Crystal Structure and Absolute Configuration of $(-)_{589}$-Tris(2,2′-bipyridine)-cobalt(III) Hexacyanoferrate(III) Octahydrate

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(Received May 17, 1980)

The crystal structure and absolute configuration of the title compound, $(-)_{589}$-$[Co(bpy)_3][Fe(CN)_6]\cdot 8H_2O$, has been determined from single-crystal X-ray data. The yellow crystals are triclinic; unit-cell dimensions $a=12.174(3)$, $b=16.742(7)$, $c=10.651(3)$ Å, $\alpha=103.25(3)$, $\beta=104.09(2)$, $\gamma=94.71(3)°$, space group Pl, $Z=2$. The structure was solved by the heavy-atom method and refined to $R=0.076$. The $(-)_{589}$-isomer of $[Co(bpy)_3]^{3+}$ has Δ configuration. The $[Co(bpy)_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ ions have an approximate D_3 symmetry and nearly the same structure as those in other related complexes. All the N atoms in $[Fe(CN)_6]^{3-}$ and the water molecules participate in a three-dimensional hydrogen-bond network.

The absolute configurations of $[Co(bpy)_3]^{3+}$ and tris(1,10-phenanthroline)cobalt(III), $[Co(phen)_3]^{3+}$, have been controversial. Mason and co-workers[1-4] have applied the exciton theory, based on the CD active, long-axis polarized (π, π^*) ligand transition. Hawkins and co-workers[5-7] have proposed an alternative procedure, involving an empirical analysis of both CD and isotropic absorption data of the (d, d*) ligand-field band. The absolute configurations derived by the two methods are not consistent; the former suggests $(-)_{589}$-$[Co(bpy)_3]^{3+}$ to have a Δ configuration, while the latter yields a Λ assignment. The validity of the isotropic absorption analysis has been questioned[8] and the assignment for $(+)_{589}$-$[Co(phen)_3]^{3+}$ has been proposed from the Pfeiffer phenomenon,[9] but the controversy still remains unresolved.

We intend to determine the absolute configuration directly by X-ray analysis, to judge which of the two methods predicts it correctly. Preliminary results of this work have been reported.[10] The absolute configuration thus determined will furnish the basis of the CD theory.

Experimental

The complex of $(-)_{589}$-$[Co(bpy)_3](ClO_4)_3$ was prepared by the method reported,[5] potassium $(+)_{589}$-bistartratoantimonate(III) being used instead of sodium $(+)_{589}$-tartrate.

The crystals of $(-)_{589}$-$[Co(bpy)_3][Fe(CN)_6]\cdot 8H_2O$ were grown by the diffusion method, as shown schematically in Fig. 1. A small glass vessel (A) filled with a solution of $(-)_{589}$-$[Co(bpy)_3](ClO_4)_3$ was placed in the center of a beaker (C). A bent glass pipe with a small opening (B) was filled with a solution of $K_3[Fe(CN)_6]$. Distilled water was poured very carefully down the wall of the beaker until the level was about 1 mm above the opening of the pipe and the vessel. To minimize thermal and photo-racemization, the beaker was kept in the dark at 5 °C. After about 24 h, yellow prismatic crystals were grown on the wall of the central vessel. Found: C, 49.22; H, 3.89; N, 19.28%. Calcd for $[Co(C_{10}H_8N_2)_3][Fe(CN)_6]\cdot 8H_2O$; C, 48.94; H, 4.56; N, 19.02%.

Figure 2 shows the absorption and circular-dichroism spectra in solution, which were recorded on a Simadzu Model MPS-50 spectrometer and JASCO Model ORD/UV-5 spectrometer with CD attachment. These spectra exhibit essentially the same pattern as those of $(-)_{589}$-$[Co(bpy)_3](ClO_4)_3$.[8]

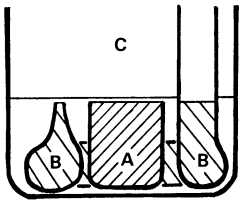

Fig. 1. A schematic drawing of the diffusion method. A small opening of the bent glass pipe is as high as the central vessel.

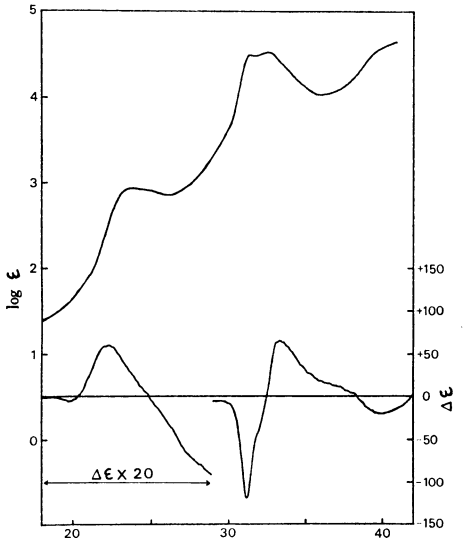

Fig. 2. The absorption (upper curve) and circular dichroism spectra (lower curve) of the $(-)_{589}$-$[Co(bpy)_3][Fe(CN)_6]$ complex in aqueous solution.

The symmetry and approximate cell dimensions of the crystal were determined from oscillation and Weissenberg photographs. The more accurate cell dimensions were obtained by least-squares analysis of 2θ measured on a Rigaku automated four-circle diffractometer. The density was measured by the flotation method in a mixture of carbon tetrachloride and hexane. The crystal data are summarized in Table 1.

Intensity data up to $2\theta \leqq 55°$ were collected on the diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) mono-

Table 1. Crystal data

Formula	$[Co(C_{10}H_8N_2)_3][Fe(CN)_6]\cdot 8H_2O$
F. W.	883.6
Space group	P1
a	12.174(3) Å
b	16.742(7) Å
c	10.651(3) Å
α	103.25(3)°
β	104.09(2)°
γ	94.71(3)°
V	2027(1) Å^3
Z	2
D_m	1.46 g/cm^3
D_x	1.4477(7) g/cm^3
μ(Mo $K\alpha$)	8.3 cm^{-1}

chromated by a graphite. An ω-2θ scan was employed with a scan rate of 4° (2θ) min^{-1}. A total of 6348 independent reflections, ($|F_o| \geqq 3\sigma(|F_o|)$), was used for the structure determination. The intensities were corrected for Lorentz and polarization factors but absorption correction was not applied.

Structure Determination

The positions of the two cobalt and two iron atoms were obtained from the three-dimensional Patterson function. Since the arrangement of these four atoms exhibits a non-crystallographic center of symmetry, the two crystallographically independent complex ions were approximately related to each other by the pseudo inversion center on the first Fourier map. The positions of the atoms in four pyridine rings, which are not related by the pseudo inversion, were selected carefully on the successive Fourier maps.

The structure was refined by the block-diagonal least-squares method. After several cycles of the refinement, sixteen oxygen atoms of the water molecules appeared on a difference map. Further refinement revealed that the eight of sixteen oxygen atoms had the decreased occupancy factors.

The positions of the hydrogen atoms in the 2,2′-bipyridine ligands were obtained from the difference map and refined with the isotropic temperature factors. The hydrogen atoms of water molecules could not be found. The weighting scheme in the final refinement, $w=0.2$ if $|F_o|<13.8$ or $|F_o|>138.1$, $w=(0.000956F_o^2-0.157|F_o|+7.58)^{-1}$ if $13.8 \leqq F_o| \leqq 138.1$, was employed. The final R value became 0.076 for 6348 observed reflections. At the final stage, no peaks higher than 0.58 e Å^{-3} were found on the difference map. Atomic scattering factors including the anomalous terms for Mo $K\alpha$ radiation were taken from the International Tables for X-Ray Crystallography.[11] Final positional parameters and their standard deviations are given in Table 2. A list of the anisotropic thermal parameters and a table of the observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 8104). The computation was done on a FACOM-HITAC system M-160 computer at this Institute.

Results and Discussion

Absolute Configuration. The intensities of fifteen

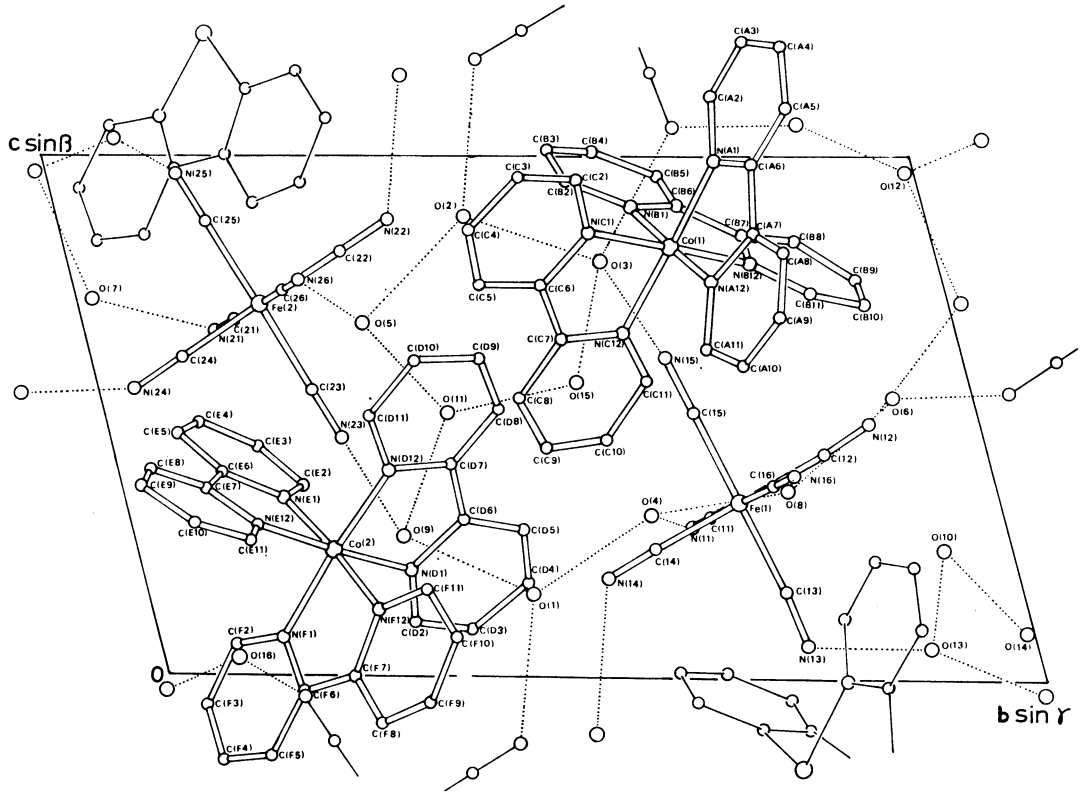

Fig. 3. The crystal structure viewed along the a axis. The hydrogen bonds are represented by dotted lines.

TABLE 2. FRACTIONAL COORDINATES, WITH THEIR STANDARD DEVIATIONS, MULTIPLIED BY 10^4 FOR THE NON-HYDROGEN ATOMS AND 10^3 FOR THE HYDROGEN ATOMS

Atom	x	y	z	B or B_{eq}[a)]	Atom	x	y	z	B or B_{eq}[a)]
Co(1)	7626(1)	7003(1)	8280(2)	25 Å^2	C(E7)	2281(11)	978(7)	3593(11)	36 Å^2
N(A1)	8526(7)	7771(5)	9925(9)	30	C(E8)	2819(13)	373(9)	3938(13)	53
C(A2)	8311(11)	7902(8)	11143(12)	42	C(E9)	3814(14)	215(8)	3611(15)	60
C(A3)	9045(13)	8428(9)	12250(13)	54	C(E10)	4268(12)	735(9)	2916(15)	55
C(A4)	10051(12)	8839(8)	12147(13)	48	C(E11)	3665(10)	1347(8)	2584(12)	39
C(A5)	10276(10)	8731(8)	10947(12)	41	N(E12)	2680(8)	1452(5)	2876(9)	33
C(A6)	9509(9)	8181(7)	9833(11)	31	N(F1)	871(8)	1450(5)	739(9)	32
C(A7)	9667(9)	7977(7)	8513(11)	30	C(F2)	−35(10)	887(7)	585(13)	42
C(A8)	10633(11)	8307(8)	8200(14)	46	C(F3)	−572(12)	349(9)	−606(15)	54
C(A9)	10717(12)	8049(9)	6883(16)	57	C(F4)	−183(14)	391(9)	−1666(15)	64
C(A10)	9806(12)	7490(10)	5963(14)	57	C(F5)	752(13)	953(10)	−1566(15)	61
C(A11)	8897(12)	7138(8)	6302(12)	46	C(F6)	1276(10)	1499(7)	−303(10)	32
N(A12)	8838(7)	7398(5)	7576(9)	29	C(F7)	2251(10)	2152(7)	−1(12)	36
N(B1)	6427(7)	6660(5)	9014(9)	35	C(F8)	2801(13)	2308(9)	−912(15)	56
C(B2)	6339(9)	5993(6)	9528(11)	33	C(F9)	3692(15)	2933(10)	−519(15)	66
C(B3)	5476(11)	5875(8)	10119(13)	50	C(F10)	4037(12)	3424(9)	754(15)	57
C(B4)	4646(12)	6384(8)	10125(15)	49	C(F11)	3436(12)	3224(8)	1659(13)	46
C(B5)	4707(12)	7060(8)	9599(14)	45	N(F12)	2597(8)	2594(5)	1270(9)	31
C(B6)	5598(10)	7183(7)	9037(11)	32	Fe(1)	2500(2)	7040(1)	3367(2)	30
C(B7)	5776(9)	7854(7)	8463(12)	34	C(11)	830(10)	6667(7)	2996(11)	34
C(B8)	5047(12)	8433(8)	8321(15)	65	C(12)	2271(10)	8147(8)	4283(13)	40
C(B9)	5272(12)	9012(9)	7643(14)	67	C(13)	2242(10)	7295(7)	1641(11)	33
C(B10)	6263(11)	9057(10)	7213(15)	54	C(14)	2685(9)	5934(6)	2445(11)	30
C(B11)	6917(10)	8466(8)	7378(12)	37	C(15)	2845(11)	6770(8)	5070(13)	43
N(B12)	6726(7)	7858(5)	7963(8)	31	C(16)	4095(10)	7486(7)	3647(12)	39
N(C1)	8454(8)	6099(6)	8522(10)	28	N(11)	−104(9)	6473(7)	2762(12)	49
C(C2)	9378(10)	6115(7)	9541(12)	30	N(12)	2171(11)	8775(7)	4918(12)	54
C(C3)	9947(12)	5444(8)	9592(14)	43	N(13)	2065(10)	7384(8)	570(11)	53
C(C4)	9554(11)	4714(9)	8550(14)	49	N(14)	2810(8)	5317(6)	1834(10)	41
C(C5)	8613(11)	4671(8)	7497(14)	49	N(15)	3019(12)	6618(8)	6118(12)	65
C(C6)	8089(9)	5387(7)	7534(11)	32	N(16)	5002(10)	7754(9)	3802(14)	71
C(C7)	7122(10)	5450(7)	6459(12)	32	Fe(2)	6727(2)	2104(1)	7114(2)	35
C(C8)	6609(14)	4813(10)	5333(18)	51	C(21)	5096(11)	1758(8)	6846(13)	43
C(C9)	5695(13)	4985(10)	4388(17)	53	C(22)	6571(10)	3188(8)	8130(11)	39
C(C10)	5390(13)	5744(8)	4555(15)	56	C(23)	6399(11)	2475(7)	5479(12)	38
C(C11)	5920(10)	6354(7)	5682(12)	40	C(24)	6859(10)	1058(7)	6054(13)	36
N(C12)	6790(7)	6211(6)	6581(9)	25	C(25)	7082(11)	1721(10)	8734(16)	60
Co(2)	1700(1)	2261(1)	2402(2)	27	C(26)	8340(10)	2434(7)	7413(12)	37
N(D1)	731(7)	3089(5)	2034(9)	30	N(21)	4168(9)	1529(7)	6754(12)	56
C(D2)	−201(10)	2988(8)	1035(12)	42	N(22)	6482(10)	3850(7)	8727(11)	56
C(D3)	−827(10)	3634(8)	893(12)	43	N(23)	6240(13)	2672(7)	4538(11)	66
C(D4)	−451(10)	4405(8)	1823(13)	40	N(24)	6931(10)	430(6)	5359(13)	53
C(D5)	533(10)	4504(7)	2862(12)	35	N(25)	7242(12)	1511(11)	9696(15)	89
C(D6)	1089(9)	3839(7)	2969(11)	32	N(26)	9321(10)	2626(7)	7598(12)	55
C(D7)	2111(9)	3863(7)	4087(11)	32	O(1)	6759(8)	4431(6)	1603(10)	58
C(D8)	2601(11)	4557(7)	5112(12)	40	O(2)	2478(8)	4696(7)	8839(10)	62
C(D9)	3514(11)	4487(7)	6090(12)	42	O(3)	1879(9)	6158(7)	7976(10)	67
C(D10)	3940(10)	3719(8)	6050(12)	42	O(4)	7740(9)	6012(8)	3137(12)	81
C(D11)	3414(10)	3061(7)	4989(11)	37	O(5)	1239(9)	3263(7)	6770(11)	75
N(D12)	2504(8)	3118(6)	3957(9)	36	O(6)	8353(10)	9083(7)	5386(10)	71
N(E1)	821(7)	1823(6)	3394(10)	34	O(7)	2801(11)	161(7)	7221(11)	80
C(E2)	−154(11)	2085(8)	3630(14)	47	O(8)	7199(10)	7602(7)	3616(14)	87
C(E3)	−830(13)	1705(10)	4386(16)	59	O(9)	7357(21)	3094(14)	2676(25)	83
C(E4)	−380(12)	1073(10)	4871(15)	56	O(10)	6214(24)	9229(17)	2439(23)	103
C(E5)	630(13)	813(9)	4643(13)	51	O(11)	9536(29)	3961(19)	5027(29)	129
C(E6)	1227(10)	1201(7)	3888(11)	37	O(12)	2833(24)	9980(15)	9727(21)	97

Table 2. Continued.

Atom	x	y	z	B or B_{eq}[a]
O(13)	3706(18)	8813(10)	665(20)	59 Å^2
O(14)	7587(23)	9926(16)	902(24)	93
O(15)	9971(24)	5518(18)	5664(28)	106
O(16)	5158(144)	883(87)	345(152)	106
H(A2)	756(8)	752(6)	1107(9)	25(22)
H(A3)	900(12)	833(9)	1280(14)	84(10)
H(A4)	1078(9)	914(7)	1301(11)	43(28)
H(A5)	1121(9)	890(7)	1089(11)	52(28)
H(A8)	1139(7)	885(5)	902(9)	17(20)
H(A9)	1144(11)	828(8)	670(13)	77(10)
H(A10)	984(10)	730(8)	508(12)	66(35)
H(A11)	827(11)	657(8)	580(13)	78(10)
H(B2)	697(9)	563(6)	928(10)	22(25)
H(B3)	558(9)	544(6)	1049(11)	61(28)
H(B4)	406(12)	633(9)	1039(14)	75(10)
H(B5)	401(9)	757(6)	958(10)	39(26)
H(B8)	427(8)	833(6)	891(9)	82(22)
H(B9)	487(8)	953(6)	774(10)	69(24)
H(B10)	639(10)	943(7)	694(12)	51(32)
H(B11)	740(10)	841(8)	712(12)	11(36)
H(C2)	950(8)	661(6)	1035(9)	34(22)
H(C3)	1062(10)	545(8)	1035(12)	52(35)
H(C4)	987(11)	430(8)	845(13)	91(10)
H(C5)	828(9)	411(7)	672(11)	35(29)
H(C8)	694(11)	428(8)	522(13)	22(10)
H(C9)	553(11)	458(8)	382(13)	25(36)
H(C10)	490(9)	595(7)	407(11)	57(29)
H(C11)	549(7)	688(5)	583(8)	67(19)
H(D2)	−48(8)	247(6)	49(9)	23(23)
H(D3)	−145(7)	356(5)	14(9)	16(20)
H(D4)	−83(10)	477(8)	180(13)	65(36)
H(D5)	79(9)	505(6)	348(10)	37(27)
H(D8)	235(8)	509(6)	509(10)	31(25)
H(D9)	376(11)	500(8)	650(13)	76(10)
H(D10)	454(10)	368(7)	653(11)	43(29)
H(D11)	365(10)	245(8)	512(12)	70(35)
H(E2)	−49(7)	268(5)	318(8)	89(18)
H(E3)	−168(12)	209(9)	482(14)	59(10)
H(E4)	−85(10)	69(7)	506(11)	50(31)
H(E5)	102(10)	37(7)	509(11)	48(32)
H(E8)	263(9)	9(7)	431(11)	57(29)
H(E9)	424(9)	−15(7)	379(11)	53(29)
H(E10)	487(10)	71(7)	268(12)	83(32)
H(E11)	395(12)	179(9)	218(14)	10(10)
H(F2)	−37(10)	85(7)	134(11)	58(32)
H(F3)	−127(9)	−3(7)	−46(11)	49(29)
H(F4)	−57(11)	12(8)	−234(13)	78(10)
H(F5)	117(11)	103(8)	−227(13)	80(10)
H(F8)	235(9)	206(7)	−194(10)	33(25)
H(F9)	412(11)	303(8)	−112(13)	76(37)
H(F10)	459(9)	395(7)	107(11)	49(29)
H(F11)	355(9)	357(6)	274(10)	38(26)

a) B_{eq} means the equivalent isotropic temperature factor, defined by $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$ where U_1, U_2, and U_3 are the principal components of U matrix. All the values of B and B_{eq} are multiplied by 10.

Table 3. Relation of $|F|$ in Friedel pairs

h	k	l	$\lvert F_c(hkl)\rvert$		$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$	$\lvert F_o(hkl)\rvert$		$\lvert F_o(\bar{h}\bar{k}\bar{l})\rvert$
$\bar{1}$	$\bar{8}$	1	24.8	>	10.8	19.6	>	8.8
1	$\bar{5}$	1	46.0	<	64.0	43.0	<	65.5
3	$\bar{3}$	1	49.6	>	26.0	59.4	>	30.6
$\bar{3}$	3	1	22.0	>	10.8	24.3	>	9.8
1	4	1	54.0	<	73.6	51.5	<	75.1
0	$\bar{5}$	2	34.0	>	23.2	28.0	>	17.2
$\bar{4}$	$\bar{1}$	2	23.6	>	15.2	23.7	>	15.5
2	1	2	20.0	<	46.8	40.0	<	64.1
0	5	2	22.8	>	14.0	25.8	>	16.8
$\bar{7}$	$\bar{12}$	3	21.2	>	11.2	16.2	>	9.9
1	1	3	68.0	>	49.2	58.3	>	43.3
$\bar{4}$	4	3	21.2	>	12.8	22.3	>	14.7
$\bar{2}$	$\bar{7}$	4	25.2	>	15.6	19.2	>	9.1
1	$\bar{4}$	5	20.0	<	30.0	19.2	<	30.5
1	4	7	12.0	<	20.0	9.1	<	17.0

Friedel pairs (hkl and $\bar{h}\bar{k}\bar{l}$), for which differences in intensities were the largest, were measured on the diffractometer using Ni-filtered Cu $K\alpha$ radiation. The observed and calculated structure factors are compared in Table 3, the anomalous scattering terms being taken from the International Tables.[11] All the relations between $|F_c(hkl)|$ and $|F_c(\bar{h}\bar{k}\bar{l})|$ are consistent with those between $|F_o(hkl)|$ and $|F_o(\bar{h}\bar{k}\bar{l})|$, indicating that $(-)_{589}$-$[Co(bpy)_3]^{3+}$ has the Δ configuration.[12]

The Structure of $[Co(bpy)_3]^{3+}$ *and* $[Fe(CN)_6]^{3-}$. The crystal structure viewed along the a axis is shown in Fig. 3, in which the numbering of the atoms is also given. The two crystallographically independent complexes are approximately related by a non-crystallographic inversion center except for the four pyridine rings including N(A12), N(B1), N(E1), and N(F12). The structures of the two crystallographically independent complexes are not significantly different. Both of the $[Co(bpy)_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ ions, which are shown in Fig. 4(a) and (b), have approximate point-group symmetry D_3.

Bond distances and angles in the coordination sphere of $[Co(bpy)_3]^{3+}$ are given in Table 4. The average Co–N distance and N–Co–N angle are 1.93 Å and 83.3°, respectively. These value are in good agreement with those found in $[Co(bpy)_2(NO_3)]^{2+}$ (1.929 Å and 83.27°, respectively),[13] and distinct from those in $[Co(en)_3]^{3+}$ (en: ethylenediamine), (1.978±0.004 Å and 85.4±0.3°, respectively).[14]

For the $[Co(en)_3]^{3+}$ and other trisbidentate complexes with five-membered rings, the following empirical rule has been proposed; those complexes which show prominent positive circular dichroism in the first absorption region possess Δ absolute configuration.[16] The absolute configuration of the present $(-)_{589}$-$[Co(bpy)_3]^{3+}$ complex conflicts with the empirical rule because the prominent positive circular dichroism is found at 22×10^3 cm^{-1} as shown in Fig. 2. The octahedron around the cobalt atom in the $[Co(bpy)_3]^{3+}$ is compared with that of $[Co(en)_3]^{3+}$ [15] in Fig. 5, in which the characteristic values are given.

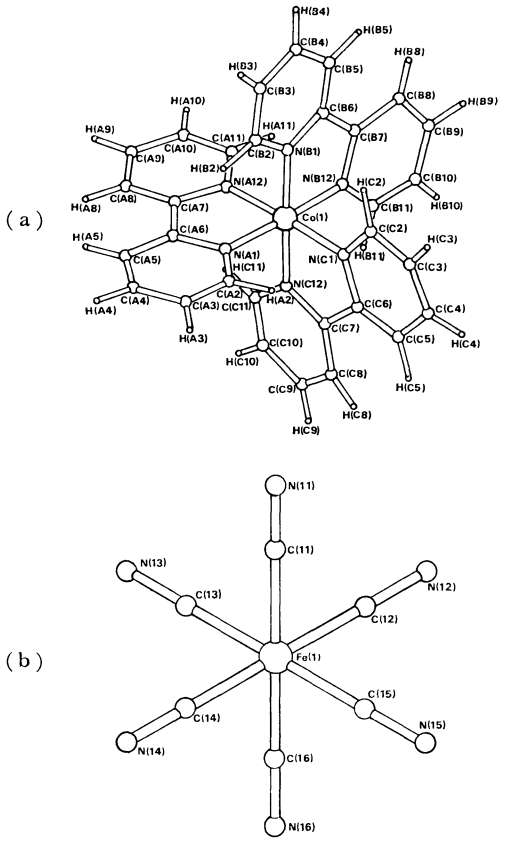

Fig. 4. The molecular structures of $[Co(bpy)_3]^{3+}$, (a), and $[Fe(CN)_6]^{3-}$, (b), viewed along the pseudo three-fold axis. These structures are not significantly different from those of the other crystallographically independent ions.

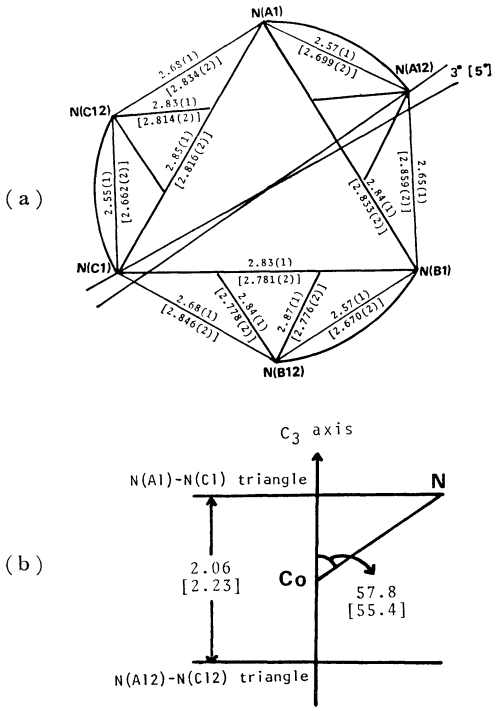

Fig. 5. Comparison of the octahedrons in $[Co(bpy)_3]^{3+}$ and $[Co(en)_3]^{3+}$ (in brackets). (a) Projection down and (b) normal to the pseudo three-fold axis. The values are taken from the present complex including Co(1) and $[Co(en)_3]^{3+}$ in $[Co(en)_3]^{3+}\cdot C_4H_4O_6^{2-}\cdot Cl^-\cdot 5H_2O$.[15]

TABLE 4. BOND DISTANCES(l/Å) AND ANGLES(ϕ/°) IN THE COORDINATION SPHERE OF $[Co(bpy)_3]^{3+}$

	Distances		
Co(1)-N(A1)	1.93(1)	Co(2)-N(D1)	1.94(1)
Co(1)-N(A12)	1.95(1)	Co(2)-N(D12)	1.91(1)
Co(1)-N(B1)	1.92(1)	Co(2)-N(E1)	1.89(1)
Co(1)-N(B12)	1.96(1)	Co(2)-N(E12)	1.95(1)
Co(1)-N(C1)	1.92(1)	Co(2)-N(F1)	1.95(1)
Co(1)-N(C12)	1.91(1)	Co(2)-N(F12)	1.95(1)
	Angles		
N(A1)-Co(1)-N(A12)	82.9(4)	N(D1)-Co(2)-N(D12)	84.1(4)
N(A1)-Co(1)-N(B1)	95.1(4)	N(D1)-Co(2)-N(E1)	94.9(4)
N(A1)-Co(1)-N(B12)	176.9(4)	N(D1)-Co(2)-N(E12)	176.9(4)
N(A1)-Co(1)-N(C1)	95.4(4)	N(D1)-Co(2)-N(F1)	92.7(4)
N(A1)-Co(1)-N(C12)	88.2(4)	N(D1)-Co(2)-N(F12)	88.8(4)
N(A12)-Co(1)-N(B1)	86.7(4)	N(D12)-Co(2)-N(E1)	90.9(4)
N(A12)-Co(1)-N(B12)	94.5(4)	N(D12)-Co(2)-N(E12)	93.5(4)
N(A12)-Co(1)-N(C1)	177.6(4)	N(D12)-Co(2)-N(F1)	175.7(4)
N(A12)-Co(1)-N(C12)	94.8(4)	N(D12)-Co(2)-N(F12)	94.2(4)
N(B1)-Co(1)-N(B12)	83.1(4)	N(E1)-Co(2)-N(E12)	83.1(4)
N(B1)-Co(1)-N(C1)	95.1(4)	N(E1)-Co(2)-N(F1)	92.3(4)
N(B1)-Co(1)-N(C12)	176.6(4)	N(E1)-Co(2)-N(F12)	174.0(4)
N(B12)-Co(1)-N(C1)	87.3(4)	N(E12)-Co(2)-N(F1)	93.3(4)
N(B12)-Co(1)-N(C12)	93.8(4)	N(E12)-Co(2)-N(F12)	93.3(4)
N(C1)-Co(1)-N(C12)	83.5(4)	N(F1)-Co(2)-N(F12)	82.9(4)

These values are not so different between the two octahedrons. It seems difficult to ascribe the opposite sign of the circular dichroism to the slight difference in geometries of the two octahedrons. A more rigorous study is necessary to explain the circular dichroism of the (d, d*) transition.

Bond distances and angles in the bipyridine ligands are listed in Table 5. The average values are given in the final column. There is no significant difference between the corresponding values in the present complex and in other related complexes, such as $[Fe(bpy)_3]^{3+}$,[17] $[Co(bpy)_2(NO_3)]^{2+}$,[13] $[Ni(bpy)_3]^{3+}$,[18,19] $[Ni(bpy)(H_2O)_2]^{2+}$,[20] and $[Cu(bpy)_3]^{2+}$.[21] The average distances of C–N, C–C, and C–C (connecting two pyridine rings) in these complexes are 1.35, 1.40, and 1.48 Å, respectively.

The geometries of the five-membered rings in the $[Co(bpy)_3]^{3+}$, $[Fe(bpy)_3]^{3+}$, and $[Ni(bpy)_3]^{2+}$ complexes are compared in Table 6. The complex of $[Cu(bpy)_3]^{2+}$ is omitted because Jahn-Teller effect distorts its octahedron. The N–M–N angle decreases with the increase of the M–N length. It is noteworthy

Table 5. Bond distances(l/Å) and angles(ϕ/°) in the 2,2′-bipyridine ligands

Atom[a]	bpy A	bpy B	bpy C	bpy D	bpy E	bpy F	Average
			Distances				
N (#1) - C (#2)	1.36(2)	1.35(2)	1.36(2)	1.32(2)	1.36(2)	1.34(2)	1.35(2)
N (#1) - C (#6)	1.37(2)	1.35(2)	1.39(2)	1.37(2)	1.35(2)	1.34(2)	1.36(2)
C (#2) - C (#3)	1.36(2)	1.37(2)	1.37(2)	1.39(2)	1.48(2)	1.35(2)	1.39(2)
C (#3) - C (#4)	1.40(2)	1.41(2)	1.38(2)	1.40(2)	1.38(2)	1.34(2)	1.39(2)
C (#4) - C (#5)	1.35(2)	1.38(2)	1.38(2)	1.39(2)	1.40(2)	1.38(2)	1.38(2)
C (#5) - C (#6)	1.39(2)	1.40(2)	1.38(2)	1.36(2)	1.43(2)	1.40(2)	1.39(2)
C (#6) - C (#7)	1.43(2)	1.46(2)	1.42(2)	1.49(2)	1.45(2)	1.47(2)	1.45(2)
C (#7) - C (#8)	1.40(2)	1.38(2)	1.38(2)	1.37(2)	1.32(2)	1.37(2)	1.37(2)
C (#7) - N (#12)	1.36(2)	1.36(2)	1.39(2)	1.36(2)	1.36(2)	1.33(2)	1.36(2)
C (#8) - C (#9)	1.40(2)	1.40(2)	1.38(3)	1.36(2)	1.37(2)	1.36(2)	1.38(2)
C (#9) - C (#10)	1.40(2)	1.34(2)	1.39(2)	1.42(2)	1.42(2)	1.36(2)	1.39(2)
C (#10) - C (#11)	1.37(2)	1.36(2)	1.34(2)	1.37(2)	1.37(2)	1.42(2)	1.37(2)
C (#11) - N (#12)	1.35(2)	1.32(2)	1.34(2)	1.38(2)	1.33(2)	1.32(2)	1.34(2)
			Angles				
Co(n) - N (#1) - C (#2)	127(1)	127(1)	127(1)	127(1)	125(1)	126(1)	127(1)
Co(n) - N (#1) - C (#6)	115(1)	116(1)	114(1)	113(1)	115(1)	114(1)	115(1)
C (#2) - N (#1) - C (#6)	118(1)	118(1)	119(1)	120(1)	120(1)	120(1)	119(1)
N (#1) - C (#2) - C (#3)	122(1)	122(1)	120(1)	121(1)	123(1)	122(1)	122(1)
C (#2) - C (#3) - C (#4)	120(1)	119(1)	122(1)	119(1)	115(1)	118(1)	119(1)
C (#3) - C (#4) - C (#5)	120(1)	121(1)	120(1)	119(1)	122(2)	122(2)	121(1)
C (#4) - C (#5) - C (#6)	119(1)	116(1)	118(1)	119(1)	120(1)	117(1)	118(1)
N (#1) - C (#6) - C (#5)	122(1)	124(1)	122(1)	121(1)	120(1)	120(1)	122(1)
N (#1) - C (#6) - C (#7)	114(1)	113(1)	114(1)	115(1)	115(1)	115(1)	114(1)
C (#5) - C (#6) - C (#7)	125(1)	123(1)	124(1)	123(1)	125(1)	126(1)	124(1)
C (#6) - C (#7) - C (#8)	123(1)	124(1)	124(1)	124(1)	126(1)	125(1)	124(1)
C (#6) - C (#7) - N (#12)	115(1)	115(1)	114(1)	112(1)	113(1)	115(1)	114(1)
C (#8) - C (#7) - N (#12)	121(1)	120(1)	121(1)	125(1)	121(1)	121(1)	122(1)
C (#7) - C (#8) - C (#9)	119(1)	117(1)	118(1)	118(1)	121(1)	119(1)	119(1)
C (#8) - C (#9) - C (#10)	117(1)	121(1)	121(1)	121(1)	118(1)	122(1)	120(1)
C (#9) - C (#10) - C (#11)	124(1)	120(1)	116(1)	118(1)	118(1)	116(1)	119(1)
C (#10) - C (#11) - N (#12)	118(1)	120(1)	126(1)	123(1)	122(1)	121(1)	122(1)
Co(n) - N (#12) - C (#7)	113(1)	113(1)	114(1)	116(1)	114(1)	114(1)	114(1)
Co(n) - N (#12) - C (#11)	125(1)	125(1)	129(1)	128(1)	126(1)	125(1)	126(1)
C (#7) - N (#12) - C (#11)	121(1)	122(1)	117(1)	116(1)	120(1)	121(1)	120(1)

a) "#" is A, B, C, D, E, or F and "n" is 1 or 2.

Table 6. Distances (l/Å) and angles (ϕ/°) in the five-membered rings of tris 2,2′-bipyridine complexes

	M-N[a]	N-C	C-C	N-M-N[a]	M-N-C[a]	N-C-C
$[Co(bpy)_3]^{3+}$	1.932	1.36	1.45	83.2	115	114
$[Fe(bpy)_3]^{3+}$	1.963	1.36	1.47	82.3	115	114
$[Ni(bpy)_3]^{2+}$	2.089	1.35	1.48	78.6	115	116

a) M means Co, Fe, and Ni atoms.

that the M–N–C angles take a constant value. This indicates that the bipyridine ligand has not a planar conformation; otherwise the M–N–C angle should increase with the increase of the M–N distance. The two rings of each bipyridine ligand in $[Ni(bpy)_3]^{2+}$ are twisted along the connecting C–C bond. The twist angles are reported as 5.8—10.9°.[18] On the other hand, the bipyridine ligands of $[Co(bpy)_3]^{3+}$ have more planar conformations. Two rings of the bipyridine ligand in $[Co(bpy)_3]^{3+}$ are not twisted but slightly bent at the connecting C–C bond. The angles between the normals to the pyridine rings in the six bipyridine ligands are 2.3° to 4.7°. For the $[Fe(bpy)_3]^{3+}$ complex, those angles have intermediate values between those in $[Ni(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$.

Bond distances and angles in $[Fe(CN)_6]^{3-}$ are given in Table 7. The average Fe–C and C–N distances, 1.94 Å and 1.14 Å, are in good agreement with those in other hexacyanoferrate(III) crystals.[22-26] Although the deviation of each Fe–C bond length from the average value is slightly large, similar distorted octahedrons, characterized by widely varying M–C bond lengths, have been observed in other hexacyanometalate(III) complexes.[22]

Hydrogen Bond. The hydrogen bonding scheme is shown in Fig. 3. All the N atoms of $[Fe(CN)_6]^{3-}$ and the water molecules participate in the hydrogen bonds to form a three-dimensional network through the O–H···N and O–H···O hydrogen bonds. The distances of O···N and O···O and angles of O···O···N and O···O···O are given in Table 8. The $[Co(bpy)_3]^{3+}$ cations are packed in the network with the van der Waals contacts.

The occupancy factors of O(9), O(10), O(11), O(12), O(13), O(14), O(15), and O(16) showed the decreased values from 0.5 to 0.2. The water molecules may be partly lost from the crystal during the data collection, as judged by the fragility of the crystal after the experiment.

Four water molecules, O(2), O(3), O(5), and O(15), are approximately related to O(1), O(9), O(4), and O(11), respectively, by the pseudo inversion center. The other water molecules occupy the positions near the bipyridine ligands which are not related by the pseudo inversion. Preliminary experiments showed that the racemic crystal of this complex has the space

TABLE 7. BOND DISTANCES (l/Å) AND ANGLES (ϕ/°) IN $[Fe(CN)_6]^{3-}$

	Distances		
Fe(1)-C(11)	1.99(1)	Fe(2)-C(21)	1.95(1)
Fe(1)-C(12)	1.96(1)	Fe(2)-C(22)	1.94(1)
Fe(1)-C(13)	1.94(1)	Fe(2)-C(23)	1.94(1)
Fe(1)-C(14)	1.95(1)	Fe(2)-C(24)	1.90(1)
Fe(1)-C(15)	1.93(1)	Fe(2)-C(25)	1.94(2)
Fe(1)-C(16)	1.95(1)	Fe(2)-C(26)	1.94(1)
C(11)-N(11)	1.11(2)	C(21)-N(21)	1.14(2)
C(12)-N(12)	1.15(2)	C(22)-N(22)	1.17(2)
C(13)-N(13)	1.16(2)	C(23)-N(23)	1.11(2)
C(14)-N(14)	1.13(2)	C(24)-N(24)	1.16(2)
C(15)-N(15)	1.15(2)	C(25)-N(25)	1.14(3)
C(16)-N(16)	1.12(2)	C(26)-N(26)	1.17(2)
	Angles		
C(11)-Fe(1)-C(12)	88.8(5)	C(21)-Fe(2)-C(22)	88.8(6)
C(11)-Fe(1)-C(13)	90.2(5)	C(21)-Fe(2)-C(23)	90.7(6)
C(11)-Fe(1)-C(14)	89.8(5)	C(21)-Fe(2)-C(24)	90.9(6)
C(11)-Fe(1)-C(15)	92.7(5)	C(21)-Fe(2)-C(25)	90.2(7)
C(11)-Fe(1)-C(16)	174.7(5)	C(21)-Fe(2)-C(26)	178.7(6)
C(12)-Fe(1)-C(13)	93.4(5)	C(22)-Fe(2)-C(23)	90.3(6)
C(12)-Fe(1)-C(14)	178.5(5)	C(22)-Fe(2)-C(24)	177.6(6)
C(12)-Fe(1)-C(15)	88.6(6)	C(22)-Fe(2)-C(25)	90.7(7)
C(12)-Fe(1)-C(16)	88.2(6)	C(22)-Fe(2)-C(26)	91.3(6)
C(13)-Fe(1)-C(14)	86.5(5)	C(23)-Fe(2)-C(24)	87.4(6)
C(13)-Fe(1)-C(15)	176.5(6)	C(23)-Fe(2)-C(25)	178.7(7)
C(13)-Fe(1)-C(16)	85.6(5)	C(23)-Fe(2)-C(26)	90.6(6)
C(14)-Fe(1)-C(15)	91.6(6)	C(24)-Fe(2)-C(25)	91.7(7)
C(14)-Fe(1)-C(16)	93.2(5)	C(24)-Fe(2)-C(26)	89.0(6)
C(15)-Fe(1)-C(16)	91.6(6)	C(25)-Fe(2)-C(26)	88.5(6)
Fe(1)-C(11)-N(11)	178(1)	Fe(2)-C(21)-N(21)	175(1)
Fe(1)-C(12)-N(12)	174(1)	Fe(2)-C(22)-N(22)	179(1)
Fe(1)-C(13)-N(13)	175(1)	Fe(2)-C(23)-N(23)	178(1)
Fe(1)-C(14)-N(14)	174(1)	Fe(2)-C(24)-N(24)	177(1)
Fe(1)-C(15)-N(15)	177(1)	Fe(2)-C(25)-N(25)	178(2)
Fe(1)-N(16)-N(16)	179(1)	Fe(2)-C(26)-N(26)	179(1)

Table 8. Distances (l/Å) and angles (ϕ/°) of hydrogen bonds

		Distances	
O (1) - N (22)	2.92 (2)	O (6) - O (8)	2.77 (2)
O (1) - O (4)	2.77 (2)	O (7) - N (12)	2.86 (2)
O (1) - O (9)	2.81 (3)	O (7) - N (21)	2.93 (2)
O (2) - N (14)	3.03 (2)	O (7) - O (12)	2.75 (3)
O (2) - O (3)	2.89 (2)	O (8) - N (16)	2.76 (2)
O (2) - O (5)	2.87 (2)	O (9) - N (23)	2.84 (3)
O (3) - N (13)	2.99 (2)	O (9) - O (11)	3.14 (4)
O (3) - N (15)	2.88 (2)	O (10) - O (13)	3.10 (4)
O (3) - O (15)	2.86 (3)	O (10) - O (14)	2.95 (4)
O (4) - N (11)	2.82 (2)	O (11) - O (15)	2.52 (5)
O (4) - O (8)	2.76 (2)	O (12) - O (13)	2.58 (4)
O (5) - N (26)	2.90 (2)	O (12) - O (16)	2.94 (18)
O (5) - O (11)	2.94 (4)	O (13) - N (13)	2.95 (3)
O (6) - N (24)	2.95 (2)	O (16) - N (25)	2.96 (18)
		Angles	
O (4) - O (1) - O (9)	117.7 (7)	N (12) - O (7) - N (21)	110.9 (6)
O (4) - O (1) - N (22)	124.5 (5)	N (12) - O (7) - O (12)	121.6 (8)
O (9) - O (1) - N (22)	105.9 (7)	N (21) - O (7) - O (12)	123.5 (8)
O (3) - O (2) - O (5)	108.2 (5)	N (16) - O (8) - O (4)	116.2 (7)
O (3) - O (2) - N (14)	100.6 (5)	N (16) - O (8) - O (6)	99.8 (6)
O (5) - O (2) - N (14)	135.9 (5)	O (4) - O (8) - O (6)	132.4 (7)
N (13) - O (3) - N (15)	119.3 (5)	N (23) - O (9) - O (1)	119.1 (10)
N (13) - O (3) - O (2)	102.1 (5)	N (23) - O (9) - O (11)	127.3 (9)
O (13) - O (3) - O (15)	130.8 (8)	O (1) - O (9) - O (11)	100.9 (9)
N (15) - O (3) - O (2)	116.3 (5)	O (13) - O (10) - O (14)	106.7 (10)
N (15) - O (3) - O (15)	84.8 (7)	O (5) - O (11) - O (15)	110.6 (14)
O (2) - O (3) - O (15)	103.5 (7)	O (7) - O (12) - O (13)	123.3 (13)
N (11) - O (4) - O (1)	111.8 (6)	O (7) - O (12) - O (16)	81.1 (35)
N (11) - O (4) - O (8)	94.8 (6)	O (13) - O (12) - O (16)	89.1 (35)
O (1) - O (4) - O (8)	139.3 (6)	N (13) - O (13) - O (12)	116.1 (11)
N (26) - O (5) - O (2)	107.9 (5)	O (3) - O (15) - O (11)	113.0 (14)
N (26) - O (5) - O (11)	85.3 (8)	N (25) - O (16) - O (12)	155.1 (66)
O (2) - O (5) - O (11)	103.2 (8)	O (3) - N (13) - O (13)	105.4 (6)
N (24) - O (6) - O (8)	111.8 (6)		

group $P\bar{1}$ and similar unit-cell dimensions to the present crystal; $a=12.374$, $b=16.305$, $c=10.540$ Å, $\alpha=102.76$, $\beta=103.84$, $\gamma=95.48°$. These results indicate the two crystals to be isostructural except for the four pyridine rings and eight water molecules.

References

1) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc., A*, **1969**, 1428.
2) S. F. Mason and B. J. Norman, *J. Chem. Soc., A*, **1969**, 1442.
3) B. Bosnich, *Acc. Chem. Res.*, **2**, 266 (1969).
4) S. F. Mason, B. J. Peart, and R. E. Waddel, *J. Chem. Soc., Dalton Trans.*, **1973**, 944.
5) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).
6) R. G. Bray, J. Ferguson, and C. J. Hawkins, *Aust. J. Chem.*, **22**, 2091 (1969).
7) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, London (1971), Chap. 5.
8) S. F. Mason and B. J. Peart, *J. Chem. Soc., Dalton Trans.*, **1973**, 949.
9) N. A. P. Kane-Maguire and D. E. Richardson, *J. Am. Chem. Soc.*, **97**, 7194 (1975).
10) Y. Ohashi, K. Yanagi, Y. Mitsuhashi, K. Nagata, Y. Kaizu Y. Sasada, and H. Kobayashi, *J. Am. Chem. Soc.*, **101**, 4739 (1979).
11) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV, p. 72.
12) "Nomenclature of Inorganic Chemistry," 2nd ed, IUPAC, London (1970), p. 75.
13) C. W. Reinmann, M. Zocchi, A. D. Mighell, and A. Santro, *Acta Crystallogr., Sect. B*, **27**, 2211 (1971).
14) Y. Saito, "Inorganic Molecular Dissymmetry," Springer-Verlag, Berlin Heidelberg (1979), p. 57.
15) D. H. Templeton, A. Zalkin, H. W. Ruben, and L. K. Templeton, *Acta Crystallogr., Sect. B*, **35**, 1608 (1979).
16) Y. Saito, "Inorganic Molecular Dissymmetry," Springer-Verlag, Berlin Heidelberg (1979), p. 135.
17) B. N. Figgis, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, **31**, 57 (1978).
18) A. Wada, N. Sakabe, and J. Tanaka, *Acta Crystallogr., Sect. B*, **32**, 1121 (1976).
19) A. Wada, C. Katayama, and J. Tanaka, *Acta*

Crystallogr., Sect. B, **32**, 3194 (1976).
20) P. J. C. Tedenac and E. Phillippot, *Acta Crystallogr., Sect. B*, **30**, 2286 (1974).
21) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, **1972**, 2597.
22) R. C. Elder, G. J. Kennard, M. D. Payne, and E. Deutsch, *Inorg. Chem.*, **17**, 1296 (1978).
23) K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, **7**, 2333 (1968).
24) E. C. Reynhardt and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **28**, 524 (1972).
25) N. G. Vannerberg, *Acta Chem. Scand.*, **24**, 2335 (1970).
26) N. G. Vannerberg, *Acta Chem. Scand.*, **26**, 2863 (1972).