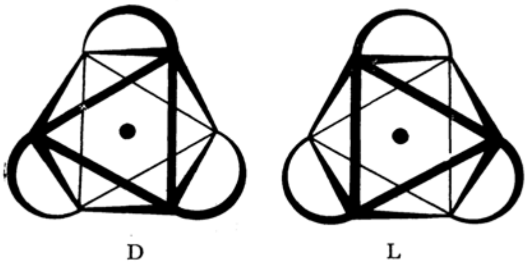

Fig. 1. Two possible configurations of a tris-(bidentate)-complex ion.

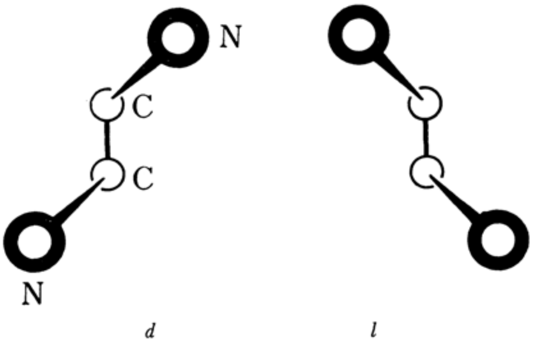

Fig. 2. Two possible gauche forms of an ethylenediamine molecule.

Now it is widely recognized that the optical rotatory dispersion (ORD) curve is diagnostic of the absolute configuration. In attempting to

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[*1] Part of this paper is taken from the Doctoral Thesis presented to the University of Tokyo by Hitoshi Iwasaki, 1965. Short Communication, This Bulletin, **36**, 1543 (1963).

[*2] Corey and Bailar2) called these two forms k and k'.

1) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **5**, 196, 475, 499 (1952).

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

3) K. Nakatsu, This Bulletin, **35**, 832 (1962).

[*3] The notations refer to Figs. 1 and 2.

4) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Cryst.*, **8**, 729 (1955); This Bulletin, **30**, 158, 795 (1957).

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

verify this convention of correlating the configurations of various complex ions, the tris(*l*-propylenediamine)cobalt(III) ion, [Co *l*-pn$_3$]$^{3+}$, has been chosen and its absolute configuration determined by means of X-rays; the ORD curve of this ion bears a close resemblance to that of [Co en$_3$]$^{3+}$, whose absolute configuration had already been established. Moreover, by the introduction of the methyl groups in the ethylenediamine ring in [Co en$_3$]$^{3+}$ ion, the ligands themselves are optically activated, actually being the *l*-forms in the present case. The absolute configuration of the *l*-pn has been chemically correlated to that of D-alanine.[6,7] Accordingly, we may expect to find a correlation between the configurational series in organic chemistry and that of the complex compounds.

Experimental

Commercial racemic propylenediamine was resolved with *d*-tartaric acid according to the method described by O'Brien and Toole.[8] 5.5 g. of the *l*-pn was heated with 5.0 g. of chloropurpureo-salt, [CoCl(NH$_3$)$_5$]Cl$_2$. The reaction mixture was then dissolved in a small amount of water. When concentrated hydrobromic acid was added to the solution, crystals of the bromide of the aimed complex were precipitated. By recrystallization from an aqueous solution, single crystals of suitable sizes for X-ray works were obtained.

The crystals are reported to have two moles of water of crystallization.[9] However, no weight loss was observed after the specimen had been kept in an air bath at 123°C for 80 min. The results of the chemical analysis*4 also showed that the specimen was anhydrous. (Found: N, 16.18%; calcd. for [Co *l*-pn$_3$]Br$_3$: N, 16.15%; calcd. for [Co *l*-pn$_3$]Br$_3$·2H$_2$O: N, 14.61%). This was supported by the present X-ray structure analysis.

The crystals are deep orange-red in color and transparent. They are hexagonal prismatic, and stable in air at room temperature. An X-ray examination showed the prismatic axis of the crystal to be coincident with the *c*-axis of the hexagonal system, and the well-developed prismatic faces are indexed as $\{11\bar{2}0\}$. Since the crystals contain only the *l*-isomer of the propylenediamine, they are optically active. In fact, the crystal was found to be laevorotatory with respect to the NaD lines under a polarizing microscope.

Oscillation photographs were taken around the *c*-axis. When one uses the Cu$K\alpha$ radiation ($\lambda=1.542$ Å), the intensity distribution on the films was approximately of a mirror symmetry with respect to the equatorial line; i. e.,

$$I(hkl) \fallingdotseq I(hk\bar{l})$$

Detailed examination, however, revealed that this was not exactly true for many weak reflections, though the deviation from the strict mirror symmetry was generally quite small. The photographs taken with the Fe$K\alpha$ radiation ($\lambda=1.937$ Å), for which the effect of the anomalous scattering is expected to be smaller than in the case of Cu$K\alpha$, had a nearly perfect mirror symmetry with respect to the equatorial line. Therefore, it may safely be concluded that the deviation from the symmetry is attributable to the anomalous dispersion occurring in the acentric crystals. The equatorial and upper-level Weissenberg photographs showed the existence of a sixfold symmetry in each reciprocal plane perpendicular to the *c*-axis. Thus the Laue symmetry group to which the intensity distribution from this crystal belongs is 6 (C_6). The space group was uniquely determined from the systematic absences to be No. 173, $P6_3$ (C_6^6).

The lattice constants were determined from the Weissenberg photographs of crystals rotating about tha *a* and *c* axes. The following values were obtained:

$$a=11.08\pm0.03, \qquad c=8.59\pm0.02 \text{ Å}$$

A unit cell contains two formula units of [Co *l*-pn$_3$]Br$_3$ (Density: observed 1.91 g. cm^{-3}, calcd. 1.90 g. cm^{-3}).

The specimen used for the collection of the final intensity data was polished by emery paper into a cylindrical form with a diameter of 0.012 cm. Equi-inclination Weissenberg photographs were taken around the *c*-axis up to the seventh layer with the filtered Cu$K\alpha$ radiation. The 0*kl* reflections were also collected by the *a*-axis rotation. Intensities were estimated visually with a standard film strip. 541 independent reflections were observed. The usual Lorentz, polarization, spot-shape and absorption corrections were then applied. For the *a*-axis data it was found that the standard deviations of the intensities among the equivalent reflections were larger than those for the *c*-axis data, probably due to the irregular shape of the specimen. Therefore, these data were not used for the final refinement.

The Determination of the Crystal Structure

Since a unit cell contains only two cobalt atoms, they must be located at one of the two kinds of two-fold special positions: 2*a* and 2*b*. However, the former was decidedly ruled out on the basis of the packing consideration. The *z*-parameter of the cobalt atom was chosen to be zero without any loss of generality.

Thus the cobalt atoms are located on the threefold axis. Consequently, the complex ion [Co *l*-pn$_3$]$^{3+}$ must possess the symmetry 3 (C_3). The positions of the bromine atoms were easily deduced from the Patterson functions projected along the *a*- and *c*-axes. By making use of the results of the structure analyses of the related complex compounds,[3,10] a structural model of the complex ion [Co *l*-pn$_3$]$^{3+}$ could be easily set up. The positions of the cobalt and bromine atoms being already fixed, only the azimuthal orientation of the complex ion around the threefold axis was left to be determined. After several trials, an optimum

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*4 The authors are indebted to Dr. Shohei Tamura for the chemical analysis of the sample.

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

[7] S. Schnell and P. Karrer, *Helv. Chim. Acta*, **38**, 2036 (1955).

[8] T. D. O'Brien and R. C. Toole, *J. Am. Chem. Soc.*, **76**, 6009 (1954).

[9] A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[10] Y. Saito and H. Iwasaki, This Bulletin, **35**, 1131 (1962).

condition was obtained in which the discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, became 0.26, where the summation was taken over all the observed *hk*0 data. Starting with this plausible position, the usual difference Fourier method was repeatedly applied to the (001) projection until the structure projected on this plane was completely established. An *a*-axis projection was also worked out at the same time. Using the results of the *c*-axis projection, together with the structural model quoted above, the *R*-factor for the 0*kl* reflections was only 0.25 for the first trial of the *z*-parametres, where the position of the bromine atoms was chosen so that it gave the N–Br contact of about 3.5 Å. Thus, these parameters were thought to be reasonable and essentially correct.

By the several Fourier refinements described below, the *R* factors were reduced to 0.12 for *hk*0 and 0.16 for 0*kl*. The final refinement was performed on the full-matrix least-squares program, ORFLS, originally written by Busing, Martin and Levy, and slightly modified by Nakatsu and Sakurai to take the effect of the anomalous scattering into account. Anisotropic temperature factors were not used since the three-dimensional electron density map and the difference Fourier map did not indicate the existence of any large anisotropic thermal motions of the atoms. After three cycles of this refinement, the *R* value dropped and converged to 0.100. All the reflections were given the weight of 1. The extinction effect was corrected for the strongest 17 reflections. Atomic scattering curves were taken from the International Tables.[11]

In the calculations of the structure factors, the effect of the anomalous dispersion was strictly considered. The correction factors for the *f*-values were assumed as follows:[12]

$$\text{for Co,}\quad \Delta f'=-2.2,\quad \Delta f''=3.9$$

and

$$\text{for Br,}\quad \Delta f'=-0.9,\quad \Delta f''=1.5$$

In the final refinement alone was the angular dependence of these quantities[13] also taken into account.

In the calculations of the Fourier syntheses, the contributions from the anomalous scattering to the structure factors were directly subtracted from F_{obs}, whose phases were given those of F_c. The remainder was used as the Fourier coefficients; i. e.,

$$F(\text{coef.})=|F_o|\exp(i\alpha)-F_c''$$

Here α is the calculated phase factor, and F_c'' is the contribution of the correction terms of the atomic scattering factors to the structure factor. F_c'' contains only the contribution from the cobalt and bromine atoms whose positional parameters are easily fixed. At each step of the refinement, this quantity may take a different value, which is in line with the improvement of the temperature factors and also with a slight change in the position of the bromine atoms. Moreover, the scale factor of F_o may be slightly changed at each step. Therefore, these Fourier coefficients had to be re-calculated at each step of the Fourier refinement. This was made possible by successive approximation. Though such a procedure seems to be rather complicated, it takes the effect of the anomalous dispersion strictly into account, and probably it is one of the best ways to solve the problem when the correction of the anomalous scattering is necessary. A computer program was written for the entire course of calculating both the structure factors and the electron densities. The shifts of the atomic parameters were read from a Fourier map, and the results were used as the next input data for the calculation of the structure factors and electron densities.

In order to obtain the Fourier coefficients by such a procedure, it is necessary to fix the absolute sign of the *z*-parameters so as to calculate F_c''. Thus, the absolute structure of the crystal had also to be determined during the course of the Fourier refinement.

On oscillation photographs taken around the *c*-axis, the diffraction spots corresponding to *hkl* and $hk\bar{l}$, the latter being equivalent to $\overline{hkl}$ due to the symmetry of the space group, are recorded at the symmetrical positions on each side of the equatorial line. These two spots are not equal in intensity as a result of the breakdown of Friedel's law. If the proper indices are given to these spots, including the correct sign of *l*, inequality

TABLE I. DETERMINATION OF THE ABSOLUTE CONFIGURATION

			Observed	Calculated
h	*k*	*l*	$\sqrt{I(hkl)/I(hk\bar{l})}$	$\lvert F(hkl)\rvert/\lvert F(hk\bar{l})\rvert$
8	1	1	0.77	0.88
9	1	1	0.72	0.86
10	1	1	0.71	0.83
8	2	1	0.91	0.88
9	2	1	0.75	0.84
1	3	1	1.31	1.50
3	4	1	0.91	0.78
4	4	1	1.10	1.07
1	5	1	1.21	1.70
3	5	1	0.60	0.43
5	5	1	1.39	1.10
1	6	1	0.73	0.59
4	6	1	0.82	0.75
6	7	1	0.80	0.88
1	9	1	0.54	0.61
2	9	1	0.86	0.75

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[11] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 164.

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

[13] Reference 10, Vol. III, p. 214.

TABLE II. ATOMIC PARAMETERS

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B (Å^2)
Co	0.6667	—	0.3333	—	0	—	1.912
Br	0.4526	0.0002	0.1189	0.0002	0.5103	0.0008	4.048
N(1)	0.4954	0.0014	0.2692	0.0014	−0.1295	0.0022	2.358
N(2)	0.5504	0.0014	0.1696	0.0014	0.1373	0.0021	2.768
C(1)	0.3863	0.0028	0.1243	0.0026	−0.0821	0.0037	4.194
C(2)	0.4011	0.0024	0.1182	0.0022	0.0998	0.0032	2.689
C(3)	0.2408	0.0018	0.0781	0.0018	−0.1389	0.0025	4.038

relations between $I\,(khl)$ and $I\,(hk\bar{l})$ will be established. The sense of the c^* direction could be easily determined with the help of a Weissenberg photograph. The differences between $I\,(hkl)$ and $I\,(hk\bar{l})$ were observed by several people independently at first, and later the intensities were estimated visually by the authors. Under the present conditions, the Lorentz, polarization and absorption factors take the same value for *hkl* and $hk\bar{l}$ reflections. Hence, the $\sqrt{I\,(hkl)/I\,(hk\bar{l})}$ ratio is equal to the ratio of the two structure factors, i. e., $|F\,(hkl)|/|F\,(hk\bar{l})|$. Some of the observed ratios, together with the calculated ratios, are listed in Table I. The latter are based on the parameters listed in Table II. Considering the general agreement in Table I, it may be concluded that these atomic parameters correspond to the absolute structure of the (—)-[Co *l*-pn$_3$]Br$_3$ crystal. A complex ion based on these parameters is illustrated in Fig. 3. Therefore, the complex ion shown in this figure must correspond to the (—)-[Co *l*-pn$_3$]$^{3+}$ ion.

The trial model with the reversed z-parameters was checked several times during the course of the Fourier refinement in order to justify the assumption of the absolute configuration of the complex ion. The calculations of the structure factor ratios were repeated at each cycle in these refinements. After the final refinement, the R values for all the *hkl* reflections became 0.100. If one takes a set of parameters in which the signs of the z-parameters of all the atoms are reversed, the R value becomes 0.123. Though the difference is small in terms of the values of the R-factors, a detailed examination of individual reflections clearly excludes the possibility of the reversal of the z-parameters.

The final set of the atomic parameters, together

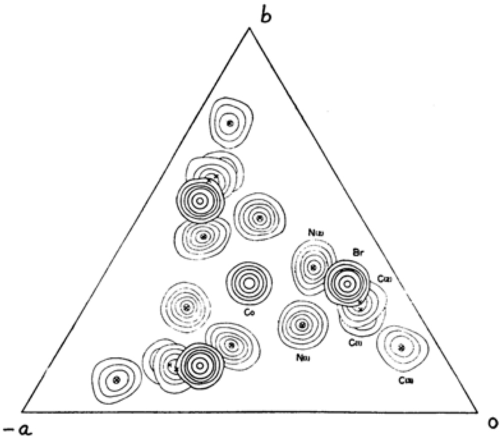

Fig. 4. Composite three dimensional Fourier diagram. Contours around the cobalt and bromine atoms are drawn at intervals of 10 e. Å^{-3}, and those for the light atoms, 2 e. Å^{-3}.

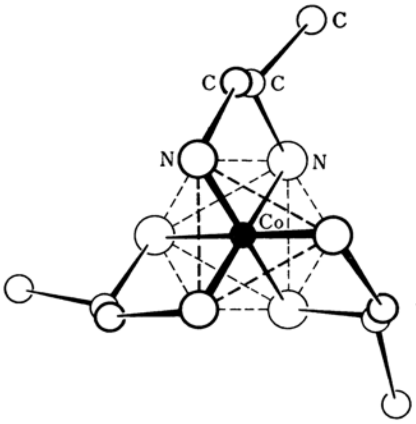

Fig. 3. The absolute configuration of a (—)-[Co *l*-pn$_3$]$^{3+}$ ion.

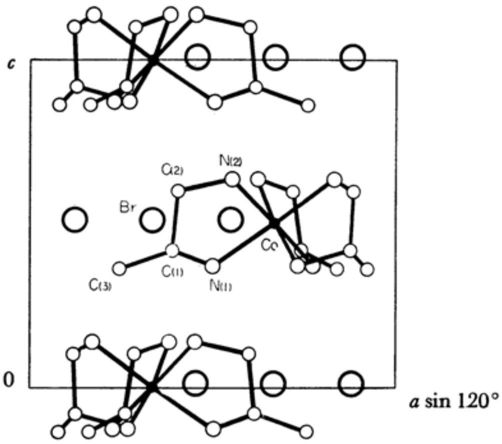

Fig. 5. Atomic arrangement projected along the a-axis.

TABLE III. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
$l=0$				3	6	24.6	20.6	5	3	45.5	47.9	6	1	42.1	41.1
1	0	83.3*	87.6	4	6	33.3	28.7	6	3	17.5	10.1	7	1	6.8	3.7
2	0	26.2	24.6	6	6	4.8	4.4	7	3	34.0	38.9	8	1	12.2	9.9
3	0	10.3	6.9	7	6	9.8	11.0	9	3	5.5	6.5	9	1	14.5	17.9
4	0	65.5	66.4	2	7	19.3	18.0	1	4	37.5	28.3	10	1	15.0	14.9
5	0	66.3	67.8	3	7	26.5	25.9	2	4	68.2	66.4	11	1	10.7	12.2
6	0	29.1	30.5	4	7	8.2	8.5	3	4	20.8	18.0	1	2	80.2*	81.3
7	0	9.0	5.0	5	7	8.7	7.6	4	4	17.9	20.9	2	2	20.2	21.8
8	0	11.1	3.7	6	7	12.3	12.2	5	4	26.9	26.8	3	2	44.1	36.2
9	0	45.1	48.5	1	8	24.3	20.5	7	4	27.4	26.2	4	2	38.9	36.1
10	0	17.0	17.9	2	8	12.3	8.8	8	4	17.1	17.4	5	2	10.8	9.0
11	0	4.1	3.0	3	8	19.3	21.2	1	5	13.3	7.2	6	2	47.9	49.6
1	1	16.0	14.5	5	8	13.4	15.3	2	5	19.2	19.0	7	2	11.9	13.3
2	1	178.9*	171.3	1	9	23.5	21.9	3	5	16.7	11.7	8	2	6.6	7.5
3	1	39.9	43.0	2	9	12.7	6.3	4	5	24.7	23.8	9	2	14.0	11.2
4	1	97.1*	100.5	4	9	9.3	13.8	5	5	7.2	9.5	10	2	12.0	12.6
5	1	14.2	15.8	1	10	6.5	12.7	7	5	25.0	22.2	1	3	50.0	44.5
6	1	57.0	57.8	2	10	8.0	5.9	1	6	16.1	13.0	2	3	26.9	24.4
7	1	5.4	4.7	3	10	12.2	16.1	2	6	69.0	69.6	3	3	30.9	31.6
8	1	19.8	15.5	1	11	12.5	15.3	3	6	18.4	17.1	4	3	32.6	32.9
9	1	13.1	12.7					4	6	12.4	8.9	5	3	29.5	23.8
10	1	14.3	13.6	$l=-1$				5	6	6.8	11.1	6	3	20.5	17.6
11	1	11.6	12.5	1	0	26.5	13.6	6	6	23.9	25.5	7	3	15.7	17.0
1	2	100.1*	105.4	2	0	41.5	45.6	1	7	40.7	41.4	8	3	23.1	25.3
2	2	39.1	38.0	3	0	15.3	14.5	2	7	21.6	26.9	9	3	9.7	4.5
3	2	27.6	24.9	4	0	52.5	55.9	3	7	7.1	12.3	1	4	101.5*	101.8
4	2	47.9	50.1	5	0	64.1	65.6	4	7	20.5	18.6	2	4	40.6	42.5
5	2	33.5	29.8	6	0	14.8	13.3	5	7	13.7	13.0	3	4	40.9	38.4
6	2	34.1	36.8	7	0	40.5	38.2	6	7	18.3	22.4	4	4	39.8	42.3
7	2	12.4	15.3	10	0	16.6	14.9	2	8	21.2	18.5	5	4	28.2	31.0
9	2	12.7	8.1	11	0	13.5	11.6	3	8	33.4	38.6	6	4	12.1	7.6
10	2	13.3	12.6	1	1	56.3*	59.9	5	8	4.7	5.4	7	4	13.8	9.9
1	3	7.7	7.3	2	1	32.7	29.7	1	9	9.7	11.6	8	4	13.4	13.4
2	3	30.2	26.3	3	1	27.4	23.9	2	9	12.6	15.0	9	4	7.5	7.5
3	3	18.8	20.7	4	1	13.0	10.4	1	10	5.9	12.0	1	5	28.8	33.2
4	3	42.6	45.6	5	1	10.3	9.5	2	10	10.1	12.6	2	5	14.8	10.8
5	3	47.4	43.9	6	1	68.6	70.4	3	10	10.7	15.3	3	5	6.6	5.0
6	3	35.4	34.6	7	1	45.8	49.8	1	11	18.0	24.2	4	5	28.7	30.7
7	3	7.8	7.4	8	1	12.5	13.2					5	5	43.2	49.9
8	3	24.7	27.4	9	1	13.7	9.9	$l=-2$				6	5	11.4	10.0
1	4	95.2*	99.3	10	1	11.8	10.1	1	0	65.2*	64.0	7	5	6.0	8.0
2	4	31.1	35.5	11	1	8.7	8.3	2	0	29.5	26.6	8	5	9.5	15.4
3	4	28.5	28.1	1	2	158.9*	151.8	3	0	30.1	27.0	1	6	41.3	42.2
4	4	49.8	55.1	2	2	70.4	68.8	4	0	70.6	70.1	2	6	43.6	43.8
5	4	40.7	43.8	3	2	45.7	47.0	5	0	64.7	63.7	3	6	24.3	22.9
6	4	11.1	7.2	4	2	23.9	25.7	6	0	33.7	35.7	4	6	27.0	22.9
7	4	5.3	4.7	5	2	28.3	26.8	7	0	14.8	14.1	5	6	11.4	12.5
9	4	6.9	7.0	6	2	36.2	37.0	8	0	11.9	11.2	7	6	10.9	12.5
1	5	29.7	34.1	7	2	36.0	39.0	9	0	46.8	51.7	1	7	9.6	5.7
2	5	31.1	21.0	8	2	23.4	22.0	10	0	14.4	16.2	2	7	15.3	16.7
3	5	10.4	6.9	9	2	19.0	20.0	11	0	7.6	6.5	3	7	21.7	19.1
4	5	26.6	27.2	10	2	16.3	22.4	1	1	13.1	8.6	4	7	0.0	3.1
5	5	42.2	48.5	1	3	26.0	16.2	2	1	122.9*	122.6	5	7	10.7	10.0
8	5	10.0	14.2	2	3	39.6	38.9	3	1	55.5	54.8	6	7	12.6	13.2
1	6	47.1	48.5	3	3	80.7	89.0	4	1	88.1	87.6	1	8	26.5	22.4
2	6	39.4	39.7	4	3	74.5	81.3	5	1	16.9	14.0	2	8	9.8	8.5

Table III. (Continued)

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
3	8	18.1	19.8	4	4	7.1	8.6	7	2	11.7	9.5	3	1	35.4	35.1
5	8	11.2	13.6	5	4	27.9	25.8	8	2	10.6	10.2	4	1	18.8	16.1
1	9	22.1	20.0	7	4	13.9	14.2	9	2	11.7	9.3	5	1	16.2	10.1
2	9	11.4	8.1	8	4	16.2	17.9	10	2	6.3	8.0	6	1	41.6	42.1
3	9	5.5	5.6	1	5	17.7	17.7	1	3	17.9	13.0	7	1	22.4	22.7
4	9	6.2	11.0	2	5	19.1	19.3	2	3	20.6	19.2	8	1	10.2	7.8
1	10	10.5	12.7	3	5	17.3	15.0	3	3	24.7	21.9	9	1	13.3	9.4
2	10	11.5	11.1	4	5	28.3	27.9	4	3	24.6	21.2	10	1	7.1	7.9
3	10	7.5	9.8	6	5	9.5	8.1	5	3	14.1	6.0	1	2	82.3*	91.0
1	11	8.8	12.4	7	5	19.9	22.2	6	3	6.6	5.6	2	2	47.1	49.0
				8	5	4.2	4.7	7	3	23.2	23.6	3	2	46.9	49.5
$l=-3$				1	6	20.3	18.9	8	3	25.4	21.9	4	2	8.2	9.3
1	0	78.6*	63.3	2	6	59.3	65.9	9	3	7.5	6.3	5	2	19.1	14.9
2	0	71.8*	67.4	3	6	10.2	10.7	1	4	71.4	75.9	7	2	24.0	24.3
3	0	12.4	11.7	5	6	11.5	16.9	2	4	37.7	37.6	8	2	15.2	12.1
4	0	41.4	40.9	6	6	17.1	19.5	3	4	39.4	39.7	9	2	9.6	11.6
5	0	51.8	51.8	7	6	6.5	7.7	4	4	28.4	28.3	1	3	24.3	25.0
6	0	6.6	1.8	1	7	36.2	38.9	5	4	15.5	16.2	2	3	20.5	18.0
7	0	30.0	32.4	2	7	20.8	23.7	6	4	9.3	6.1	3	3	50.7	53.3
8	0	7.2	8.6	3	7	12.4	14.2	8	4	12.8	12.2	4	3	34.0	36.7
9	0	6.9	0.7	4	7	21.2	20.1	1	5	31.0	31.9	6	3	13.6	9.2
10	0	11.6	9.5	5	7	10.5	12.1	2	5	12.4	12.1	7	3	23.4	23.8
11	0	7.3	9.5	6	7	11.2	19.7	4	5	27.6	30.4	8	3	10.6	12.9
1	1	84.3*	78.2	2	8	13.5	16.0	5	5	41.6	45.2	1	4	16.9	17.5
2	1	39.3	34.6	3	8	28.3	35.0	7	5	4.5	6.0	2	4	37.5	36.9
3	1	50.2	49.1	5	8	6.2	2.3	1	6	34.0	34.3	3	4	22.8	22.1
4	1	10.0	8.2	2	9	6.3	8.6	2	6	33.5	34.2	4	4	9.0	8.9
5	1	23.5	17.9	1	11	10.3	17.1	3	6	16.3	17.0	5	4	22.3	19.5
6	1	57.1	54.7					4	6	19.2	14.9	7	4	7.0	7.6
7	1	30.9	29.7	$l=-4$				5	6	13.0	14.5	8	4	11.5	14.4
8	1	6.3	7.7	1	0	36.1	34.5	1	7	6.7	5.9	1	5	14.4	13.9
9	1	13.5	9.7	2	0	15.9	12.8	2	7	13.1	10.6	2	5	19.4	19.9
10	1	10.2	9.4	3	0	35.9	34.5	3	7	6.2	12.5	3	5	11.1	8.1
11	1	3.7	9.4	4	0	49.7	49.4	4	7	8.8	5.9	4	5	21.3	18.1
1	2	126.5*	119.2	5	0	48.4	47.0	1	8	19.6	17.3	5	5	5.8	5.3
2	2	68.7	70.4	6	0	35.1	37.7	2	8	8.8	5.9	6	5	7.2	8.4
3	2	57.0	57.6	8	0	15.4	17.2	3	8	17.6	18.3	7	5	12.7	14.2
4	2	11.8	9.8	9	0	38.7	47.3	4	8	6.9	7.6	1	6	18.9	16.7
5	2	24.6	19.9	10	0	12.8	14.6	1	9	18.0	14.8	2	6	40.7	45.4
6	2	10.1	6.8	11	0	3.9	3.7	2	9	7.9	4.7	3	6	10.6	7.4
7	2	30.1	31.0	1	1	18.6	14.0	3	9	7.5	6.2	4	6	7.8	9.2
8	2	17.3	15.4	2	1	55.6	59.3	1	10	7.0	10.0	5	6	10.2	11.4
9	2	15.1	19.4	3	1	46.0	51.7	2	10	9.7	12.6	6	6	13.0	16.5
10	2	13.4	21.4	4	1	67.1	70.9					1	7	28.9	27.4
1	3	17.3	15.5	5	1	15.3	13.5	$l=-5$				2	7	6.2	10.8
2	3	39.5	39.2	6	1	25.5	23.3	1	0	41.7	38.3	3	7	10.2	11.6
3	3	71.8	73.7	7	1	13.4	10.7	2	0	53.0	54.4	4	7	12.9	11.4
4	3	49.0	49.2	8	1	9.5	4.1	3	0	11.7	8.6	5	7	8.4	10.1
5	3	10.0	7.1	9	1	13.5	13.6	4	0	35.5	33.8	1	8	5.9	9.0
6	3	13.7	11.9	10	1	11.0	11.9	5	0	38.9	38.1	2	8	14.4	14.0
7	3	27.5	31.0	1	2	53.0	52.6	6	0	14.9	8.6	3	8	22.9	26.3
8	3	11.9	13.4	2	2	16.4	14.7	7	0	27.9	26.9	4	8	6.0	8.1
9	3	4.8	5.2	3	2	29.0	28.3	8	0	10.5	7.5	2	9	7.4	7.2
1	4	23.2	21.2	4	2	25.1	20.6	10	0	8.9	8.3				
2	4	51.6	50.2	5	2	23.0	26.3	1	1	57.2*	59.2	$l=-6$			
3	4	18.4	19.3	6	2	49.8	50.8	2	1	28.5	24.5	1	0	30.0	28.5

Table III. (Continued)

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
2	0	7.3	1.2	2	3	23.5	21.3	2	8	7.8	6.0	7	2	16.7	17.8
3	0	16.1	15.1	3	3	12.4	8.7	3	8	13.3	15.8	8	2	9.9	9.4
4	0	28.9	28.1	4	3	21.9	21.1	1	9	11.8	9.0	1	3	17.4	17.9
5	0	31.7	30.6	5	3	14.4	12.2					2	3	6.4	8.0
6	0	25.5	26.1	6	3	13.8	11.9	$l=-7$				3	3	32.7	34.3
7	0	8.0	4.6	7	3	15.0	13.8	1	0	15.0	13.5	4	3	30.0	32.7
8	0	13.7	12.1	8	3	14.1	17.0	2	0	28.8	29.9	5	3	14.5	17.8
9	0	26.1	29.8	1	4	36.7	36.4	3	0	10.3	5.4	6	3	10.0	4.8
10	0	8.3	12.3	2	4	25.7	27.2	4	0	27.0	27.6	7	3	15.2	17.3
1	1	19.7	18.8	3	4	24.9	24.4	5	0	27.4	26.9	1	4	6.5	3.9
2	1	35.8	37.4	4	4	24.0	26.0	6	0	9.4	4.7	2	4	24.3	24.8
3	1	29.6	30.3	5	4	14.9	15.5	7	0	20.0	18.1	3	4	19.9	16.9
4	1	47.6	54.9	6	4	8.7	6.8	8	0	5.8	5.8	5	4	13.2	11.4
5	1	14.0	11.4	1	5	23.0	24.5	1	1	30.5	32.1	6	4	6.5	4.5
6	1	22.2	20.8	2	5	9.7	8.2	2	1	12.4	13.8	1	5	6.4	7.7
7	1	10.9	10.6	3	5	6.0	6.8	3	1	18.7	14.0	2	5	14.2	13.0
8	1	5.3	5.8	4	5	21.2	22.9	4	1	11.2	9.5	3	5	6.9	5.0
9	1	8.8	9.5	5	5	28.8	30.6	5	1	11.2	8.1	4	5	14.3	10.3
1	2	34.6	37.4	1	6	29.3	29.4	6	1	29.1	30.7	1	6	11.2	9.4
2	2	14.8	15.7	2	6	20.0	18.0	7	1	17.2	18.2	2	6	24.5	24.5
3	2	10.7	8.0	3	6	9.1	9.0	8	1	5.1	4.1	3	6	8.1	5.4
4	2	14.1	12.8	4	6	15.3	11.8	1	2	47.6	56.0	1	7	18.5	15.2
5	2	11.2	10.3	5	6	6.9	9.3	2	2	28.2	26.6	2	7	5.6	6.0
6	2	28.7	28.3	1	7	7.7	9.4	3	2	28.2	28.5	3	7	7.6	6.7
7	2	9.6	8.8	2	7	15.6	18.7	4	2	11.2	12.9	1	8	5.1	7.9
8	2	6.2	8.1	3	7	13.4	13.3	5	2	11.5	10.2	2	8	8.4	8.6
1	3	15.7	13.9	1	8	11.5	8.9	6	2	11.3	14.1				

with their standard deviations, is shown in Table II. The standard deviations are calculated from the usual treatment of the errors, using the disagreement of the structure factors.[14] This corresponds to the standard errors of the positions of an average of about 0.007 Å for Br, 0.027 Å for N and 0.046 Å for C.

The observed and calculated structure factors are listed in Table III. In the table the asterisk * denotes those reflections which have already been corrected for the extinction effects.

A composite electron density diagram made from the sections of the three-dimensional Fourier synthesis is shown in Fig. 4. The structure projected along the a-axis is illustrated in Fig. 5.

The Description of the Structure and Discussion

The atomic arrangement in the crystal is shown in Figs. 4 and 5. The interatomic distances and bond angles are given in Table IV.

The structure is essentially ionic and consists of the positively-charged $[\mathrm{Co}\ l\text{-pn}_3]^{3+}$ ions and Br^- ions. The Br–Br separation is 4.11_2 Å, corresponding to twice the ionic radius of Br^-. The cobalt and bromine atoms lie in approximately one

TABLE IV. INTERATOMIC DISTANCES AND BOND ANGLES (Å, degree)

Co–N(1)	1.998±0.030
Co–N(2)	2.001±0.030
N(1)–C(1)	1.50 ±0.07
N(2)–C(2)	1.49 ±0.06
C(1)–C(2)	1.58 ±0.07
C(1)–C(3)	1.51 ±0.07
Br–Br	4.112±0.011**
Br–N(1)	3.432±0.037*
Br–N(2)	3.339±0.037*
Br–C(1)	3.584±0.048*
Br–C(2)	3.573±0.040*
Br–C(3)	3.705±0.040**
Co–Br	4.985±0.007*
Co–Br	4.830±0.007*
Co–Br	4.499±0.007**
∠N Co N	86.5±1.5°
∠Co N(2)C(2)	108 ±3°
∠Co N(1)C(2)	110 ±4°
∠N(1)C(1)C(2)	106 ±5°
∠N(2)C(2)C(1)	108 ±5°
∠N(1)C(1)C(3)	115 ±6°
∠C(2)C(1)C(3)	115 ±6°

* Distances between layers.
** Distances within one layer.

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[14] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

layer, perpendicular to the *c*-axis. The whole structure can be obtained if exactly similar layers are placed on the first in such a way that they are all related by the operation of 6_3. A complex ion is surrounded by three Br$^-$ ions within the same layer at a distance of 4.49_9 Å and by six anions at the apices of a trigonal prism. The Co atom lies approximately at the center of this prism, the Co–Br distances being 4.98_5 and 4.83_0 Å. The atomic group composed of three Br$^-$ ions is surrounded by the complex ions in just the same way as the latter is surrounded by the anions.

There are some possibilities of the formation of weak hydrogen bonds between the Br$^-$ and the nitrogen atoms in the propylenediamine rings. Two of the closest N–Br approaches occur at the distances of 3.36 and 3.43 Å. The directions of these close N–Br contacts are almost parallel to the *c*-axis. By these hydrogen bonds each layer seems to be held together. These distances are of the same order as those found in isoleucine hydrobromide[15] and 11-aminoundecanonic acid. HBr·1/2H$_2$O[16]. The existence of any water molecules is evidently excluded.

The complex ion has a three-fold symmetry because of the requirements of the space group. The three chelate rings must, therefore, be completely identical with each other. The CH–CH$_2$ bond in the chelate rings is nearly parallel to the three-fold axis of the complex ion, corresponding to the "lel" form. The shape and size of the five-membered ring, composed of Co and pn except for the methyl group, closely resembles that found in [Co en$_3$]$^{3+}$,[3-5] [CoCl$_2$en$_2$]$^+$ [17] and [CoBr$_2$-en$_2$]$^+$ [18]. The substituted methyl group does not disturb the overall features of the Co-en ring. The C–CH$_3$ bond lies in an approximately equatorial plane of the five-membered ring, in agreement with the prediction of Corey and Bailar that the equatorial orientation is of a lower energy than the axial one.[2] The shape and size of the Co-pn rings are essentially the same as those found in [CoCl$_2$ *l*-pn$_2$]$^+$.[10]

All the distances and angles within the chelate rings are normal. The Co–N separation is 2.00_0 Å, compared with 1.98−2.03 Å in [Co en$_3$]$^{3+}$ [3,5] and 1.94−2.02 Å in [CoCl$_2$*l*-pn$_2$]$^+$ [10]. Six nitrogen atoms form a slightly distorted octahedron around the central cobalt atom, the N–Co–N angle being 86.5°. The ligand molecule assumes a gauche configuration with an azimuthal angle of 51° between the planes determined by the C–C and C–N bonds.

The complex ion [Co *l*-pn$_3$]$^{3+}$ shown in Fig. 3 corresponds to the laevorotatory form with respect to the NaD lines. This form can be denoted as the L*lll* configuration.

If three methyl groups of L-(−)-[Co *l*-pn$_3$]$^{3+}$ are replaced by hydrogen atoms, the absolute configuration of the complex ion L-[Co en$_3$]$^{3+}$ is obtained. The latter is known also to be laevorotatory with respect to the NaD lines.[3,4] Smirnoff found that the ORD curves of (−)-[Co en$_3$]$^{3+}$ and (−)-[Co *l*-pn$_3$]$^{3+}$ correspond well to one another.[9] From this fact it has been deduced, without verification, that these two ions would possess the same absolute configuration; that is, the latter would also take the L-form. The present investigation has revealed that this is actually the case. Thus, the conventional method of correlating the absolute configurations with the ORD curves has been proved for the first time to be useful and reliable.

The absolute configuration of the propylenediamine, which has an asymmetric carbon atom in the molecule, could be determined at the same time. The result corresponds to the configuration correlated to D-alanine, which is in agreement with the previous conclusion about [CoCl$_2$ *l*-pn$_2$]$^+$ [10] and also with the chemical convention[6,7].

One of the most important conclusions of this study is that the absolute configuration of a series of tris(bidentate)-complexes can be successfully correlated to the configurational series in organic compounds. The complex ion [Co en$_3$]$^{3+}$, which is the simplest and the most familiar of the tris(bidentate)-complexes, has been correlated to the *l*-pn and, consequently, to the whole system of the organic compounds through the intermediation of the absolute configuration of [Co *l*-pn$_3$]$^{3+}$. This was possible because the complex ion possesses a remarkable stereospecificity.[2] When three bidentates, en or pn, are co-ordinated to the cobalt atom, the central C–C bonds prefer the "lel" configuration to the oblique one. In the five-membered chelate rings, the C–CH$_3$ bond has a tendency to take the equatorial configuration rather than the axial one. Furthermore, the complex ion seems to favor the highest attainable symmetry, so that the three bidentates become identical with each other, as was pointed out by Jaeger et al.[19] If one accepts these three conditions, there is only one way in which three molecules of the *l*-pn can be co-ordinated to the cobalt atom. It may readily be seen that the resultant complex ion must assume the L-form shown in Fig. 1. These results are expected to be applied to the whole series of tris(bidentate)-complexes. Investigations along these lines are now in progress for crystals of [Co cptn$_3$]X$_3$·4H$_2$O and [Co chxn$_3$]X$_3$·4H$_2$O.

The calculations of the structure factors and electron densities were carried out on the PC 2

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