(with voluminous documentation) by Rillema and Endicott[16] so the present result is not unexpected. When Mn(III) is the oxidant, the agreement is rather poor—but this is the only system considered in which the metal ion exchange reaction has not been directly measured. For the other entries it is evident that there is a reasonable correlation between the theoretical and experimental values.

The result that the absolute values calculated for ΔF^* in the oxidation of benzo- and toluhydroquinones by Np(VI) and Fe(III) are in such good agreement with experimental results may be, in part, fortuitous. This is evident for the systems in which Fe(III) is the oxidant. For these cases there is an ambiguity in the mechanism that arises from the term in the rate law inverse in hydrogen ion concentration. Marcus[9] assumed that this term was a reflection of the pre-equilibrium $QH_2 = QH^- + H^+$. The differences $\Delta F^*_{\text{calcd}} - \Delta F^*_{\text{exptl}}$ he reported were 1.1 and 1.6 kcal/mol for the benzo- and toluhydroquinones, respectively. In spite of some reservations, however, it appears that the Marcus cross relation concept may be applicable to the class of reversible organic redox reactions.

Registry No. Neptunium, 7439-99-8; H_2Q, 123-31-9; CH_3H_2Q, 95-71-6.

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Crystal Structure of *l*-Tris(1,10-phenathroline)iron(II) Bis(antimony(III) *d*-tartrate) Octahydrate[1]

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The compound *l*-tris(1,10-phenanthroline)iron(II) bis(antimony(III) *d*-tartrate) octahydrate, $Fe(C_{12}N_2H_8)_3(C_4O_6H_2Sb)_2 \cdot 8H_2O$, crystallizes in the trigonal space group $P3_221$. Three formula units occupy a unit cell of dimensions $a = 18.58$ (2) and $c = 12.04$ (2) Å. Intensities were measured by the stationary-crystal, stationary-counter technique using a scintillation counter and Mo Kα X-rays. The structure was refined by full-matrix least-squares to a conventional R factor of 0.048 for 1600 reflections whose intensities were observed to be greater than their estimated standard deviations. The structure consists of a ferrous tris(1,10-phenanthroline) cation and a bis(antimonous *d*-tartrate) anion. The iron atom lies on a twofold axis and is octahedrally coordinated to the nitrogen atoms of the three phenanthroline groups at an average distance of 1.97 (1) Å. The antimony tartrate complex is a dimer in which each of the two antimony atoms is coordinated to four oxygen atoms of the tartrate; Sb–O distances average 1.94 (1) and 2.13 (2) Å, respectively, for alcohol and carboxyl oxygen atoms. The absolute configurations of the complex ions were determined by the anomalous dispersion effect. The cation Λ-$(-)_{589}[Fe(phen)_3]^{2+}$, phen = phenanthroline, has a pseudo-threefold axis and resembles a three-bladed left-handed propeller, the blades being the planar phenanthroline ligands. The configuration of the *d*-tartrate in the $[Sb(+)tart]_2{}^{2-}$ ion is in agreement with previous determinations.

Introduction

Ferrous ion and 1,10-phenanthroline make octahedral complexes which exist in enantiomers that can be resolved by precipitation of the *l* isomer with antimony *d*-tartrate as shown by Dwyer and Gyarfas.[2] Professor R. E. Powell of this University provided us with crystals of this precipitate and suggested that we determine the structure and absolute configuration by X-ray diffraction to permit a check of methods of configuration determination by theoretical analysis of the optical properties. This paper reports such a study.[3] We show that the $(-)[Fe(phen)_3]^{2+}$ which precipitates with *d*-tartrate is in the conformation of a left-handed propeller, in agreement with the assignment of McCaffery, Mason, and Norman[4] on the basis of analysis of circular dichroism, thus providing a confirmation of the validity of that method.

Another result of this study is that the antimony tartrate, which has been formulated classically in tartar emetic and similar salts as "antimonyl tartrate," $SbO(C_4H_4O_6)^-$, or sometimes[5] as $H_2OSb(C_4H_2O_6)^-$, exists in this crystal as a cyclic dimer of composition $((C_4H_2O_6)Sb)_2{}^{2-}$. In this complex Sb(III) has displaced hydrogen from the alcohol groups as well as the carboxyl groups and is complexed only by tartrate. The same complex anion has been found by Kiosse, Golovastikov, and Belov[6] in *dl*-$(NH_4)_2Sb_2(C_4H_2O_6)_2 \cdot 4H_2O$, by Kiosse, Golovastikov, Ablov, and Belov[7] in *d*-$(NH_4)_2Sb_2(C_4H_2O_6)_2 \cdot 3H_2O$, and by Kamenar, Grdenic, and Prout[8] in *dl*-$K_2Sb_2(C_4H_2O_6)_2 \cdot 3H_2O$. Earlier reports[9] of a different structure for this anion in the *d,l* K salt have been revised,[8] and the dimer structure is the only one known in crystals.

Experimental Section

The sample of *l*-ferrous tris(1,10-phenanthroline) bis(antimonous *d*-tartrate) octahydrate consisted of crystals in the form of small deep red needles. A fragment ~0.1 mm in diameter and ~0.3 mm in length was glued to a Pyrex fiber, and subsequent Weissenberg photography showed the needle axis to be c of a trigonal unit cell. Cell dimensions and intensities were measured with a manual General

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, 83, 263 (1950).

[3] For a preliminary account, see D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr.*, 21, A154 (1966).

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[8] B. Kamenar, D. Grdenic, and C. K. Prout, *Acta Crystallogr., Sect. B*, 26, 181 (1970).

[9] D. Grdenic and B. Kamenar, *Acta Crystallogr.*, 16, A40 (1963); 19, 197 (1965).

Electric XRD-5 X-ray diffraction apparatus equipped with a quarter-circle Eulerian-cradle goniostat and a scintillation counter with pulse height discrimination. Mo Kα X-rays, λ 0.70926 Å for Kα_1, filtered by a 0.003 in. thick Zr filter on the receiving slit were used for the measurements. The X-ray tube was operated at 40 kV and 20 mA. The crystal was so oriented that the c axis was parallel to the ϕ axis of the instrument.

Counts of 10-sec duration were made of 1748 independent reflections using a stationary-counter, stationary-crystal technique; these include all the reflections whose indices are positive and whose Bragg angles are less than 22.5°. The diffractometer was set at a 4° takeoff angle to the tube. Background was plotted as a function of 2θ and these values were used for most of the intensities; in cases where background was affected by streaking, individual backgrounds were measured. Typical backgrounds between 20 and 45° of 2θ were from 2 to 4 counts/sec. The 032 reflection was the most intense (7856 cps). The net intensity was less than its estimated standard deviation for 144 reflections. In the least-squares refinements these data were assigned zero weights. The data were corrected for the Lorentz–polarization factors, and no correction was made for absorption. The absorption coefficient μ is estimated to be 15 cm^{-1}. No extinction correction was found necessary.

In the course of some experiments using Cu Kα radiation, the cell dimensions were observed to be very much affected by relative humidity. When the relative humidity, as read from a simple Abbeon relative humidity indicator, read 30%, the trigonal cell dimensions were calculated to be $a = 18.55$ and $c = 12.00$ Å; at 46% they swelled to 18.61 and 12.04 Å. This behavior is somewhat similar to that we observed in collecting data for Ferrichrome A.[10] Had we had fluctuations to the limits of the two extremes in humidity reported above, the error in the 2θ angle at 45° with Mo X-rays would have been about 0.15°; this would not produce a serious setting error, and in fact no problem was noticed during the manual collection of the data. With copper radiation, setting errors are serious; at a comparable $(\sin\theta)/\lambda$ value the error would be about 0.6°. We collected some 8000 scanned intensities on a second crystal using Cu Kα radiation with an automatic diffractometer, but we abandoned the set for two reasons. We lacked confidence in the settings due to humidity changes that occurred during the 2 weeks required to collect the data, even though we attempted daily modifications of the cell dimensions. Second, Cu data suffer much more from absorption. We made some refinements using the Cu data, and the resulting coordinates were within two standard deviations of the results from the manually collected Mo data we report here.

Fourier, least-squares, and distance calculations were performed using our own unpublished programs on a Control Data Corp. 6600 computer. The full-matrix least-squares program minimizes the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$; F_o and F_c are the observed and calculated structure factors, and w is the weighting factor. Atomic scattering factors for Sb^{3+}, Fe^{2+}, neutral O, N, C, and H were used,[11,12] and both the real and imaginary parts of the anomalous dispersion correction[13] for Sb and Fe were included in the least-squares calculations. Anisotropic temperature factors used have the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; for convenience the thermal parameters are reported here as B_{ij}, in units Å^2, where $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$ and $a_i{}^*$ is the ith reciprocal cell length. The weighting on each reflection, w, was set to $(\sigma(F_o))^{-2}$ with the exception that $w = 0$ when I(net count) $\leqslant \sigma(I)$. The standard deviation of the observed structure factor was calculated as $\sigma(F_o) = F_o - (F_o{}^2 - s\sigma(I)/Lp)^{1/2}$, where s is a scaling factor, $F_o = (sI/Lp)^{1/2}$, and Lp is the Lorentz–polarization correction. $\sigma(I) = (I + p^2I^2 + 2B)^{1/2}$, where p is an estimated fractional uncertainty in I, and B is the background. A value of $p = 0.07$ was found necessary to reduce the weights of the intense reflections so that their weighted residuals were comparable to those of lesser intensity.

Table I. Atomic Coordinates[a]

ATOM	X	Y	Z
FE	-.3985(1)	0	-1/3
SB	-.48029(7)	-.34732(6)	-.39066(7)
O(1)	-.2399(9)	-.2714(8)	-.3044(9)
O(2)	-.3769(9)	-.3256(7)	-.2931(8)
O(3)	-.3931(6)	-.3003(7)	-.5013(7)
O(4)	-.6430(7)	-.5199(8)	-.6147(8)
O(5)	-.5627(6)	-.3996(7)	-.5308(7)
O(6)	-.5023(6)	-.4609(6)	-.3872(6)
O(7)	.110(1)	.069(1)	-.399(1)
O(8)	.277(1)	.079(1)	-.421(1)
O(9)	.155(2)	.229(1)	-.298(2)
O(10)	-.066(2)	-.317(2)	-.099(2)
N(1)	-.3499(6)	-.0604(6)	-.2624(7)
N(2)	-.3582(6)	.0845(6)	-.2140(8)
N(3)	-.4396(6)	.0705(6)	-.3976(7)
C(1)	-.307(1)	-.291(1)	-.344(1)
C(2)	-.310(1)	-.272(1)	-.464(1)
C(3)	-.589(1)	-.476(1)	-.544(1)
C(4)	-.559(1)	-.5182(9)	-.465(1)
C(5)	-.3820(9)	-.1206(9)	-.191(1)
C(6)	-.339(1)	-.156(1)	-.145(1)
C(7)	-.262(2)	-.132(1)	-.176(1)
C(8)	-.139(1)	-.029(1)	-.298(1)
C(9)	-.222(1)	-.065(1)	-.255(1)
C(10)	-.2703(8)	-.0325(9)	-.296(1)
C(11)	-.3121(8)	.0927(8)	-.125(1)
C(12)	-.2835(8)	.1602(9)	-.056(1)
C(13)	-.3052(8)	.2193(8)	-.0698(9)
C(14)	-.3784(9)	.2716(9)	-.190(1)
C(15)	-.4249(8)	.2618(8)	-.279(1)
C(16)	-.4924(8)	.1826(8)	-.453(1)
C(17)	-.5072(9)	.117(1)	-.522(1)
C(18)	-.4803(7)	.0623(8)	-.4919(9)
C(19)	-.3547(8)	.2125(8)	-.161(1)
C(20)	-.4488(7)	.1931(7)	-.3564(9)
C(21)	-.4245(7)	.1355(8)	-.3308(9)
C(22)	-.3774(8)	.1448(8)	-.2329(9)
H(1)	-.443	-.142	-.167
H(2)	-.368	-.206	-.089
H(3)	-.231	-.158	-.143
H(4)	-.103	-.051	-.271
H(5)	-.298	.048	-.110
H(6)	-.247	.166	.012
H(7)	-.284	.268	-.015
H(8)	-.363	.321	-.141
H(9)	-.443	.304	-.295
H(10)	-.512	.222	-.475
H(11)	-.537	.111	-.594
H(12)	-.492	.013	-.542
H(13)	-.271	-.212	-.490
H(14)	-.610	-.566	-.424

[a] Numbers in parentheses here and in subsequent tables indicate estimated standard deviations of the least significant digits.

Table II. Anisotropic Thermal Parameters, Å^2 [a]

ATOM	B11	B22	B33	B12	B13	B23
FE	3.24(8)	2.76	2.12(8)	1.38(6)	-.07(4)	-.14
SB	7.16(7)	4.92(5)	3.54(4)	4.12(5)	1.03(4)	.31(4)
O(1)	8.3(8)	8.0(7)	5.7(5)	4.1(6)	-2.9(6)	-1.9(5)
O(2)	8.6(8)	5.0(6)	3.7(5)	2.8(5)	.1(5)	.2(4)
O(3)	5.9(5)	6.5(6)	3.9(4)	3.6(5)	.4(4)	1.7(4)
O(4)	6.2(6)	8.5(7)	5.6(5)	5.1(6)	-1.7(5)	.4(5)
O(5)	6.0(5)	5.5(6)	4.8(5)	4.2(5)	-.4(4)	.6(4)
O(6)	5.7(5)	4.7(5)	2.2(4)	3.1(4)	-.4(3)	.2(3)
O(7)	12.9(13)	10.0(11)	9.1(8)	5.1(9)	.1(8)	-.2(8)
O(8)	15.0(14)	14.6(15)	8.5(9)	3.1(12)	1.1(9)	-5.7(9)
O(9)	17.7(19)	15.4(17)	17.8(16)	10.0(15)	-6.1(15)	-5.1(14)
O(10)	27.3(27)	18.8(20)	20.1(19)	17.5(19)	11.1(19)	5.9(16)
N(1)	3.6(6)	2.7(5)	3.1(4)	1.4(4)	.2(4)	.1(4)
N(2)	3.5(5)	3.5(5)	2.6(4)	1.9(4)	-.4(4)	.1(4)
N(3)	3.8(5)	3.5(5)	2.0(4)	1.9(4)	.2(4)	-.0(4)
C(1)	7.6(11)	5.4(9)	4.3(8)	3.9(9)	-2.1(9)	-1.5(7)
C(2)	7.4(10)	5.5(8)	3.8(7)	3.5(8)	-.4(6)	.4(6)
C(3)	5.7(8)	6.0(9)	2.2(5)	4.3(8)	-.4(6)	.3(6)
C(4)	4.2(7)	6.2(8)	3.2(6)	3.1(7)	.7(6)	.1(6)
C(5)	4.8(8)	3.9(7)	3.8(6)	2.8(6)	-.8(6)	-.9(5)
C(6)	7.1(11)	6.2(9)	3.4(7)	4.1(8)	.1(7)	.3(6)
C(7)	9.6(13)	7.9(11)	6.1(9)	7.2(10)	-2.8(10)	-2.4(9)
C(8)	7.3(11)	11.9(18)	5.8(10)	7.0(12)	-.3(8)	.0(9)
C(9)	5.5(9)	7.4(10)	4.7(7)	4.0(8)	-.4(7)	.0(8)
C(10)	3.8(7)	4.6(8)	3.3(6)	1.9(6)	-1.0(5)	-1.0(5)
C(11)	2.9(6)	3.5(7)	3.7(6)	1.4(5)	-.4(5)	.5(5)
C(12)	3.8(7)	4.0(7)	3.2(6)	1.4(6)	-.4(5)	-.8(5)
C(13)	3.6(6)	3.7(7)	2.7(5)	.9(5)	-.6(5)	-1.6(5)
C(14)	4.7(8)	4.6(8)	3.4(6)	2.3(6)	.4(6)	-.2(5)
C(15)	4.6(7)	2.7(6)	5.0(7)	2.7(6)	1.5(6)	1.1(5)
C(16)	4.3(7)	3.8(6)	4.2(6)	2.3(6)	-.3(5)	.9(5)
C(17)	3.8(7)	5.8(8)	2.9(5)	2.4(6)	-1.0(5)	.0(5)
C(18)	3.3(6)	3.6(6)	2.5(5)	1.2(5)	-.2(5)	.5(4)
C(19)	3.9(6)	2.3(5)	3.1(5)	1.5(5)	.5(5)	-.6(5)
C(20)	3.2(5)	2.8(6)	3.2(5)	1.6(5)	.3(4)	.2(5)
C(21)	3.2(6)	3.7(6)	2.2(5)	1.5(5)	.5(4)	.3(5)
C(22)	2.9(6)	3.6(6)	2.1(5)	1.3(5)	.6(4)	1.1(5)

[a] For Fe, $B_{22} = 2B_{12}$ and $B_{23} = 2B_{13}$ because of the site symmetry.

Results

Unit Cell and Space Group. The cell dimensions are $a = 18.58 \pm 0.02$ and $c = 12.04 \pm 0.02$ Å at ~24°; the accuracy is limited by the humidity effect and these reported values are estimated to have been measured when the relative humidity was between 35 and 40%. The observed Laue symmetry of the reflections is $\bar{3}m1$. The observed setting of the symmetry, $I(hkl) = I(kh\bar{l})$, the known asymmetry of the molecules, and the observed absences of $00l$ if $l \neq 3n$ indicate the enantiomorphic pair of space groups $P3_121$ and $P3_221$ as the sole choices; anomalous dispersion effects established the space group to be $P3_221$ ($D_3{}^6$). Allowing for three formula units per unit cell, the calculated X-ray density is 1.77 g/cm^3.

Structure Determination. The positions of the iron and antimony atoms were readily determined from a three-di-

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(10) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Amer. Chem. Soc.*, 88, 1810 (1966).

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Table III. Distances and Angles in the $Fe(phen)_3$ Cation

Distances, Å

Fe-N(1)	1.96 (1)	C(5)-C(6)	1.39 (2)	C(13)-C(19)	1.39 (2)
Fe-N(2)	1.98 (1)	C(6)-C(7)	1.32 (3)	C(14)-C(15)	1.33 (2)
Fe-N(3)	1.97 (1)	C(7)-C(9)	1.44 (3)	C(15)-C(20)	1.46 (2)
N(1)-C(5)	1.30 (2)	C(8)-C(8)	1.26 (4)	C(16)-C(17)	1.38 (2)
N(1)-C(10)	1.36 (2)	C(8)-C(9)	1.44 (3)	C(16)-C(20)	1.37 (2)
N(2)-C(11)	1.33 (2)	C(9)-C(10)	1.39 (2)	C(17)-C(18)	1.39 (2)
N(2)-C(22)	1.35 (2)	C(10)-C(10)	1.38 (3)	C(19)-C(22)	1.41 (2)
N(3)-C(18)	1.33 (2)	C(11)-C(12)	1.38 (2)	C(20)-C(21)	1.39 (2)
N(3)-C(21)	1.36 (2)	C(12)-C(13)	1.36 (2)	C(21)-C(22)	1.43 (2)

Angles, Deg

N(1)-Fe-N(1)	82.9 (3)	C(6)-C(7)-C(9)	119 (2)	C(16)-C(17)-C(18)	120 (2)
N(1)-Fe-N(2)	92.2 (5)	C(8)-C(8)-C(9)	123 (2)	N(3)-C(18)-C(17)	122 (2)
N(1)-Fe-N(2)	89.4 (5)	C(7)-C(9)-C(8)	128 (2)	C(13)-C(19)-C(14)	125 (2)
N(1)-Fe-N(3)	94.7 (6)	C(7)-C(9)-C(10)	116 (2)	C(13)-C(19)-C(22)	117 (2)
N(1)-Fe-N(3)	174.6 (7)	C(8)-C(9)-C(10)	116 (2)	C(14)-C(19)-C(22)	118 (2)
N(2)-Fe-N(2)	177.9 (3)	N(1)-C(10)-C(9)	123 (2)	C(15)-C(20)-C(16)	124 (2)
N(2)-Fe-N(3)	82.9 (5)	N(1)-C(10)-C(10)	116 (2)	C(15)-C(20)-C(21)	117 (2)
N(2)-Fe-N(3)	95.6 (5)	C(9)-C(10)-C(10)	121 (2)	C(16)-C(20)-C(21)	118 (2)
N(3)-Fe-N(3)	88.1 (3)	N(2)-C(11)-C(12)	122 (2)	N(3)-C(21)-C(20)	123 (1)
C(5)-N(1)-C(10)	118 (2)	C(11)-C(12)-C(13)	122 (2)	N(3)-C(21)-C(22)	116 (1)
C(11)-N(2)-C(22)	117 (2)	C(12)-C(13)-C(19)	118 (2)	C(20)-C(21)-C(22)	120 (2)
C(18)-N(3)-C(21)	117 (2)	C(15)-C(14)-C(19)	122 (2)	N(2)-C(22)-C(19)	123 (2)
N(1)-C(5)-C(6)	123 (2)	C(14)-C(15)-C(20)	122 (2)	N(2)-C(22)-C(21)	116 (1)
C(5)-C(6)-C(7)	120 (2)	C(17)-C(16)-C(20)	119 (2)	C(19)-C(22)-C(21)	121 (2)

Table IV. Distances and Angles in the Bis(antimony tartrate) Anion

Distances, Å

Sb-O(3)	1.94 (1)	O(5)-C(3)	1.27 (2)
Sb-O(6)	1.94 (1)	O(3)-C(2)	1.44 (2)
Sb-O(2)	2.11 (2)	O(6)-C(4)	1.41 (2)
Sb-O(5)	2.16 (2)	C(1)-C(2)	1.50 (2)
O(1)-C(1)	1.21 (2)	C(3)-C(4)	1.50 (2)
O(4)-C(3)	1.26 (2)	C(2)-C(2)	1.49 (4)
O(2)-C(1)	1.28 (2)	C(4)-C(4)	1.56 (3)

Angles, Deg

O(2)-Sb-O(3)	79.7 (6)	O(1)-C(1)-C(2)	117 (2)
O(2)-Sb-O(5)	153.5 (7)	O(2)-C(1)-C(2)	116 (2)
O(2)-Sb-O(6)	82.7 (5)	O(3)-C(2)-C(1)	111 (2)
O(3)-Sb-O(5)	84.9 (5)	O(3)-C(2)-C(2)	109 (2)
O(3)-Sb-O(6)	100.3 (6)	C(1)-C(2)-C(2)	112 (2)
O(5)-Sb-O(6)	79.1 (5)	O(4)-C(3)-O(5)	123 (2)
Sb-O(2)-C(1)	115.3 (8)	O(4)-C(3)-C(4)	119 (2)
Sb-O(3)-C(2)	117.3 (7)	O(5)-C(3)-C(4)	118 (2)
Sb-O(5)-C(3)	113.0 (7)	O(6)-C(4)-C(3)	111 (2)
Sb-O(6)-C(4)	118.6 (7)	O(6)-C(4)-C(4)	112 (2)
O(1)-C(1)-O(2)	127 (2)	C(3)-C(4)-C(4)	108 (2)

Table V. Distances and Angles Involving Water Oxygen Atoms

Distances, Å

O(7)-O(7)	2.73 (4)	O(8)-O(10)	2.90 (4)
O(7)-O(7)	2.77 (3)	O(9)-O(1)	2.88 (3)
O(7)-O(9)	2.93 (3)	O(10)-O(10)	2.69 (5)
O(7)-O(8)	3.03 (3)	O(10)-O(4)	2.73 (3)
O(8)-O(1)	2.74 (2)		

Angles, Deg

O(7)-O(7)-O(7)	135 (1)	O(1)-O(8)-O(10)	105 (1)
O(7)-O(7)-O(8)	109 (1)	O(7)-O(8)-O(10)	76 (1)
O(7)-O(7)-O(9)	94 (1)	O(1)-O(9)-O(7)	108 (1)
O(7)-O(7)-O(8)	95 (1)	O(4)-O(10)-O(8)	112 (1)
O(7)-O(7)-O(9)	119 (1)	O(4)-O(10)-O(10)	113 (1)
O(8)-O(7)-O(9)	103 (1)	O(8)-O(10)-O(10)	128 (1)
O(1)-O(8)-O(7)	101 (1)		

mensional Patterson map. The iron occupies a special position on a twofold axis, and all of the other atoms occupy the general sixfold set. A Fourier map phased on the Fe and Sb atoms resulted in the location of 19 of the 35 nonhydrogen atoms. The partial structure was refined to an R factor, $R = \Sigma|\Delta F|/\Sigma|F_o|$, of 0.20. A second Fourier map revealed the remaining atoms with the exception of the hydrogen and the water oxygen atoms. Further refinement of the structure followed by a difference Fourier map revealed four water oxygen atoms. Hydrogen atoms did not show up very well on the difference Fourier maps, and eventually the parameters of all but the water hydrogens

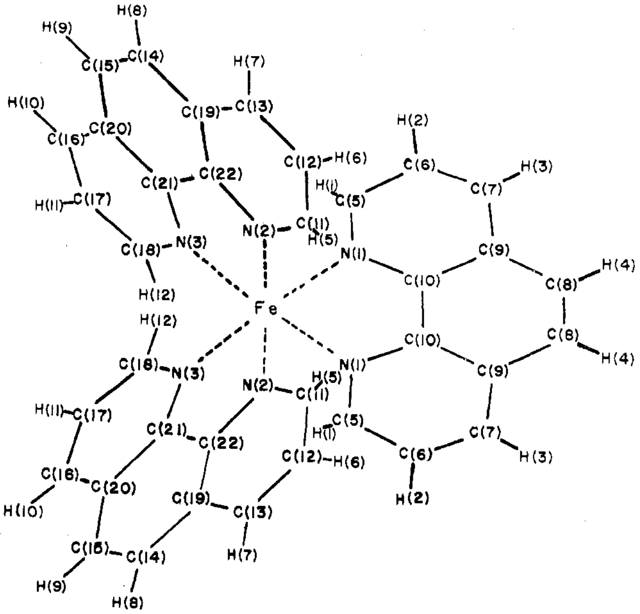

Figure 1. Diagram of the tris(1,10-phenathroline)iron(II) cation indicating the numbering system used.

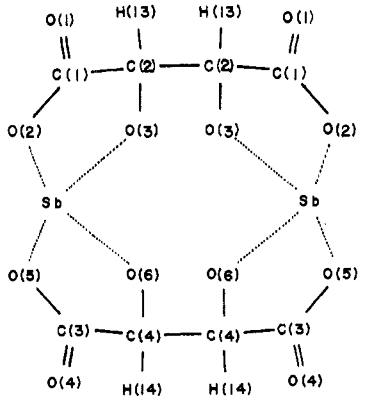

Figure 2. Diagram of the bis(antimony tartrate) anion indicating the numbering system used.

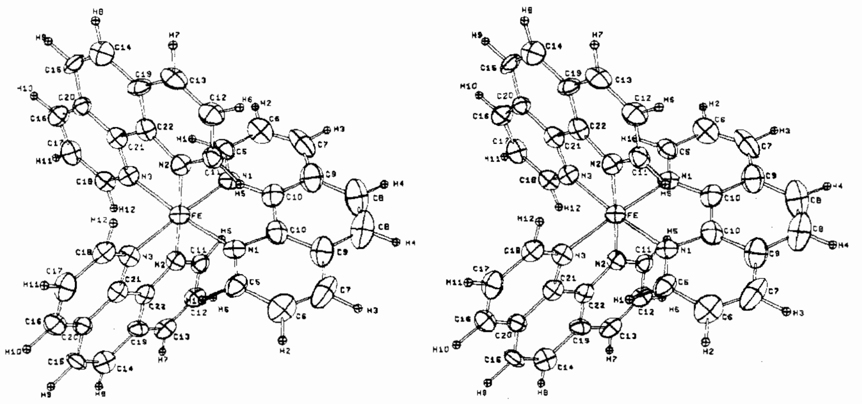

Figure 3. Stereoscopic view of the $(-)_{589}[Fe(phen)_3]^{2+}$ ion.

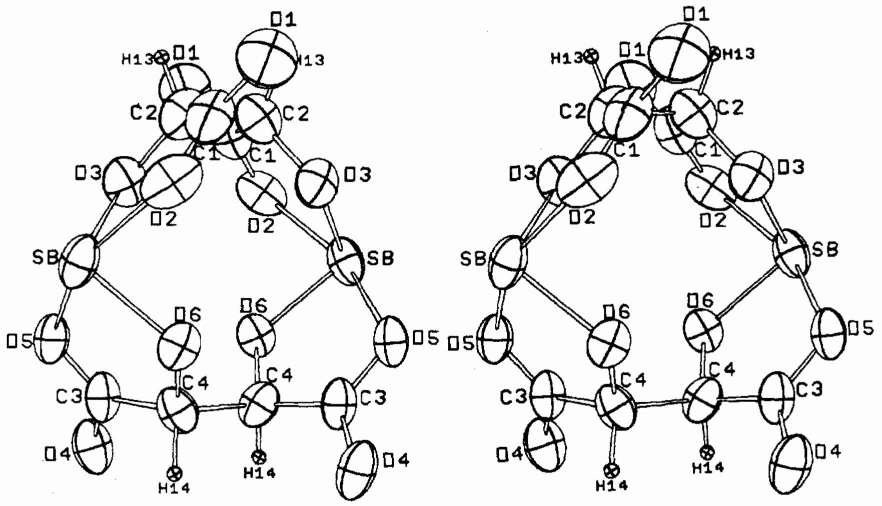

Figure 4. Stereoscopic view of the bis(antimony *d*-tartrate)$^{2-}$ ion.

were included but constrained to their estimated positions with a fixed isotropic thermal parameter of 5.0 Å^2. From the humidity effect it is evident that water is loosely bound in this crystal and most probably occurs in its sites with partial occupancy. This conclusion is supported by the large temperature parameters of the water oxygen atoms. Since there is no clear-cut ordered hydrogen-bond pattern in the water substructure, we could not estimate the hydrogen positions of the water molecules.

The results of the least-squares refinement are shown in Tables I and II. Figures 1 and 2 serve as guides to the numbering system. The refinement was arbitrarily started in space group $P3_121$, but this was changed to $P3_221$ in order that the configuration of the *d*-tartrate would be the same as that reported by van Bommel and Bijvoet.[14] The final R factor on 1600 nonzero weighted data is 0.048; the weighted R_2, $(\Sigma w(\Delta F)^2/\Sigma w|F_o|^2)^{1/2}$, is 0.056; the standard deviation of an observation of unit weight is 1.07; and the R factor for all 1748 data, including the zero-weighted ones, is 0.057. A table of observed and calculated structure factors is available upon request.[15]

A difference Fourier map based on the final set of parameters was calculated. The maximum peak height on this map was 0.8 e/Å^3. The largest peaks appear near the antimony atom, but no attempt was made to associate them with any electron pair structure.

A series of refinements made with the anomalous dispersion reversed resulted in R increasing from 0.048 to 0.052 and R_2 from 0.056 to 0.062. This is in agreement with the configuration for the *d*-tartrate determined by van Bommel and Bijvoet.[14] An additional experiment to check absolute configuration was performed using Cu Kα radiation to measure some 528 data including representatives of 117 Bijvoet pairs. The majority of these pairs showed significant differences in intensity, and the signs of these differences agreed in almost every case with the signs of the calculated differences of structure factor amplitudes. Refinement with this data set adjusting only the scale factor and the coordinates and anisotropic thermal parameters of Fe and Sb (hydrogen atoms omitted, other atoms with isotropic thermal parameters) reduced R to 0.06 with the correct configuration but only to 0.10 with the reverse configuration. For Cu Kα radiation, the imaginary terms for Fe and Sb are 3.5 and 5.8 electrons, respectively.

Description of the Structure

The cation consists of an iron atom complexed by three planar phenanthroline ligands to form a left-handed propeller-type structure; see Figure 3. In keeping with recent nomenclature proposals[16] this ion would be described as Λ-$(-)_{589}[Fe(phen)_3]^{2+}$, phen = phenanthroline. The ion itself lies on a crystallographic twofold axis, but its molecular symmetry is also very nearly threefold. The iron atom

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(14) A. J. van Bommel and J. M. Bijvoet, *Acta Crystallogr.*, 11, 61 (1958).

(15) A listing of structure factor amplitudes, standard deviations, and differences between observed and calculated amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1641.

(16) *Inorg. Chem.*, 9, 1 (1970).

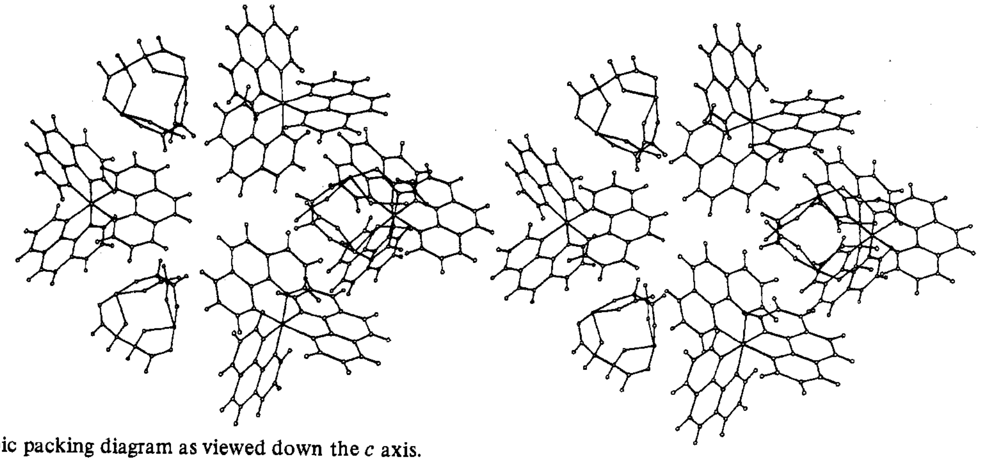

Figure 5. Stereoscopic packing diagram as viewed down the *c* axis.

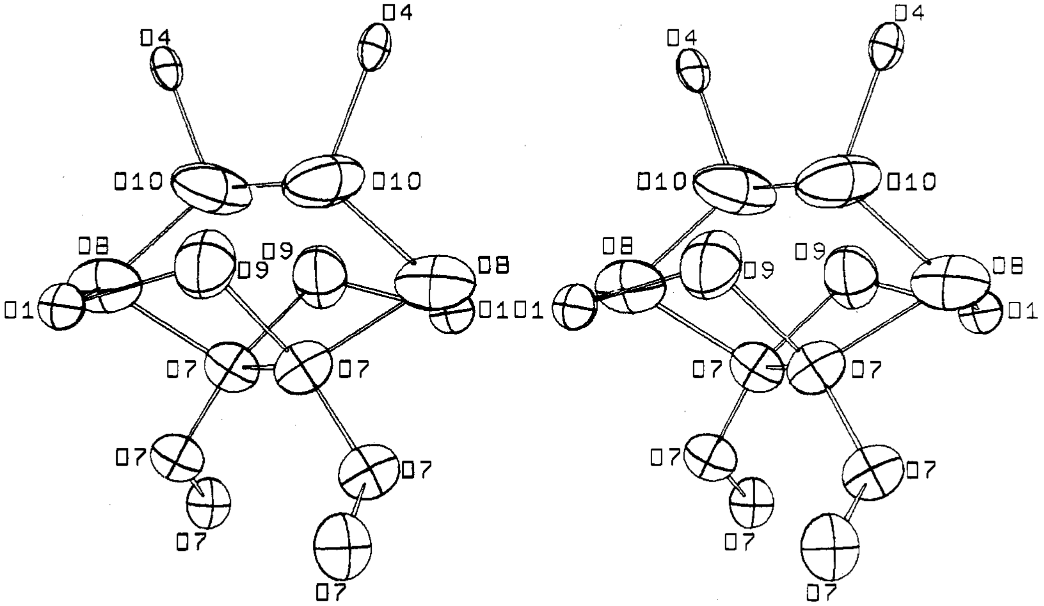

Figure 6. Stereoscopic view showing the water oxygen structure. Atoms O(7) through O(10) represent water oxygen atoms; O(1) and O(4) represent tartrate oxygen atoms.

is coordinated to all six nitrogen atoms of the three phenanthroline groups at an average distance of 1.97 ± 0.01 Å. A list of distances and angles in the cation is presented in Table III.

The anion consists of a dimer of antimony tartrate on a crystallographic twofold axis. Figure 4 shows a stereoscopic view of this ion. A list of distances and angles of this anion is shown in Table IV. Each antimony is coordinated to four oxygen atoms from the tartrate ligands, and there is no evidence in this study of any further coordination to the antimony, *i.e.*, an antimonyl oxygen. The nearest neighbors of Sb on its back side are atoms of the phenanthroline moieties, with Sb–C distances ranging upward from 3.79 Å. The same complex has been reported with very similar shape in the studies cited above.[6-8] Average distances are 2.13 Å for Sb–O (carbonyl) and 1.94 Å for Sb–O (alcohol), somewhat shorter than the corresponding average values reported for the other crystals: 2.15, 2.04 Å;[6] 2.18, 2.02 Å;[7] 2.20, 2.01 Å.[8]

The anion and cation pack in a way which is not simple to describe. A stereographic view of the structure looking down the threefold axis is shown in Figure 5. The closest approach of the cation to the anion occurs between O(6) in the anion and H(12) in the cation at a distance of 2.35 Å; the closest nonhydrogen approach is between O(5) in the anion and C(13) in the cation at a distance of 3.16 Å.

The water structure in this crystal is indicated in Figure 6; in this figure all contact distances less than 3.04 Å are indicated with a connection. The O(7) water molecules form a spiral in the direction of the *c* axis, and waters O(8), O(9), and O(10) form a structure with hydrogen bonding to O(1) and O(4) of the tartrate groups. The thermal parameters of the water molecules are large, suggesting incomplete occupancy and disorder. The observation that the cell dimensions change reversibly and radically with humidity is indicative that water can readily enter and leave the crystal and suggests that these sites were partially occupied under the conditions of the experiment. Disorder in the water structure is evident in the close approach across twofold axes of O(7) to another O(7) and similarly O(10) to O(10); for if the close approaches are due to hydrogen bonding, one must invoke disorder to describe the hydrogen atom positions.

One can identify three hydrogen bonds in Table V which must be ordered, since they are between water and carbonyl oxygen atoms. The other distances in the table provide only 4.5 bonds for the other five hydrogen atoms in the asymmetric unit, and all of these bonds have the possibility of alternate configurations for the hydrogen. The lack of a satisfactory unique hydrogen-bond configuration may contribute to the ease with which water can escape from the structure.

It is a common practice to identify a phase by its ideal composition when variable composition exists, and we refer to this crystalline phase as the octahydrate because that would be the composition if all the water sites were occupied.

Registry No. $Fe(C_{12}N_2H_8)_3(C_4O_6H_2Sb)_2 \cdot 8H_2O$, 40354-54-9.

Acknowledgment. We thank Professor Richard E. Powell for bringing this problem to our attention and providing us with crystals.

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Crystallographic Studies on Sulfur Dioxide Insertion Compounds. IV. Structure of μ-(Sulfur dioxide)-bis(π-cyclopentadienyldicarbonyliron), Including the Location and Refinement of Hydrogen Atoms

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The species μ-(sulfur dioxide)-bis(π-cyclopentadienyldicarbonyliron), $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 7.7028$ (17), $b = 17.1559$ (45), $c = 12.8488$ (27) Å; $\beta = 117.48$ (1)°; $Z = 4$. X-Ray diffraction data, complete to $2\theta = 55°$ (Mo Kα radiation), were collected with a Picker FACS-1 diffractometer, and the structure was solved by means of Patterson and Fourier syntheses. All atoms, including hydrogens, have been located; convergence of the least-squares refinement process occurred with $R_F = 3.01\%$ and $R_{wF} = 3.63\%$ for the 3472 independent reflections. The SO_2 moiety is "inserted" symmetrically between two iron atoms, with Fe(1)-S = 2.2790 (6) Å and Fe(2)-S = 2.2814 (7) Å. Sulfur-oxygen distances are S-O(1) = 1.4797 (15) Å and S-O(2) = 1.4764 (14) Å.

Introduction

The "insertion"[1] of sulfur dioxide into transition metal-carbon bonds has been studied in detail, principally by Wojcicki and his coworkers.[2] We have previously determined the crystal and molecular structures of diverse products of this class of reaction, *viz.*, $C_4H_6Fe(CO)_3 \cdot SO_2 \cdot BF_3$,[3] $\pi\text{-}C_5H_5Fe(CO)_2C_4H_5SO_2$,[4] and $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2\text{-}CH_2CH{=}CHC_6H_5$,[5] and are now extending our studies to species in which an SO_2 molecule is inserted into a metal-metal bond. The present article concerns the structure of $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$ which is formed by the reaction of $\pi\text{-}C_5H_5Fe(CO)_2Na$ and SO_2 in tetrahydrofuran.[6] $[\pi\text{-}C_5H_5\text{-}Fe(CO)_2]_2SO_2$ represents the first example of a neutral molecule in which two transition metal atoms are linked together solely by means of an SO_2 "bridge." It should be noted, however, that certain ionic species, *e.g.*, $[(NC)_5Co(SO_2)Co(CN)_5{}^{6-}]$[7] and $[(OC)_5M(SO_2)M(CO)_5{}^{2-}]$ (M = Cr, W),[8] have previously been synthesized. Examples of Sn-(SO_2)-Sn and Fe-(SO_2)-Sn systems have also been documented.[9]

Collection and Correction of the X-Ray Diffraction Data

Red crystals of $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$ were provided by Professor A. Wojcicki of the Ohio State University. A preliminary survey of $h(0\text{-}2)l$ and $(0\text{-}2)kl$ precession photographs, together with a and b cone-axis photographs, yielded approximate cell dimensions, indicated C_{2h} ($2/m$) Laue symmetry, and showed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14).

The crystal used for data collection had an approximately rectangular cross section with the bounding faces being (100), $(\bar{1}00)$, $(0\bar{1}0)$, and a slightly damaged and rounded (010) face which approximated in orientation to the (1,17.6,0) plane. [Dimensions were (100) → $(\bar{1}00)$ = 0.41 mm and $(0\bar{1}0)$ → "(1,17.6,0)" = 0.23 mm.] The crystal was 0.42 mm in length with one end truncated by $(1\bar{1}\bar{1})$ and $(\bar{2}\bar{1}7)$ and the other end truncated by $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, and $(0\bar{2}1)$.

The crystal was accurately centered on a Picker FACS-1 diffractometer and was orientated such that its $\bar{1}04$ axis was coincident with the instrumental ϕ axis.

Unit cell dimensions, determined from the 2θ, ω, and χ settings of the resolved Mo Kα_1 ($\lambda = 0.70926$ Å) peaks of 12 high-angle reflections ($2\theta = 37\text{-}52°$), measured under "high resolution" conditions[10] at 26° are $a = 7.7028$ (17), $b = 17.1559$ (45), $c = 12.8488$ (27) Å; and $\beta = 117.48$ (1)°. The unit cell volume is 1506.5 Å^3, yielding a calculated density of 1.844 g cm^{-3} for $M = 417.99$ and $Z = 4$. (The density was not measured experimentally due to an insufficient quantity of sample.)

Intensity data were collected[10] using Mo Kα radiation (*i.e.*, molybdenum radiation filtered through niobium foil) by executing a coupled θ-2θ (crystal-counter) scan from 1.0° in 2θ below the Kα_1 peak to 1.0° in 2θ above the Kα_2 peak. Each scan was executed at 1.0 deg min^{-1}, accumulating P counts in t_P seconds. Stationary background counts, of 40-sec duration each, were recorded at the low and high 2θ limits of the scan, giving B_1 and B_2 counts (respectively) for a total background counting time of t_B = 80 sec. Copper foil attenuators, whose transmission factors for Mo Kα

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(1) The term "insertion" is here used to describe a situation whereby a species X interacts with an A-B bond to form an A-X-B moiety. No *mechanistic* connotations are implied.

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(7) A. A. Vlcek and F. Basolo, *Inorg. Chem.*, 5, 156 (1966).

(8) J. K. Ruff, *Inorg. Chem.*, 6, 2080 (1967).

(9) R. E. J. Bichler and H. C. Clark, *J. Organometal. Chem.*, 23, 427 (1970).

(10) Exhaustive details of the apparatus and experimental procedure have appeared previously: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).