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The Crystal Structure of *cis*-Ammonium Disulfitotetramminecobaltate(III) Trihydrate, $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$[1]

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The structure of $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$ has been determined by the heavy-atom method and refined to $R=0.12$ by a least-squares analysis based on 874 three-dimensional visual data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with unit cell dimensions of $a=10.995$, $b=17.563$, $c=6.834$ Å, and $Z=4$. The two sulfito groups in the complex anion are coordinated to the central cobalt atom in *cis* positions through their sulfur atoms, with Co-S distances of 2.23 Å (mean). The *cis*-configuration of brown sodium salt, with an absorption spectrum similar to that of the trihydrate of ammonium salt, has also been established.

There are two stereoisomers conceivable for the disulfitotetramminecobaltate(III) complex anion: the *cis* and *trans* forms. In fact, in the case of the ammonium salt of this complex, the two isomers have been known as the dark brown trihydrate and the reddish brown tetrahydrate respectively. The absorption spectrum of the dark brown ammonium salt in an aqueous solution has a chage-transfer band at 265 mμ and a sulfito-specific band at 297 mμ in the ultraviolet region, whereas that of the reddish brown ammonium salt has only a sulfito-specific band at 274 mμ. In the sodium salts, the spectra are nearly identical with those of the corresponding ammonium salts; that is, the brown salt corresponds to the dark brown ammonium salt, and the golden-yellow salt, to the reddish brown ammonium salt. These spectra were first measured by Shimura[2] and are followed in the present work (Fig.1).

The assignment of the configurations of these salts has not yet been established; Hofmann and Jenny,[3] who first prepared the two isomers of sodium salts, designated a brown, less soluble dihydrate as the *cis* form and another golden-yellow, more soluble tetrahydrate as the *trans* form. They also concluded that the dark brown and reddish brown ammonium isomers correspond to the brown or golden-yellow sodium salts, respectively. Schwarz and Tede[4] showed, from their studies of the photochemical decomposition of the ammonium salts, that the dark brown, more decomposable salt is the *cis*-isomer and the reddish brown, less

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[1] T. Nomura, M. Nakahara, and Y. Kondo, presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] Y. Shimura, *J. Amer. Chem. Soc.*, **73**, 5079 (1951); This Bulletin, **25**, 46 (1952).

[3] K. A. Hofmann and A. Jenny, *Ber.*, **34**, 3855 (1901).

[4] R. Schwarz and K. Tede, *ibid.*, **60**, 63 (1927).

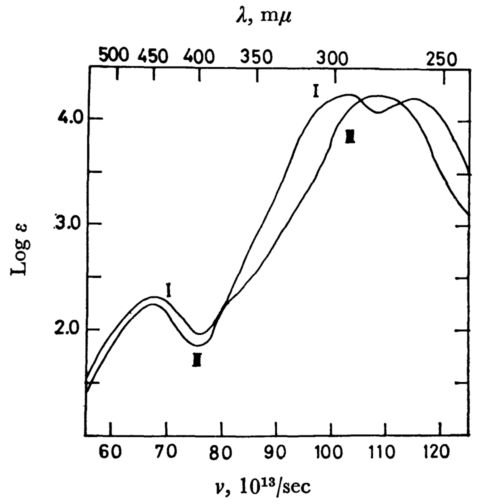

Fig. 1. Absorption spectra of the dark brown isomer (I) and of the reddish brwon isomer (II) of ammonium salt in a 3% aqueous solution of ammonia.

decomposable salt is the *trans*-isomer. Klement[5] and Bailar and Peppard[6] also concluded that the sulfito groups of the dark brown trihydrate must be located in the *cis* positions, in view of the fact that only two ammonia molecules are replaced by an ethylenediamine molecule. On the other hand, in view of the position of the charge-transfer band, Shimura[2] suggested that the dark brown salt has a *trans* configuration with respect to the sulfito groups and assumed, from the first absorption band at 465 mμ, that the sulfito groups in the complex anion were more symmetrical or more stable than a free SO_3 radical, that is, that they were bonded through the sulfur atom to the central atom.

In the present work, the dark brown trihydrate, $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$, has been subjected to a three-dimensional X-ray analysis in order to establish the structure of the complex anion and in order to elucidate in detail the way of the coordination of the sulfito groups to the metal.

Experimental

Ammonium disulfitotetramminecobaltate(III) trihydrate was prepared by the method of Bailar and Peppard.[6] This compound crystallizes in dark brown pillars elongated along the *c* axis, the shortest crystallographic axis. The specimens used for the collection of the intensity data were reformed into cylinders with diameters of 0.024 cm and of 0.026 cm, the axes of which were parallel to the *c* and *a* axes respectively. Using Fe*K*α radiation, Weissenberg photographs with spot-integrating procedure were taken from the zero to fourth levels and from the zero to seventh levels about the *c* and *a* axes respectively. The intensities were measured visually by use of standard calibrated scales and were converted to structure amplitude values in the usual way. Corrections were also applied for absorption, the crystal being assumed to be perfectly cylindrical.[7] A total of 874 independent intensity data were collected.[8]

The crystal data are as follows: $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$, F.W.=359.3, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19); $a=10.995(6)$, $b=17.563(15)$, $c=6.834(5)$ Å, $U=1322$ Å^3; $D_m=1.81$ g·cm^{-3}. $Z=4$, $D_x=1.80$ g·cm^{-3}; linear absorption coefficient for Fe*K*α radiation, $\mu=94.5$ cm^{-1}.

Determination of the Structure

The location of the cobalt atom could be readily determined from Patterson projections, $P(u, v)$ and $P(v, w)$ (Fig. 2).

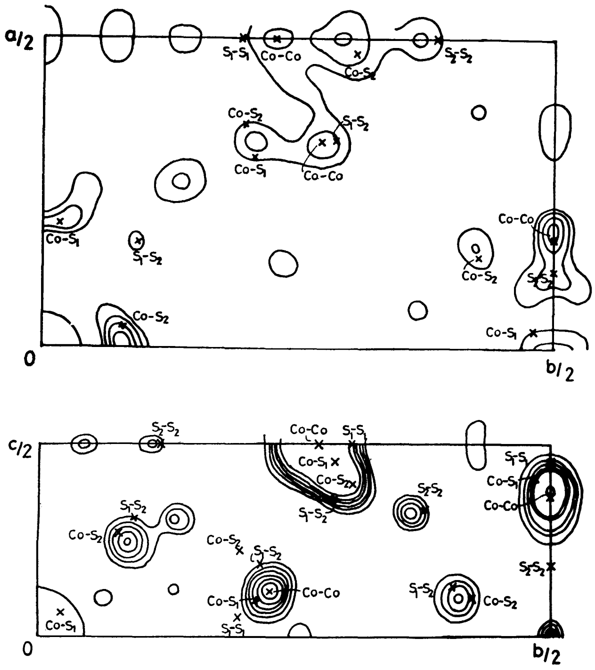

Fig. 2. Patterson projections, $P(u,v)$ and $P(v,w)$, where the vectors between heavy atoms are shown by the crosses.

However, the positions of the two sulfur atoms of the sulfito groups could not be definitely fixed from Patterson maps until a three-dimensional Fourier synthesis has been calculated by the use of phases based on the cobalt atom. The coordinates of these heavy atoms were refined by the block-diagonal, least-squares method.[9] The discrepancy factor, $R=\sum(|F_o|-|F_c|)/\sum|F_o|$, decreased to 0.30. A three-dimensional Fourier synthesis with phases determined by the heavy atoms allowed the four nitrogen atoms to be located around the cobalt atom. Successive refinements were carried out and the positions of all the remaining lighter atoms except those of the hydrogen atoms were revealed, though the nitrogen atom of the ammonium ion and the oxygen atoms of the water molecules were not sufficiently distingushed from each other. These syntheses also indicated that

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[5] R. Klement, *Z. Anorg. Chem.*, **150**, 117 (1926).

[6] J. C. Bailar, Jr., and D. F. Peppard, *J. Amer. Chem. Soc.*, **62**, 105 (1940).

[7] International Tables for X-Ray Crystallography, Vol. II, Kynoch Press, Birmingham (1959).

[8] A FFLP program written by Dr. F. Iwasaki and Dr. H. Iwasaki was used for the Lorentz and polarization corrections of the intensity data.

[9] The Fourier synthesis and least-squares program used was HBLS-4 (in the "Universal Crystallographic Computation Program System" edited by Dr. T. Sakurai and published by the Crystallographic Society of Japan), written by Dr. T. Ashida. The weights at the final least-squares refinement were assumed to be as follows: $w=(3.52/F_0)^2$ if $F_0\geq 3.52$, and $w=1$ if $F_0\leq 3.52$.

anisotropic temperature factors should be used for all the atoms.

After several cycles of least-squares refinement with anisotropic thermal parameters, the discrepancy fractor became 0.12. A final difference Fourier synthesis gave no significant indications of the positions of the hydrogen atoms. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[10]

At a later stage of the refinement, extinction corrections were applied for some of the larger F_o values.

The final three-dimensional electron density map is shown in Fig. 3. The final parameters are given in Tables 1 and 2.

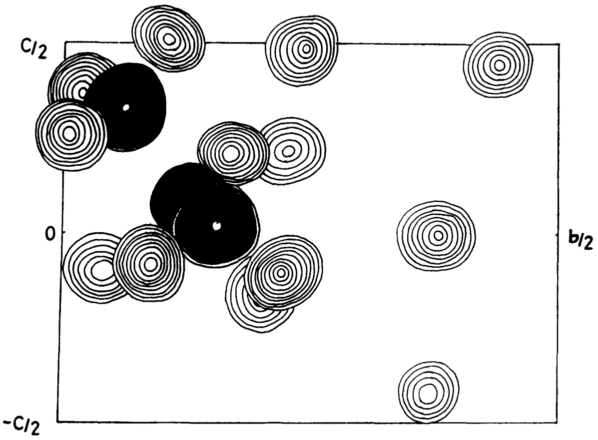

Fig. 3. The final three-dimensional electron density map composed of sections through the atomic centers parallel to (100). The contours are drawn at intervals of 1.0 e.Å^{-3} starting with 1.0 e.Å^{-3}.

The agreement between the observed and calculated structure amplitudes is reasonable.[11]

The standard deviations of the coordinates, estimated from the least-squares results, are 0.004 Å (mean) for the cobalt and sulfur atoms and 0.02 Å (mean) for the others.

Description of the Structure and Discussion

A projection of the contents of an asymmetric unit along the *a* axis is presented in Fig. 4. The bond lengths

TABLE 1. FINAL FRACTIONAL COORDINATES AND THEIR e.s.d.'s

Atom	$x(\sigma(x))\times 10^4$	$y(\sigma(y))\times 10^4$	$z(\sigma(z))\times 10^4$
Co	0891(2)	1326(1)	0747(5)
S (1)	−1101(4)	1529(3)	0238(7)
S (2)	0538(4)	0595(3)	3327(8)
N (1)	0894(18)	2276(10)	2351(29)
N (2)	2655(16)	1194(9)	1250(26)
N (3)	0864(17)	0384(10)	−0916(25)
N (4)	1290(17)	1988(10)	−1681(35)
N (5)	0244(21)	3686(12)	−4179(33)
O (1)	−1796(17)	1673(9)	2093(23)
O (2)	−1730(15)	0845(7)	−0816(25)
O (3)	−1288(13)	2209(8)	−1064(21)
O (4)	0161(17)	1069(9)	5128(21)
O (5)	1645(14)	0157(8)	3745(25)
O (6)	−0530(16)	0035(9)	2826(22)
O (7)	3339(17)	2368(9)	4850(28)
O (8)	0655(15)	3739(10)	−0037(26)
O (9)	2305(16)	4360(10)	4598(25)

TABLE 2. FINAL THERMAL PARAMETERS AND THEIR e.s.d.'s
Temperature factors are of the form:
$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$

Atom	$\beta_{11}\times 10^6$	$\beta_{22}\times 10^6$	$\beta_{33}\times 10^6$	$\beta_{12}\times 10^6$	$\beta_{13}\times 10^6$	$\beta_{23}\times 10^6$
Co	0532(0)	0241(0)	1672(2)	0008(0)	0031(0)	0011(0)
S (1)	0500(0)	0193(0)	1225(2)	0013(0)	−0136(1)	0132(0)
S (2)	0397(0)	0191(0)	1392(2)	−0091(0)	0046(1)	0046(0)
N (1)	0644(1)	0292(0)	2431(11)	0045(0)	0362(4)	0377(1)
N (2)	0681(1)	0267(0)	1447(9)	−0201(0)	−0177(3)	0200(1)
N (3)	0911(2)	0314(0)	1000(8)	−0089(1)	−0043(3)	0051(1)
N (4)	0438(1)	0274(0)	3225(13)	0251(0)	−0108(4)	−0035(1)
N (5)	1195(2)	0530(0)	1958(11)	−0245(1)	0397(4)	−0274(2)
O (1)	0941(1)	0359(0)	1924(9)	−0001(0)	−0139(3)	−0018(1)
O (2)	0851(1)	0155(0)	2664(10)	−0049(0)	0527(3)	−0049(1)
O (3)	0457(1)	0355(0)	1602(8)	−0172(0)	−0141(1)	0050(1)
O (4)	1424(2)	0379(0)	0556(7)	−0062(0)	0904(3)	−0007(1)
O (5)	0583(1)	0314(0)	2786(10)	0082(0)	0243(3)	0398(1)
O (6)	1002(2)	0462(0)	1675(9)	−0404(1)	−0074(3)	−0064(1)
O (7)	1104(2)	0308(0)	2918(10)	0062(0)	−0313(4)	0133(1)
O (8)	0903(1)	0453(0)	2147(9)	0266(1)	0147(3)	0333(1)
O (9)	1128(2)	0375(0)	2310(10)	−0031(1)	0193(4)	0158(1)

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10) International Tables for X-Ray Crystallography Vol. III, Kynoch Press, Birmingham (1962).

11) A complete list of the observed and calculated structure factors has been submitted to, and is kept as Document No. 7105 by, the office of the Bulletin of the Chemical Society of Japan, 1—5 Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be secured by citing the Document number and by remitting, in advance, ¥400 for photo prints. Pay by check or money order payable to: Chemical Society of Japan.

Table 3. THE INTERATOMIC DISTANCES AND BOND ANGLES IN THE COMPLEX ANION, $[Co(SO_3)_2(NH_3)_4]$
Their e.s.d.'s are given in parentheses

Co–S(1)	2.245(6)Å	S(1)–O(6)	3.24(2)	N(3)–N(4)	2.90(3)Å	O(4)–O(5)	2.47(2)
Co–S(2)	2.215(6)	S(2)–N(1)	3.05(2)	N(3)–O(1)	4.23(2)	O(4)–O(6)	2.50(2)
Co–N(1)	2.00(2)	S(2)–N(2)	2.92(2)	N(3)–O(2)	2.96(2)	O(5)–O(6)	2.47(2)
Co–N(2)	1.98(2)	S(2)–N(3)	2.94(2)	N(3)–O(3)	3.98(2)	S(1)–Co–S(2)	92.5(2)°
Co–N(3)	2.01(2)	S(2)–N(4)	4.29(2)	N(3)–O(4)	4.37(2)	S(1)–Co–N(1)	87.4(6)
Co–N(4)	2.07(2)	S(2)–O(1)	3.30(2)	N(3)–O(5)	3.32(2)	S(1)–Co–N(2)	177.4(5)
S(1)–O(1)	1.50(2)	S(2)–O(2)	3.80(2)	N(3)–O(6)	3.06(2)	S(1)–Co–N(3)	91.6(5)
S(1)–O(2)	1.56(1)	S(2)–O(3)	4.59(1)	N(4)–O(1)	4.30(3)	S(1)–Co–N(4)	89.6(5)
S(1)–O(3)	1.50(1)	N(1)–N(2)	2.81(3)	N(4)–O(2)	3.92(3)	S(2)–Co–N(1)	92.7(6)
S(2)–O(4)	1.54(2)	N(1)–N(3)	4.00(3)	N(4)–O(3)	2.89(2)	S(2)–Co–N(2)	88.0(5)
S(2)–O(5)	1.47(2)	N(1)–N(4)	2.83(3)	N(4)–O(4)	5.08(3)	S(2)–Co–N(3)	88.3(5)
S(2)–O(6)	1.56(2)	N(1)–O(1)	3.14(3)	N(4)–O(5)	4.92(3)	S(2)–Co–N(4)	177.6(5)
Co–O(1)	3.15(2)	N(1)–O(2)	4.39(2)	N(4)–O(6)	5.04(3)	N(1)–Co–N(2)	90.1(8)
Co–O(2)	3.19(2)	N(1)–O(3)	3.35(2)	O(1)–O(2)	2.46(2)	N(1)–Co–N(3)	178.6(8)
Co–O(3)	3.11(1)	N(1)–O(4)	2.96(2)	O(1)–O(3)	2.42(2)	N(1)–Co–N(4)	88.3(8)
Co–O(4)	3.13(2)	N(1)–O(5)	3.93(2)	O(1)–O(4)	3.17(2)	N(2)–Co–N(3)	90.9(7)
Co–O(5)	3.02(2)	N(1)–O(6)	4.25(2)	O(1)–O(5)	4.76(2)	N(2)–Co–N(4)	89.8(7)
Co–O(6)	3.11(2)	N(2)–N(3)	2.84(2)	O(1)–O(6)	3.24(2)	N(3)–Co–N(4)	90.7(8)
S(1)–S(2)	3.227(7)	N(2)–N(4)	2.86(3)	O(2)–O(3)	2.45(2)	O(1)–S(1)–O(2)	107.1(9)
S(1)–N(1)	2.93(2)	N(2)–O(1)	5.00(2)	O(2)–O(4)	4.58(2)	O(1)–S(1)–O(3)	107.2(9)
S(1)–N(2)	4.23(2)	N(2)–O(2)	5.06(2)	O(2)–O(5)	4.99(2)	O(2)–S(1)–O(3)	106.1(8)
S(1)–N(3)	3.05(2)	N(2)–O(3)	4.95(2)	O(2)–O(6)	3.17(2)	O(4)–S(2)–O(5)	110.5(10)
S(1)–N(4)	3.05(2)	N(2)–O(4)	3.82(2)	O(3)–O(4)	4.94(2)	O(4)–S(2)–O(6)	107.4(9)
S(1)–O(4)	3.71(2)	N(2)–O(5)	2.73(2)	O(3)–O(5)	5.85(2)	O(5)–S(2)–O(6)	109.4(9)
S(1)–O(5)	4.54(2)	N(2)–O(6)	4.20(2)	O(3)–O(6)	4.74(2)		

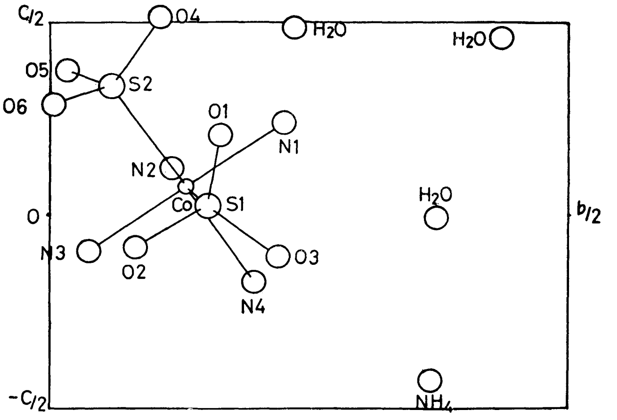

Fig. 4. The structure in an asymmetric unit, viewed along the *a* axis.

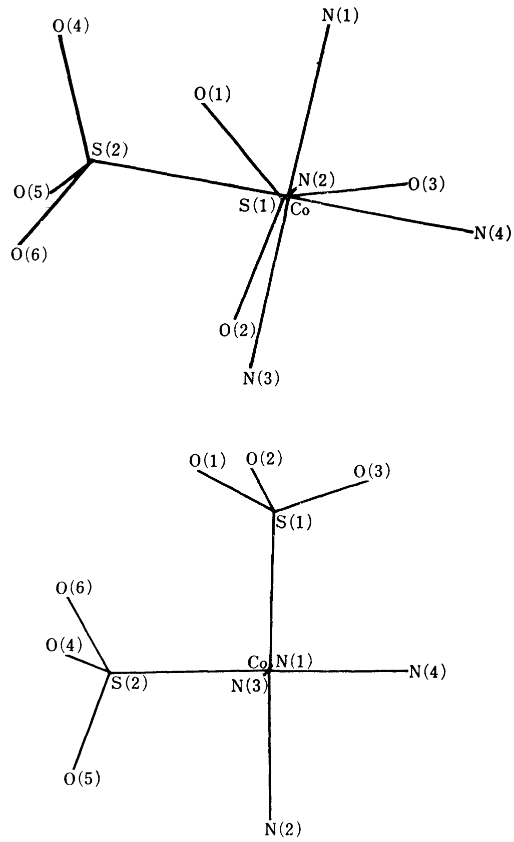

Fig. 5. Projections of the complex anion onto (a) the plane defined by the three oxygen atoms of O(1), O(2), and O(3) in a sulfito group and (b) the least-squares plane for Co, S(1), S(2), N(2), and N(4).

and angles with their e.s.d.'s are listed in Table 3, while the pertinent intermolecular contacts (*i.e.*, those less than 3.22 Å) are given in Table 5.

In the complex anion, the two sulfito groups are coordinated to the central cobalt atom in *cis* positions through their sulfur atoms, the Co-S distances of 2.22 Å and 2.25 Å. These bond lengths are somewhat shorter than the sum of the covalent radii (2.26 Å) obtained from the radius of 1.22 Å for Co(III) and that of 1.04 Å for tetrahedral sulfur, while they are a little longer than the Co-S distance of 2.20 Å found in the crystal of $[Co(SO_3)(SCN)en_2]$,[12] whose crystal structure was first determined among the Co(III) complexes containing the sulfito group as a ligand. The sulfito groups are of a somewhat distorted trigonal-pyramidal struc-

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12) S. Baggio and L.N. Becka, *Acta Crystallogr.*, **B25**, 946 (1969).

ture, three oxygen atoms and a lone pair of electrons being bound tetrahedrally around the central sulfur atom; they do not possess a strict three-fold symmetry. The O–S distances range from 1.47 to 1.56 Å, the values of the S–O–O angles being 106°—111°. In the crystals of $(NH_4)_2SO_3\cdot H_2O$[13] and $NiSO_3\cdot 6H_2O$[14] containing ionic sulfito groups, the mean values of the S–O distances and the O–S–O angles are 1.53 Å and 104° respectively, whereas, in the crystals of $[Co(SO_3)(SCN)en_2]$ and $[Pd(SO_3)(NH_3)_3]$[15] involving the coordinated sulfito groups, the corresponding values are 1.49 Å and 110° respectively.

The planes formed by O(1), O(2), and O(3), and O(4), O(5), and O(6), are approximately perpendicular to the Co–S(1) and Co–S(2) bonds respectively (*cf.*, Fig. 5(a)).

The intermolecular distances, Co–N(NH_3), are 1.98—2.01 Å and are quite normal, with the exception only of 2.07 Å of Co–N(4), which is slightly longer.

The nitrogen and sulfur atoms are displaced from the regular octahedral positions around the central cobalt atom. The displacement is irregular, though the geometry is partially kept almost regular as may be seen in, for example, the dimensions of two of the triangles formed by three nitrogens. Mainly as a result of the repulsions between the non-bonded oxygen atoms belonging to different sulfito groups, the S-Co-S angle is larger than 90° (Fig. 5(b)) and two sulfito groups are located so as to keep their oxygen atoms at distances longer than 3.17 Å from those in another (Fig. 6 and Table 3). This distortion of the complex anion from the regular octahederal configuration seems to make the complex more photochemically decomposable than another isomer.[4]

The crystal is essentially ionic. The layers of the complex anions and those of the ammonium ions are alternately piled up, approximately parallel with the (120) and (1$\bar{2}$0) planes. The interstices among the complex anions form channels, which are elongated along the *c* and *a* axes and which are packed with ammonium ions and water molecules (Fig. 7).

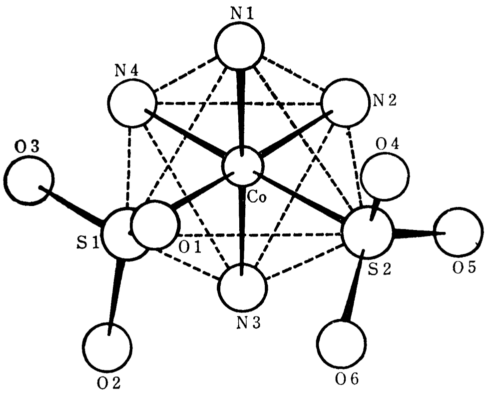

Fig. 6. A drawing of the complex anion, viewed along the direction perpendicular to the plane composed of three nitrogen atoms, N(2), N(3), and N(4). The displacement of sulfur and nitrogen atoms from their regular octahedral positions and the relative locations of oxygen atoms belonging to different SO_3 groups are also shown.

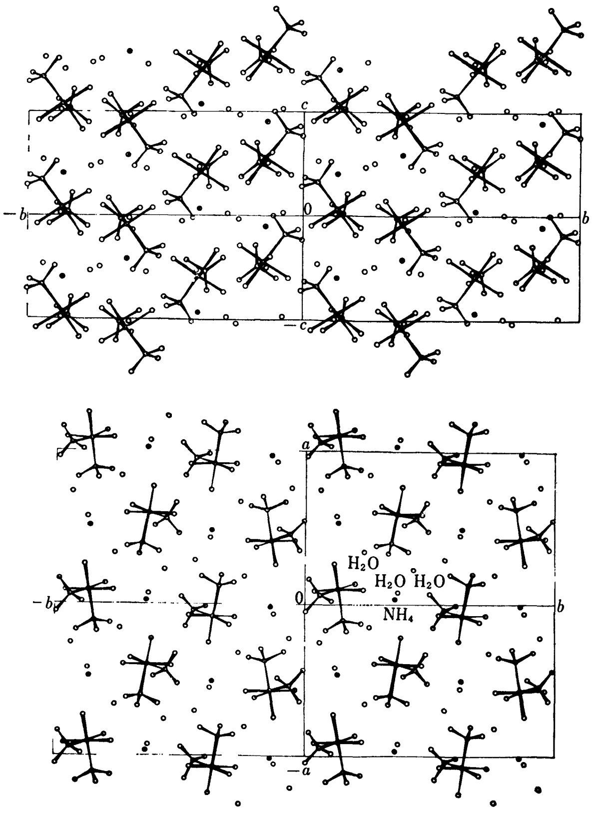

Fig. 7. Arrangement of the complex anions, ammonium ions, and water molecules in the crystal lattice.

A complex anion is surrounded by six ammonium ions: four closest $N\cdots NH_4$ and two $O\cdots NH_4$ approaches can be found at distances ranging from 3.22 to 3.62 Å (Table 4).

TABLE 4. SIX CLOSER APPROACHES FROM AMMONIUM IONS TO NITROGEN AND OXYGEN ATOMS IN ANIONS

Reference atom at (*x*,*y*,*z*)	Distances
N(1)-N(5) at (*x*, *y*, 1+*z*)	3.50(3)Å
N(2)-N(5) at (1/2+*x*, 1/2−*y*, −*z*)	3.48(3)
N(3)-N(5) at (−*x*, −1/2+*y*, −1/2−*z*)	3.22(3)
N(4)-N(5) at (*x*, *y*, *z*)	3.62(3)
O(1)-N(5) at (−1/2+*x*, 1/2−*y*, −*z*)	3.61(3)
O(6)-N(5) at (−*x*, −1/2+*y*, −1/2−*z*)	3.47(3)

The closest $O\cdots N$ contact occurs at a distance of 2.69 Å between NH_4 and H_2O (9^a), the closest $O\cdots O$ distance being 2.69 Å between O(1) and H_2O (7^f) and the closest $N\cdots N$ distance being 3.22 Å between N(3) and $NH_4{}^d$, while the van der Waals radii are 1.50 Å for nitrogen and 1.40 Å for oxygen. Intermolecular contacts less than 3.22 Å are presented in Table 5, while the short contacts in the structure are shown in Fig. 8. The complex anions are held together in the crystal by hydrogen bonds of the $N-H\cdots O$ and $O-H\cdots O$ types. These bonds involve each complex anion in a three-dimensional bonding network.

In the present structural study, the configuration of the dark brown ammonium trihydrate salt, NH_4-

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[13] L. F. Battle and K. N. Trueblood, *Acta Cryst.*, **19**, 531 (1965).

[14] S. Baggio and L. N. Becka, *ibid.*, **B25**, 1150 (1969).

[15] M. A. Spinnler and L. N. Becka, *J. Chem. Soc.*, *A*, **1967**, 1195.

TABLE 5. INTERMOLECULAR CONTACTS LESS THAN 3.22 Å AND THEIR e.s.d.'s. IN PARENTHESES

Superscripts used are as follows:

No symbol	x,	y,	z
a)	x,	y,	$-1+z$
b)	$1/2+x$,	$1/2-y$,	$-z$
c)	$1/2-x$,	$-y$,	$-1/2+z$
d)	$-x$,	$-1/2+y$,	$-1/2-z$
e)	$-1/2+x$,	$1/2-y$,	$-z$
f)	$-1/2+x$,	$1/2-y$,	$1-z$
g)	$-x$,	$-1/2+y$,	$1/2-z$

N(1)-O(7)	3.17(3)Å	N(5)-O(7^e)	2.83(3)Å
N(1)-O(8)	3.05(3)	O(1)-O(7^f)	2.69(2)
N(2)-O(3^b)	3.04(2)	O(1)-O(9^e)	3.06(2)
N(2)-O(5^c)	3.02(3)	O(2)-O(8^e)	3.02(2)
N(3)-O(4^a)	3.06(2)	O(2)-O(9^e)	2.82(2)
N(3)-O(5^c)	2.91(2)	O(2)-O(9^g)	2.81(2)
N(3)-N(5^d)	3.22(3)	O(3)-O(7^e)	2.72(2)
N(4)-O(4^a)	2.98(3)	O(6)-O(9^f)	3.13(2)
N(4)-O(1^b)	3.17(2)	O(6)-O(8^g)	2.72(2)
N(5)-O(9^a)	2.69(3)	O(6)-O(9^g)	2.83(2)
N(5)-O(8)	2.87(3)	O(1)-O(8^e)	3.22(2)

$[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$, has been established as the *cis* form. It may also be concluded that the brown sodium salt with an absorption spectrum similar to that of the present substance is the *cis* isomer. The results thus obtained are consistent with those of several other studies.[3-6]

Both of the sulfito groups are pyramidal and are bonded to the cobalt through the sulfur atom.This is consistent with the prediction of Shimura.[2] The large value of the molar extinction coefficient in the charge-transfer band (log $\varepsilon=4.20$) can be reasonably explained by the coordination of the sulfito group through the sulfur.

During the preparation of the manuscript of this report, a short communication about the structure of this complex anion has been published by other workers.[16]

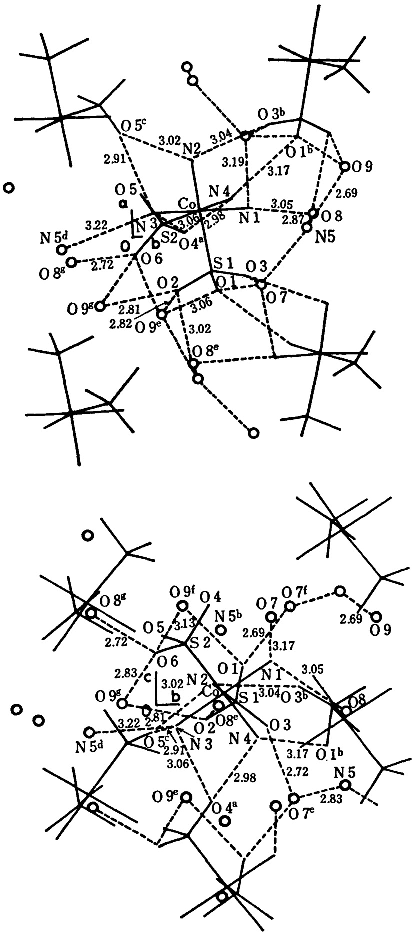

Fig. 8. Intermolecular contacts less than 3.22 Å.

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