Studies on Crystals of Metallic Tris-ethylenediamine Complexes. III. The Determination of the Absolute Configuration of Optically Active Complex Ion, [Co en$_3$]$^{3+}$, by Means of X-rays

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Introduction

In 1951, Bijvoet, Peerdeman and van Bommel[1] first succeeded in determining the absolute configuration of *d*-tartaric acid by means of X-rays, using absorption edge technique.

However, no attempt has ever been made to determine the absolute configuration of optically active tris-ethylenediamine-cobaltic complex ion, [Co en$_3$]$^{3+}$ (en: ethylenediamine), one of the most familiar complex ions in the chemistry of complex compounds. The present paper deals with this problem, including a brief description of the principle of the method and the experimental procedure. A brief account of this work has been published already[2].

Principle of the Method

As is well known, Friedel's law states that it is not possible, by ordinary methods in X-ray diffraction study, to detect the presence or the absence of centrosymmetry in a crystal, from which it follows immediately that in the case of non-centrosymmetry one can not conclude whether a model or its inversion actually corresponds with a given optically active crystal, say—dextro compound. However, it is not true when use is made of X-rays whose wave length is a little shorter than the absorption edge of a particular atom in the crystal. If this condition is fulfilled, a difference in intensity between the reflections from (hkl) and $(\bar{h}\bar{k}\bar{l})$ can be observed for non-centrosymmetrical crystal.

This is due to the scattering of X-rays by the particular atom with anomalous phase and amplitude. From the difference between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$, one can determine the absolute configuration of a structure which belongs to one of the pairs of enantiomorphous space groups, provided that the crystal structure is fully known in all respects except that of "hand". The actual intensities $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ can be calculated on the basis of a final set of atomic coordinates determined in the usual way, taking the anomalous dispersion into account. If the observed inequality relations are the reverse of those calculated, the real atomic parameters must be the inversion of the initial set.

Besides these inequality relations, the following equality exists:

$$I_d(hkl)=I_l(\bar{h}\bar{k}\bar{l}) \tag{1}$$

where the subscript *d* and *l* are used to distinguish the two enantiomorphous crystals. It follows immediately:

$$\text{if } I_d(hkl)\lessgtr I_d(\bar{h}\bar{k}\bar{l}),\text{ then } I_l(hkl)\gtrless I_l(\bar{h}\bar{k}\bar{l}), \tag{2}$$

that is, the inequality relations must be reversed in the case of *d*-compound and *l*-compound.

Since the wave length of Cu $K\alpha$ radiation (λ=1.5418 Å) is a little shorter than the *K*-absorption edge of the cobalt atom (λ_k=1.6081 Å), anomalous dispersion is expected to take place. The crystal structures of D- and L-2[Co en$_3$]Cl$_3$·NaCl·6H$_2$O are fully known except that of "hand" as reported previously[3]. Therefore, the absolute configuration of these compounds can be determined without ambiguity, if the difference between $I(hkil)$ and $I(\bar{h}\bar{k}\bar{i}\bar{l})$ can be observed when Cu $K\alpha$ radiation is used.

The phase change on scattering may be included in the usual expression for the structure factor without changing its form, if we consider the atomic scattering factor to be complex numbers[4]:

$$f=f^0+\Delta f'+i\Delta f'' \tag{3}$$

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* Present adress; Momotani Juntenkan Co. Ltd., Osaka.

[1] J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature*, **168**, 271 (1951).

[2] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Cryst.*, **8**, 729 (1955).

[3] K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, This Bulletin, **30**, 158 (1957).

[4] R. W. James, "The Optical Principles of the Diffraction of X-rays", G. Bell and Sons, Ltd., London (1948), Chap. IV.

where f^0 is the scattering factor for wave lengths far from any one of the absorption edges of electrons and $\Delta f'$ and $\Delta f''$ represent the corrections to be applied to the real and the imaginary part of the scattering factor because of dispersion.

When Cu $K\alpha$ radiation is used to take diffraction photographs of the complex compound above mentioned, the K-level electrons of the cobalt atom are excited. Therefore, we have for the scattering factor of the cobalt atom:

$$f_{\mathrm{Co}}=f^0{}_{\mathrm{Co}}+\Delta f'{}_{\mathrm{Co}}+i\Delta f''{}_{\mathrm{Co}} \qquad (4)$$

The structure factor $F(hkil)$ for $l=2n$ can be written as follows, if we assume regular structure postulated in the previous paper:

$$F(hkil)=A(hkil)+iB(hkil), \qquad (5)$$

where

$$A(hkil)=\sum_j m_jf_j \cos 2\pi lz_j \{\cos 2\pi(hx_j+ky_j)$$
$$+\cos 2\pi(kx_j+iy_j)+\cos 2\pi(ix_j+hy_j)\}$$
$$B(hkil)=\sum_j \mathrm{m}_jf_j \sin 2\pi lz_j \{\cos 2\pi(hx_j+ky_j)$$
$$+\cos 2\pi(kx_j+iy_j)+\cos 2\pi(ix_j+hy_i)\}$$

and

f_j: atomic scattering factor for the j-th atom

m_j: a suitable factor to allow for the reduced multiplicity for atoms on the special positions

x_i, y_j, z_j: atomic coordinates for the j-th atom.

It can easily be shown from the above expression that $F(hki\bar{l})$ is equivalent to $F(\bar{h}\bar{k}\bar{i}\bar{l})$ and is a complex conjugate of $F(hkil)$. Because of eq. (4), $|F(hkil)|$ is no more equal to $|F(hki\bar{l})|$, hence, the intensity $I(hkil)$ is unequal to $I(hki\bar{l})$. Accordingly, to observe the effect of anomalous dispersion, it is more convenient to compare the reflections from $(hkil)$ and $(hki\bar{l})$ instead of those from $(hkil)$ and $(\bar{h}\bar{k}\bar{i}\bar{l})$. These reflections can be observed on the same oscillation photograph taken around the c-axis and moreover, various correction factors come out exactly the same for these two reflections.

Experimental Procedure and the Determination of the Absolute Configuration

i) *Observation of Inequality Relations by Oscillation Photographs.*

Thin needle-like crystals of about 0.2 mm. in diameter were selected. First, a few oscillation photographs were taken using Fe $K\alpha$ radiation, in order to confirm that the crystal setting is perfect and $(hkil)$ and $(hkil)$ intensities are practically equal. Photographs were then taken with Cu $K\alpha$ radiation, which is scattered by the cobalt atoms anomalously. In Fig. 1, the effect of anomalous dispersion is shown, where reflections of Fe $K\alpha$ and Cu $K\alpha$ from the plane $(32\bar{5}2)$ and $(32\bar{5}\bar{2})$ are recorded on one film, the latter being equivalent to $(\bar{3}\bar{2}5\bar{2})$ because of symmetry. For D-compound the intensity of reflection of Cu $K\alpha$ from the plane $(32\bar{5}\bar{2})$ is clearly stronger than that from the plane (3252), while they are equal in intensity in case of Fe $K\alpha$ radiation. The inequality relation is reversed for L-compound.

There are many such pairs of reflections for which slight but discernible differences in intensities were observed, whereas no such differences could be found when Fe $K\alpha$ radiation was used.

It was also found that the intensity relations observed for the one crystal are the reverse of those found for its enantiomorph. This observation strongly suggests that these differences are due to the anomalous dispersion of cobalt atoms in the crystal. In Table I observed and calculated relations between $I(hkil)$ and $I(hki\bar{l})$ are compared for all the observed pairs. The visual estimates of the last two columns are the results of observations by a few persons independently. In Table I the inequality sign $>$ or $<$ shows that the observed intensity for $(hkil)$ is greater or smaller than that for $(hki\bar{l})$. The sign $?>$ or $?<$ means that the inequality is not so definite as that without the symbol ?. The symbol ? shows that the inequality could not be observed or was different according to different observers. In the calculation of intensities of reflections, $\Delta f'$ and $\Delta f''$ were calculated according to the formula derived by Hönl[5]. They amount to $\Delta f'=-3.0$ and $\Delta f''=3.4$, respectively. The calculated values shown in the first column are based on the regular model. Those shown in the second column were calculated on the basis of a model having disorder due to submicroscopic twinning. In this case, $F(hki2\mathrm{n})$ is not exactly equal but very near to the complex conjugate of $F(hki\overline{2n})$ even when no anomalous dispersion occurs. Thus the difference between $I_c(hkil)$ and $I_c(hki\bar{l})$ calculated for Fe $K\alpha$ radiation is

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[5] H. Hönl, *Zeit. f. Physik*, **84**, 1 (1933); *Ann. Physik*, **18**, 625 (1933).

TABLE I

OBSERVED AND CALCULATED INTENSITIES

	Calculated on the Basis of				Observed for	
	Regular Model		Twinned Model			
hkil	$I(hkil)$	$I(hki\bar{l})$	$I(hkil)$	$I(hki\bar{l})$	D-Cryst.	L-Cryst.
1012	1985	1810	2300	2140	?	<
1122	2.9	159	17	100	<	>
1232	86	173	196	381	<	>
1342	965	910	921	865	? >	? <
1452	781	705	824	738	? >	? <
1562	312	296	300	292	>	<
1892	51	47	50	47	? >	<
1, 9, 10, 2	33	34	33	37	—	? >
2022	148	269	334	423	<	>
2132	3710	3460	3310	3200	>	<
2242	38	159	30	102	<	>
2352	418	448	444	485	? <	? >
2462	112	99	124	112	?	?
2572	15	17	17	14	?	?
2682	6.4	7.1	6.8	11.5	—	>
2792	71	65	67	62	? >	?
2, 8, 10, 2	84	75	101	89	? >	?
2, 9, 11, 2	47	41	45	41	? <	—
3032	72	167	146	171	<	>
3142	315	434	514	557	<	>
3252	141	82	120	82	>	<
3362	165	194	212	241	? <	? >
3472	34	46	25	35	? <	?
3582	146	141	149	146	? >	? <
3, 7, 10, 2	58	61	59	68	? <	?
3, 8, 11, 2	39	32	35	29	? >	?
4042	1252	1160	1106	1083	? >	? <
4152	21	27	45	25	<	>
4262	291	310	310	329	?	?
4482	3.3	28	2.2	24	<	>
4, 7, 11, 2	0.4	6.9	2.1	4.1	<	>
5052	412	394	371	363	?	?
5272	0.7	11	3.3	6.7	<	>
5382	86	76	84	77	? >	<
5492	99	104	105	115	? <	? >
6172	43	37	41.3	41.1	>	<
6282	88	86	84	86	? <	>
6392	187	169	207	178	? >	?
6, 4, 10, 2	125	112	112	106	? >	<
7072	233	213	219	196	?	?
7292	164	131	123	120	>	<
7, 3, 10, 2	93	94	92	94	?	? <
7, 4, 11, 2	0.1	6.2	2.7	4.8	? >	?
8192	5.1	7.9	6.0	10.4	—	>
8, 2, 10, 2	9.4	4.9	13.4	5.2	>	<
8, 3, 11, 2	5.2	5.4	5.2	6.9	?	—
9, 1, 10, 2	37	40	40	44	?	?
10, 0, 10, 2	14	12	12	9.8	? >	—

small and within the errors of experiments for most cases, and the calculated intensities based on the latter model for Cu $K\alpha$ radiation lead to the same inqeuality relations with only a few exceptions. Therefore, the same conclusion was drawn from both models.

Namely, the concordance, in general, of intensity signs in the observed and the calculated intensities seen in the Table I indicates that the drawing of a complex ion $[\text{Co en}_3]^{3+}$ shown in Fig. 2 corresponds to the dextrorotatory form with respect to Na D line. This result has been indeed verified by computing the $P_s(\mathbf{u})$ function of Okaya, Saito and Pepinsky[6,7].

ii) *Observation of Inequality Relations by Laue Photographs.*

Grenville-Wells and Lonsdale[8] showed that the effect of anomalous dispersion could also be observed by means of Laue photographs. This method has certainly some advantages over the one using oscillation photographs. However, when applied to the present case, the observation could not be carried out without experimental difficulties. Since the crystals disintegrated by losing their water of crystallization when exposed in the X-ray beam for several hours, it was difficult to set the crystal perfectly and obtain appropriate Laue photographs before decomposition. Moreover, no suitable pairs of reflections could be found which were of high order and strong enough in intensity to reduce the influence of the setting error of the crystal.

Though not satisfactorily, the inequality relations were observed about a few pairs of $(hki2)$ reflections in accord with the results obtained by using oscillation photographs.

Some Remarks on Experimental Procedure

It is to be noted here that the same coordinate system must be used in the indexing of the oscillation photographs and calculation of the structure factors. The right handed system was used throughout this investigation. As pointed out by Bijvoet and his coworkers, the calculation of the differences between (hkl) and $(\bar{h}\bar{k}\bar{l})$ intensities does not need very accurate F-values. Theoretically, observation of a single pair of reflections is enough to decide the diffraction model and its mirror image. However, it is advisable to observe the difference of as many corresponding spots as possible. From this point, the Laue photographic method might be laborious.

When anomalous dispersion occurs in the crystal, incident beam is in general heavily absorbed and fluorescent radiation is copiously excited, so that the photograph shows weak diffraction spots on a rather heavily blackened background. Usually its takes a pretty long time to take a diffraction photograph. To avoid the blackening as much as possible and to obtain a picture with clear background in a relatively short time, it is necessary to make the range of oscillation of the crystal small.

Practically it is a rather difficult task to compare the intensities from a front (hkl) and a rear face $(\bar{h}\bar{k}\bar{l})$ of a crystal, since it is not easy to obtain a crystal whose front and rear surface are exactly at the same condition with regard to their perfection etc. However, in most cases it is possible to avoid this difficulty. If, for instance, $F(hkl)$ is equivalent to $F(hk\bar{l})$ because of the symmetry of the space group, it is more convenient to use the reflection $(hk\bar{l})$ instead of $(\bar{h}\bar{k}\bar{l})$, as pointed out in the previous section.

The best method to measure the difference of $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ would be to use two Geiger counters arranged in such a way that the two reflections are received at the same time and to use a circuit by which the difference can be read off directly.

Summary

The absolute configuration of an optically active complex ion $[\text{Co en}_3]^{3+}$ has been determined by means of X-ray absorption edge technique. Cu $K\alpha$ radiation was used to excite the cobalt atoms in the crystals of D- and L-$2[\text{Co en}_3]\text{Cl}_3\cdot\text{NaCl}\cdot 6\text{H}_2\text{O}$. The effects of the anomalous dispersion were observed by single crystal oscillation photographs as well as Laue photographs. A brief description of the principle of the method and the experimental procedure is included.

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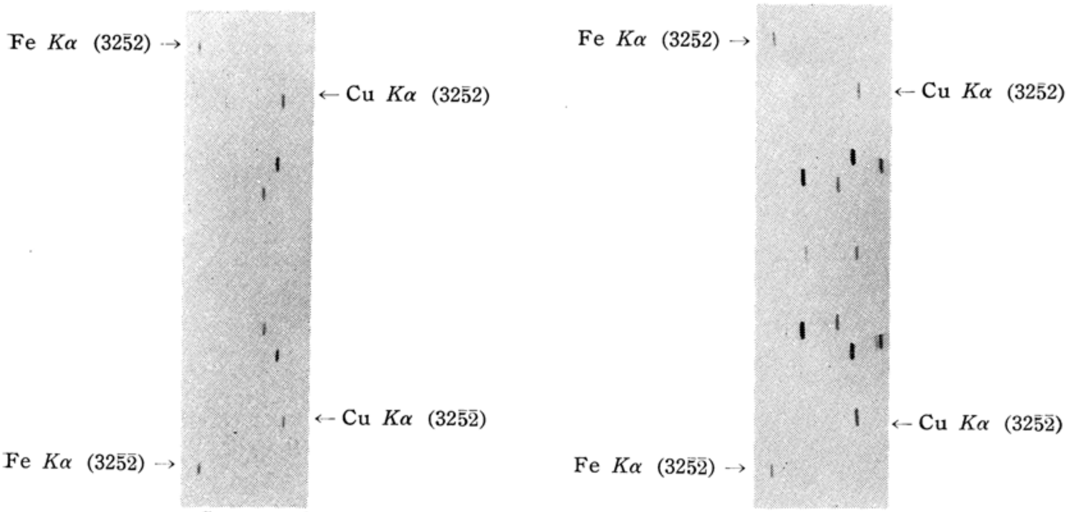
[6] Y. Okaya, Y. Saito and R. Pepinsky, *Phys. Rev.*, **98**, 1857 (1955).

[7] Y. Saito, Y. Okaya and R. Pepinsky, In press; cf. also, Phys. Rev., **100**, 970 (1955).

[8] H. J. Grenville-Wells and K. Lonsdale, *Nature*, **173**, 1145 (1954).



D-Compound L-Compound

Fig. 1. Parts of oscillation photographs of D- and L-2[Co en$_3$]Cl$_3$·NaCl·6H$_2$O, showing the effect of anomalous dispersion.

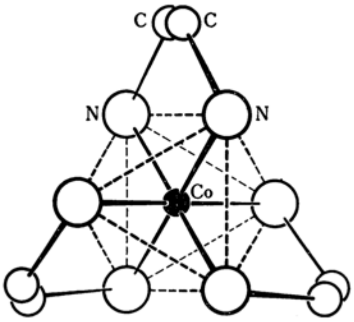


Fig. 2. Drawing of the D(+)- [Co en$_3$]$^{3+}$ complex ion.