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Crystal and Molecular Structure of (+)-(3*R*,4*S*,8*R*,9*S*)-Quinidinium Δ-$(-)_{546}$-Bis(oxalato)(1,10-phenanthroline)chromate(III) Monohydrate and Its Implication in the Pfeiffer Effect of the Corresponding System

Hiroyuki Ohbo, Hiroshi Okazaki, Katsuhiko Miyoshi, and Hayami Yoneda*
Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima 730

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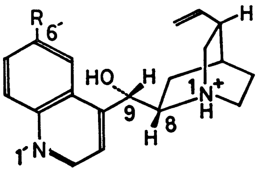
The crystal structure of the title compound *d*-quinidinium $(-)_{546}$-$[\mathrm{Cr(ox)_2(phen)}]\cdot\mathrm{H_2O}$ has been determined by a single-crystal X-ray analysis and refined to $R=0.078$ for 2172 reflections. The crystals are orthorhombic, space group $P2_12_12_1$ with unit cell dimensions of $a=9.943(2)$, $b=11.265(2)$, $c=30.716(6)$ Å, and $Z=4$. The known configurations of *d*-quinidinium ion revealed that $(-)_{546}$-$[\mathrm{Cr(ox)_2(phen)}]^-$ has a Δ configuration in accord with the earlier assignment based on its CD spectrum. Following characteristics were noted with regard to intermolecular interactions in the crystal; i) complex anions are linked with one another through the hydrogen bonds to intervening water molecules, to form chains along two-fold screw axes parallel to the a-axis, ii) intermolecular hydrogen bonds connect the complex anion closely with *d*-quinidinium cation which is further hydrogen-bonded to each other forming infinite chains along two-fold axes parallel to the b-axis, and iii) partial stacking is observed between aromatic phen and quinoline rings. These interaction modes were discussed in relation to the Pfeiffer Effect of the corresponding system in water.

The Pfeiffer Effect[1)] is a shift in chiral equilibrium between two antipodes of an initially racemic complex upon the addition of a certain chiral compound called an environment substance in solution. It is, thus, a prototype of so-called first-order asymmetric transformations of coordination compounds. In our previous paper,[2)] it was reported that an appreciable equilibrium shift is attained for a mixed-chelate complex, $[\mathrm{Cr(ox)_2(phen)}]^-$ (ox=oxalate dianion and phen=1,10-phenanthroline), when monohydrochloride salts of cinchona alkaloids are mixed with in water. In particular, *d*-quinidinium chloride (=6′-methoxy-*d*-cinchoninium chloride) and *l*-quininium chloride (=6′-methoxy-*l*-cinchonidinium chloride) are found much more effective in inducing an equilibrium shift of $[\mathrm{Cr(ox)_2(phen)}]^-$ than their parent alkaloids *d*-cinchoninium and *l*-cinchonidinium chlorides, suggesting some important roles played by the MeO group on the quinoline ring in the stereoselective interaction with the complex anion in water. These observations led us to presume that more extensive association takes place between the cinchona alkaloid cations and the complex anion than is expected for usual 1:1 electrolytes. In fact, molecular model consideration indicates that hydrophobic stacking interaction is possible between aromatic phen and quinolyl groups in addition to electrostatic and/or hydrogen-bonding interactions of ox ligand(s) with the protons on the N(1) atom and of the OH group on the C(9) atom of the alkaloid cation.



R = H; cinchoninium ion
R = MeO; quinidinium ion

In the present study, an X-ray analysis was performed on a diastereomeric salt of *d*-quinidinium ion with $(-)_{546}$-$[\mathrm{Cr(ox)_2(phen)}]^-$ to get some information on their intermolecular interactions in the solid state, which, we expect, might help us to elucidate their stereoselective interactions involved in the Pfeiffer Effect of the corresponding system in water.

Experimental

Preparation of Compounds. Potassium salt of $[\mathrm{Cr(ox)_2(phen)}]^-$ was prepared as described in the literature,[3)] and was identified by its absorption spectrum.[4)] Aqueous *rac*-$\mathrm{K[Cr(ox)_2(phen)]\cdot 4H_2O}$ (8 mM, 50 ml) was mixed with aqueous *d*-quinidinium chloride dihydrate (8 mM, 50 ml), and a small amount of ethanol (1—2 ml) was added to facilitate the crystal formation. After the solution was allowed to stand at room temperature in the dark for 2 d, purple-red plate-like crystals were separated out. Found: C, 57.67; H, 4.57; N, 7.59%. Calcd for $\mathrm{C_{36}H_{35}CrN_4O_{11}}$: C, 57.52; H. 4.69; N, 7.45%.

Data Collection. A crystal with the size of $0.49\times0.42\times0.09\ \mathrm{mm^3}$ was used for reflection data collection. Determination of the unit cell dimensions and data collection were carried out on a Syntex R3 automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate ($\lambda=0.71069$ Å). In Table 1 are given cell constants and their estimated standard deviations which were derived from a least-squares refinement for 22 strong, general reflections ($20°<2\theta<35°$). Other crystal data are also collected in Table 1. From systematic absences for $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd, the space group was uniquely identified as $P2_12_12_1$. Reflection intensities were measured up to $2\theta=50°$ using the ω-scan technique with a scan speed of 3—30°/min (50 kV, 20 mA). Three reference reflections monitored after every cycle of 200 measurements, showed no significant variation in intensity during the data collection. Out of 3470 reflections measured, 2172 reflections with $|F_o|>3\sigma(F_o)$ were selected and were used for the structure determination. They were corrected for the Lorentz-polarization factor, but no absorption correction was

Table 1. Crystal data

Orthorhombic Space Group $P2_12_12_1$	
$a=9.943(2)$ Å	$D_o=1.41\ \mathrm{g\,cm^{-3}}$
$b=11.265(2)$ Å	$D_c=1.43\ \mathrm{g\,cm^{-3}}$
$c=30.716(9)$ Å	$Z=4$
$U=3440(1)$ Å^3	$\mu(\mathrm{Mo}\ K\alpha)=4.2\ \mathrm{cm^{-1}}$

applied since the linear absorption coefficient was low.

Solution and Refinement of Crystal Structure

The structure was solved by a conventional heavy-atom method. Atomic scattering factors for all atoms were taken from Ref. 5 and were corrected for real and imaginary parts of anomalous scattering.[6]

The position of the Cr atom was deduced from the three-dimensional Patterson synthesis. The remaining atoms were located from successive difference Fourier syntheses. After all nonhydrogen atoms were located, the block-diagonal least-squares refinement using anisotropic thermal parameters for these atoms reduced an R value, $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, to 0.091. At this stage, initial positions of hydrogen atoms were deduced from the geometrical calculations, and the least-squares refinement was continued with all the parameters fixed for hydrogen atoms. Two cycles of the refinement finally performed with all parameters variable, converged an R value to 0.078 and an R_w value,

Table 2. Atomic coordinates and thermal parameters

Atom	x	y	z	B_{eq}/Å^2 [a]	Atom	x	y	z	B_{eq}/Å^2 [a]
Cr	−0.00086(19)	0.23326(12)	0.39232(5)	3.61	C(E5)	0.1913(9)	0.2764(8)	0.2090(3)	3.12
N(A1)	0.1510(8)	0.1734(6)	0.3526(2)	3.56	C(E6)	0.0853(10)	0.3359(10)	0.2276(3)	4.33
C(A2)	0.1429(10)	0.1163(9)	0.3158(3)	4.63	C(E7)	0.0992(10)	0.4088(10)	0.2640(3)	4.71
C(A3)	0.2540(12)	0.0726(9)	0.2940(3)	5.25	C(E8)	0.2223(10)	0.4303(9)	0.2807(3)	4.41
C(A4)	0.3805(12)	0.0879(9)	0.3118(4)	6.33	C(E9)	−0.0683(10)	0.2589(11)	0.1761(3)	5.81
C(A5)	0.5169(11)	0.1762(10)	0.3725(4)	7.40	C(E10)	0.3362(10)	0.3724(8)	0.2632(3)	4.09
C(A6)	0.5203(11)	0.2338(10)	0.4100(4)	7.52	C(E11)	0.3207(9)	0.2952(7)	0.2271(3)	2.90
C(A7)	0.3979(12)	0.3356(11)	0.4714(4)	7.19	O(E12)	−0.0445(6)	0.3248(7)	0.2139(2)	5.52
C(A8)	0.2799(14)	0.3713(10)	0.4883(3)	7.50	O(W)	−0.2583(11)	0.4742(10)	0.5251(3)	13.70
C(A9)	0.1622(11)	0.3503(9)	0.4663(3)	5.07	H(CA2)	0.048(8)	0.095(8)	0.302(3)	4.6
N(A10)	0.1614(8)	0.2947(6)	0.4272(2)	4.07	H(CA3)	0.240(9)	0.028(7)	0.264(2)	3.2
C(A11)	0.2820(9)	0.2567(8)	0.4099(3)	4.11	H(CA4)	0.466(9)	0.059(8)	0.295(3)	4.6
C(A12)	0.2769(9)	0.1948(8)	0.3695(3)	4.11	H(CA5)	0.596(8)	0.149(7)	0.356(3)	4.2
C(A13)	0.3952(9)	0.1525(9)	0.3502(4)	5.82	H(CA6)	0.608(8)	0.246(8)	0.425(3)	3.6
C(A14)	0.4032(10)	0.2791(9)	0.4307(3)	5.13	H(CA7)	0.484(9)	0.352(8)	0.487(2)	3.1
O(B1)	−0.0262(6)	0.3817(5)	0.3607(2)	4.20	H(CA8)	0.271(9)	0.417(8)	0.516(3)	5.4
O(B2)	−0.1294(6)	0.3041(5)	0.4321(2)	4.84	H(CA9)	0.072(8)	0.373(7)	0.481(2)	2.7
C(B3)	−0.1184(10)	0.4464(9)	0.3762(3)	4.49	H(ND1)	0.341(9)	0.099(8)	0.095(3)	4.3
C(B4)	−0.1780(10)	0.4039(9)	0.4184(3)	4.60	H(CD2a)	0.499(8)	0.059(7)	0.045(2)	2.2
O(B5)	−0.1563(8)	0.5411(6)	0.3611(3)	7.12	H(CD2b)	0.564(8)	0.076(8)	0.095(2)	3.4
O(B6)	−0.2646(8)	0.4599(6)	0.4376(2)	6.76	H(CD3)	0.601(7)	0.215(7)	0.020(2)	1.8
O(C1)	−0.1362(6)	0.1480(6)	0.3606(2)	4.76	H(CD4)	0.615(8)	0.404(8)	0.065(3)	4.1
O(C2)	0.0120(7)	0.0876(5)	0.4257(2)	4.84	H(CD5a)	0.365(9)	0.430(8)	0.066(3)	6.6
C(C3)	−0.1585(11)	0.0423(9)	0.3735(4)	5.74	H(CD5b)	0.423(8)	0.377(8)	0.018(3)	4.1
C(C4)	−0.0681(11)	0.0056(9)	0.4119(4)	5.68	H(CD6a)	0.232(8)	0.273(7)	0.066(2)	2.5
O(C5)	−0.2405(8)	−0.0250(6)	0.3599(3)	7.76	H(CD6b)	0.330(8)	0.203(7)	0.027(2)	4.9
O(C6)	−0.0717(8)	−0.0930(7)	0.4288(3)	8.99	H(CD7a)	0.622(7)	0.284(7)	0.137(2)	1.3
N(D1)	0.3951(7)	0.1665(7)	0.0887(2)	2.78	H(CD7b)	0.520(8)	0.402(7)	0.136(2)	3.5
C(D2)	0.5237(10)	0.1180(9)	0.0705(3)	4.46	H(CD8)	0.330(8)	0.294(7)	0.134(2)	1.3
C(D3)	0.6109(9)	0.2227(9)	0.0540(3)	4.78	H(CD9)	0.352(8)	0.108(7)	0.173(2)	3.2
C(D4)	0.5525(10)	0.3364(9)	0.0722(3)	4.50	H(CD10)	0.832(9)	0.279(8)	0.050(3)	6.1
C(D5)	0.4170(11)	0.3569(10)	0.0507(4)	5.56	H(CD11a)	0.766(9)	0.056(7)	0.094(2)	4.6
C(D6)	0.3298(10)	0.2472(9)	0.0558(3)	4.41	H(CD11b)	0.932(9)	0.139(8)	0.086(3)	4.7
C(D7)	0.5355(9)	0.3230(8)	0.1218(3)	3.31	H(OD12)	0.546(8)	0.021(8)	0.184(2)	4.3
C(D8)	0.4168(9)	0.2410(8)	0.1293(3)	2.98	H(CE2)	0.656(9)	0.349(8)	0.280(2)	3.3
C(D9)	0.4309(9)	0.1583(8)	0.1702(3)	3.09	H(CE3)	0.641(8)	0.217(7)	0.218(2)	2.4
C(D10)	0.7609(12)	0.2125(10)	0.0644(3)	6.47	H(CE5)	0.180(8)	0.220(7)	0.183(2)	1.4
C(D11)	0.8205(13)	0.1327(12)	0.0823(4)	8.55	H(CE7)	0.015(8)	0.445(7)	0.279(2)	2.3
O(D12)	0.5503(6)	0.0907(6)	0.1658(2)	4.26	H(CE8)	0.231(9)	0.486(8)	0.306(3)	2.7
N(E1)	0.4592(8)	0.3936(7)	0.2823(2)	4.12	H(CE9a)	0.020(8)	0.280(7)	0.153(2)	3.9
C(E2)	0.5625(10)	0.3350(9)	0.2662(3)	4.43	H(CE9b)	−0.156(9)	0.278(8)	0.162(3)	5.8
C(E3)	0.5580(9)	0.2583(9)	0.2309(3)	3.94	H(CE9c)	−0.065(8)	0.171(8)	0.181(3)	4.2
C(E4)	0.4384(9)	0.2412(9)	0.2105(3)	3.13					

a) For the nonhydrogen atoms, anisotropic thermal parameters are listed in Table 6 (supplementary material). $B=8\pi^2(U_{11}+U_{22}+U_{33})/3$.

$[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_c|^2]^{1/2}$, to 0.055. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$ and the weighting scheme employed was $w=[\sigma^2+g^2|F_o|^2]^{-1}$ for the final refinement, where σ is a standard deviation obtained from the counting statistics for each reflection and the value of g used is 0.01. The final electron density difference map showed no unusual features, and there was no residual peak higher than 0.3 e/Å^3.

Fourier syntheses, least-squares refinement, and geometrical calculations were performed using programs $P2_12_12_1$,[7] HBLS,[8] and DAPH[9] with slight modification, respectively on a HITAC M-200H computer at the Hiroshima University Information Processing Center.

The final atomic parameters and their estimated standard deviations are listed in Table 2 with averaged isotropic thermal parameters. Anisotropic thermal parameters and complete lists of the $|F_o|$ and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8327).

Results and Discussion

The asymmetric unit within the unit cell is illustrated in Fig. 1 with the numbering scheme adopted for respective atoms.

Molecular Structure of Complex Anion. The bond distance and selected bond angles in $[Cr(ox)_2(phen)]^-$ are given in Table 3. The mean C–O bond distance is 1.939(7) Å somewhat shorter than the corresponding distances of 1.969(2) Å found in *rac*-$K_3[Cr(ox)_3]\cdot 3H_2O$[10] and of 1.965(2), 1.952(7), and 1.962(5) Å in *fac*-$[Cr(gly)_3]\cdot H_2O$,[11] *rac*-$[Cr(acac)_3]$,[12] and Δ-$[Cr(acac)_3]$,[13] respectively. Somewhat greater anisotropy in the thermal parameters might be in part responsible for the shorter Cr–O distances found in the present crystal. The mean Cr–N bond distance found is 2.065 (8) Å, which coincides well with the corresponding distances of 2.066(10) Å in $[Cr(phen)_2(OH)]_2I_4\cdot 4H_2O$[14] and of 2.068(5) Å in *fac*-$[Cr(gly)_3]\cdot H_2O$.[11]

The averaged O–Cr–O and N–Cr–N bond angles are 83.5(3)° and 81.5(3)°, respectively. They compare well within e.s.d.'s with the values of 82.3(1)° and 79.7(3)° reported for *rac*-$K_3[Cr(ox)_3]\cdot 3H_2O$[10] and $[Cr(phen)_2(OH)]_2I_4\cdot 4H_2O$,[14] respectively.

Intramolecular bond distances within phen and ox chelate ligands are all in good agreement with the comparable values reported in the literature.[10,14] Ox chelates have two kinds of C–O bonds; one forms a "free" carbonyl group and the other is directly associated with the complex formation with Cr(III) ion. A general trend[10] that the latter bond is longer, is also noted in this case. In a phen chelate, the N(A1)–C(A2) and N(A10)–C(A9) distances, for example, are a little shorter than the N(A1)–C(A12) and N(A10)–C(A11) distances, respectively, as is usually the case.[14] Similarly, some deviations are also seen in the C–C bond distances. If e.s.d.'s are taken into account, the C–N and C–C bond distances in a phen chelate seem to correlate with their π-bond orders estimated.[14,15]

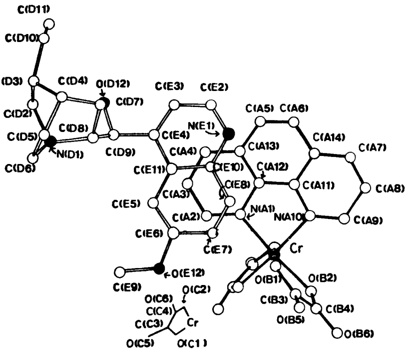


Fig. 1. Asymmetric unit within the unit cell of *d*-quinidinium Δ-$[Cr(ox)_2(phen)]\cdot H_2O$ with the numbering scheme.

In Table 4 are presented the equations of the least-squares plane through the chelate ligands and the distances from the plane to the respective atoms. The Cr(III) atom lies approximately on the plane of one ox chelate (C), but off the plane of another ox chelate (B) which is hydrogen-bonded to both the H–N$^+$(D1) and H–O(W) protons. Similarly, the Cr(III) atom is not coplanar with the phen chelate plane (A), which is probably due to the repulsive interaction with the neighboring quinolyl group of *d*-quinidinium ion.

The absolute configuration of $(-)_{546}$-$[Cr(ox)_2(phen)]^-$ forming a less-soluble diastereomer with *d*-quinidinium cation is assigned as Δ on the basis of the known configurations (3*R*,4*S*,8*R*,9*S*) of *d*-quinidinium cation.[16] This assignment is in accord with that made earlier by the CD spectrum.[4]

Molecular Structure of d-*Quinidinium Cation.* The bond distances and angles within *d*-quinidinium cation (Table 3) are very close to those reported earlier by an X-ray analysis on several cinchona alkaloids,[16–18] with somewhat a shorter C(D10)–C(D11) bond distance. The quinuclidine part has a skew conformation. When it is viewed along the N(D1)–C(D4) direction, the bonds N(D1)–C(D2), N(D1)–C(D6), and N(D1)–C(D8) are rotated about 10° from the eclipsed position over the bonds C(D4)–C(D3), C(D4)–C(D5), and C(D4)–C(D7), in keeping with the results obtained by earlier studies.[16,17] The quinoline ring is regarded as planar within experimental error.

Crystal Packing. The molecular packing in the crystal seen down the a-axis is depicted in Fig. 2. The crystal structure is characterized simply by four types of intermolecular hydrogen bonds by which the composite molecules, complex ion, *d*-quinidinium ion, and water are held together; other intermolecular

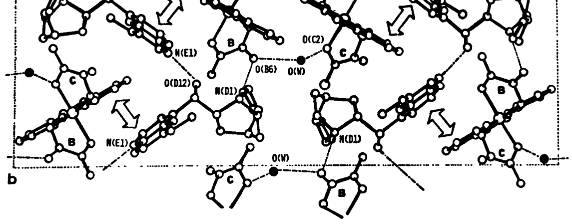


Fig. 2. Crystal packing in *d*-quinidinium Δ-$[Cr(ox)_2(phen)]\cdot H_2O$ viewed down the a-axis.

contacts being due to normal van der Waals interactions. The intermolecular distances shorter than 3.4 Å are given in Table 5. In the following, the crystal packing is discussed with particular reference to intermolecular interactions involved.

First of all, infinite chains of *d*-quinidinium cations hydrogen-bonded to one another (O(D12)–H···N(E1)) are aligned along the two-fold screw axes parallel to the b-axis (O(D12)···N(E1) 2.74 Å). Each *d*-quinidinium cation in the chain is further connected to the ox chelate (B) through the N$^+$(D1)–H···O(B6) hydrogen bond (N(D1)···O(B6) 2.78 Å). In short, a particular *d*-quinidinium ion participates in the two types of intermolecular hydrogen-bonding, *i.e.*, the N(E1) and H–O(D12) atoms are employed for the interaction with another *d*-quinidinium ion and the H–N$^+$(D1) proton for the interaction with the complex anion.

The crystal structure of *d*-quinidinium salt with 1,1′-dimethylferrocene-3-carboxylate has been reported.[16] In this crystal, both of the H–N$^+$(D1) and H–O(D12) protons are associated with the hydrogen

TABLE 3. SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular distances	l/Å		l/Å
Cr-N(A1)	2.058(8)	Cr-O(B1)	1.948(6)
Cr-N(A10)	2.071(8)	Cr-O(B2)	1.943(7)
N(A1)-C(A2)	1.291(13)	Cr-O(C1)	1.920(7)
N(A10)-C(A9)	1.322(14)	Cr-O(C2)	1.943(7)
N(A1)-C(A12)	1.385(12)	O(B1)-C(B3)	1.265(12)
N(A10)-C(A11)	1.371(12)	O(B2)-C(B4)	1.291(12)
C(A2)-C(A3)	1.391(15)	O(C1)-C(C3)	1.281(13)
C(A9)-C(A8)	1.399(18)	O(C2)-C(C4)	1.298(13)
C(A3)-C(A4)	1.381(16)	C(B3)-O(B5)	1.212(13)
C(A8)-C(A7)	1.334(18)	C(B4)-O(B6)	1.223(13)
C(A4)-C(A13)	1.377(16)	C(C3)-O(C5)	1.189(14)
C(A7)-C(A14)	1.357(16)	C(C4)-O(C6)	1.235(15)
C(A13)-C(A5)	1.416(17)	C(B3)-C(B4)	1.514(14)
C(A14)-C(A6)	1.423(16)	C(C3)-C(C4)	1·533(16)
C(A12)-C(A13)	1.405(15)		
C(A11)-C(A14)	1.412(14)		
C(A5)-C(A6)	1.346(17)		
C(A11)-C(A12)	1.439(14)		
N(D1)-C(D2)	1.510(12)	N(E1)-C(E2)	1.300(13)
C(D2)-C(D3)	1.544(15)	C(E2)-C(E3)	1.398(14)
C(D3)-C(D4)	1.518(15)	C(E3)-C(E4)	1.351(14)
C(D4)-C(D5)	1.528(15)	C(E4)-C(E11)	1.399(13)
C(D4)-C(D7)	1.551(14)	C(E5)-C(E11)	1.422(13)
C(D5)-C(D6)	1.534(15)	C(E5)-C(E6)	1.355(14)
C(D6)-N(D1)	1.501(13)	C(E6)-C(E7)	1.414(15)
C(D7)-C(D8)	1.524(12)	C(E7)-C(E8)	1.325(15)
C(D8)-N(D1)	1.518(11)	C(E8)-C(E10)	1.403(15)
C(D8)-C(D9)	1.556(12)	C(E10)-N(E1)	1.372(13)
C(D9)-O(D12)	1.426(11)	C(E10)-C(E11)	1.440(14)
C(D9)-C(E4)	1.567(13)	C(E6)-O(E12)	1.371(13)
C(D3)-C(D10)	1.548(16)	C(E9)-O(E12)	1.396(14)
C(D10)-C(D11)	1.192(17)		
Intramolecular angles	ϕ/°		ϕ/°
N(A1)-Cr-N(A11)	81.5(3)	C(D10)-C(D3)-C(D2)	115(1)
O(B1)-Cr-O(B2)	82.8(3)	C(D10)-C(D3)-C(D4)	111(1)
O(C1)-Cr-O(C2)	84.2(3)	C(D3)-C(D10)-C(D11)	128(1)
Cr-N(A1)-C(A2)	129.2(7)	C(D9)-C(D8)-N(D1)	111(1)
Cr-N(A10)-C(A9)	128.3(7)	C(D9)-C(D8)-C(D7)	114(1)
Cr-N(A1)-C(A12)	112.5(6)	C(D8)-C(D9)-O(D12)	109(1)
Cr-N(A10)-C(A11)	111.4(6)	C(D8)-C(D9)-C(E4)	107(1)
Cr-O(B1)-O(B3)	114.0(6)	C(D12)-C(D9)-C(E4)	111(1)
Cr-O(B2)-O(B4)	113.6(6)	C(E5)-C(E6)-O(E12)	124(1)
Cr-O(C1)-O(C3)	115.1(7)	C(E7)-C(E6)-O(E12)	113(1)
Cr-O(C2)-C(C4)	112.3(7)	C(E5)-C(E6)-C(E7)	123(1)
		C(E6)-O(E12)-C(E9)	117(1)

TABLE 4. LEAST-SQUARES PLANES

Deviations of atoms from the planes in Å

plane(A)		plane(B)		plane(E)	
N(A1)	−0.010	O(B1)	−0.014	N(E1)	0.030
C(A2)	−0.013	O(B2)	0.003	C(E2)	−0.021
C(A3)	−0.016	C(B3)	0.020	C(E3)	−0.028
C(A4)	−0.036	C(B4)	0.003	C(E4)	0.026
C(A5)	0.009	O(B5)	−0.003	C(E5)	−0.014
C(A6)	−0.000	O(B6)	−0.010	C(E6)	−0.007
C(A7)	−0.042	Cr*	0.134	C(E7)	−0.039
C(A8)	−0.047			C(E8)	0.019
C(A9)	−0.010	plane(C)		C(E9)	0.061
N(A10)	0.043	O(C1)	0.020	C(E10)	0.018
C(A11)	0.033	O(C2)	−0.028	C(E11)	0.005
C(A12)	0.042	C(C3)	0.011	O(E12)	−0.042
C(A13)	0.019	C(C4)	0.006		
C(A14)	0.032	O(C5)	−0.027		
Cr*	−0.155	O(C6)	0.018		
		Cr*	−0.003		

Dihedral angles between the planes

plane(A)-plane(B)	103.2°	plane(B)-plane(C)	89.1°
plane(A)-plane(C)	85.0°	plane(A)-plane(E)	9.5° (stacking)

Plane equations[a)]

plane	l	m	n	p
A	0.0809	0.8646	−0.4959	3.5504
B	−0.6998	−0.4940	−0.5161	7.6448
C	0.6878	−0.3340	−0.6445	8.6477
E	0.1528	0.7735	−0.6151	1.2365

* The Cr atom is not included for plane calculations. a) The equation of a plane is expressed as $lx'+my'+nz'+p=0$, where x', y', and z' are coordinates in Å. All atoms are given equal weight.

bonds to the carboxylate group on the ferrocene, and the N(E1) atom on the quinolyl group is completely indifferent to the intermolecular interaction. Similarly, the N(E1) atom does not participate at all in any intermolecular interactions in the crystal of free *d*-cinchonine where both of the H–O(D12) and N(D1) atoms are used for the hydrogen-bonding interactions with another *d*-cinchonine molecule.[18)] In this way, our present crystal structure seems peculiar in that the N(E1) atom plays as a proton acceptor an essential role in the crystal packing.

Remaining two types of hydrogen bonding found in the present crystal structure are associated with water molecules of crystallization; the complex anions are linked with one another through the hydrogen bonds to the intervening water molecules (O(W)–H···O(B6) and O(W)–H···O(C2)) to form another screw chain parallel to the a-axis. The intermolecular distances are as follows; O(W)···O(B6) 2.69 Å and O(W)···O(C2) 2.83 Å.

One more interaction mode to be noted is partial intermolecular stacking between aromatic phen and quinoline rings (Fig. 1). The spacing between the two rings is 3.3—3.5 Å and the tilt angle between the normals of the ring planes is 9.5°. Similar stacking is often observed in the crystal structures of mixed-ligand metal complexes having phen or bpy ligand(s) as a chelate.[19)]

Implication to the Interactions Involved in the Pfeiffer Effect. As noted in the introduction, the chiral equilibrium of $[Cr(ox)_2(phen)]^-$ is substantially shifted in favor of its *Δ*- and *Λ*-enantiomers in the presence of *d*-quinidinium and *l*-quininium cations, respectively. Under certain experimental conditions, the enantiomer excess actually attained amounts to almost 20%, which is by far greater than those usually observed (2—3%).[2)] In order to account for the much greater Pfeiffer Effect observed, a following association model is proposed for the stereoselective interaction between *Δ*-$[Cr(ox)_2(phen)]^-$ and *d*-quinidinium ions in aqueous solution (Fig. 3-a).

In this model, it is one ox chelate(B) of the complex anion that interacts with quinidinium cation through the two hydrogen bonds; one between the free carbonyl oxygen atom and the H–N$^+$(1) proton, and the other between another carbonyl oxygen atom coordinated to the Cr(III) ion and the OH group on the C(9) atom. Similar hydrogen-bonding interactions have been actually found between the carboxylate group and *d*-quinidinium ion in the solid state.[16)] The other ox chelate(C) is not concerned at all with the interaction with *d*-quinidinium ion. In addition to these hydrogen bonds, hydrophobic stacking[20)] interaction between the aromatic phen and quinoline rings contributes to the stereoselective association. The presence of stacking interaction is suggested by the findings

Table 5. Intermolecular distances

No.	A-H···B		tr.[a]	A-H···B *l*/Å
1) Hydrogen bonds of the type A-H···B				
1	O(W)	O(B6)	1	2.69
2	O(W)	O(C2)	2	2.83
3	O(D12)	N(E1)	3	2.74
4	N(D1)	O(B6)	4	2.78
2) Contacts related to hydrogen bonds				
No.[b]	A′	B′	tr.[a]	A′···B′ *l*/Å
1	C(A7)	O(B2)	5	3.37
1	C(A8)	O(B2)	5	3.27
2	O(W)	C(A11)	2	3.30
3	O(D12)	C(E8)	3	3.33
4	N(D1)	O(B5)	4	3.16
4	C(D9)	O(B5)	4	3.18
4	C(D2)	O(B6)	4	3.14
4	C(D6)	O(B6)	4	3.31
3) Other close contacts (<3.4 Å)				
	A′	B′	tr.[a]	A′···B′ *l*/Å
	C(A3)	C(E11)	1	3.31[c]
	O(B1)	C(E7)	1	3.24
	C(D6)	O(C6)	6	3.17
	C(D8)	O(C5)	6	3.18
	C(E5)	O(C5)	6	3.12
	C(D4)	O(W)	7	3.29
	C(A5)	O(C5)	8	3.33
	C(E9)	C(D11)	8	3.40

a) tr. refers to the following translations of "B" atom from the coordinates listed in Table 2.: 1) x, y, z; 2) $-0.5+x, 0.5-y, 1-z$; 3) $1-x, -0.5+y, 0.5-z$; 4) $-x, -0.5+y, 0.5-z$; 5) $0.5+x, 0.5-y, 1-z$; 6) $-x, 0.5+y, 0.5-z$; 7) $0.5-x, 1-y, -0.5+z$; 8) $-1+x, y, z$. b) Number given to the hydrogen bond listed in 1). c) Related to stacking interaction. The e.s.d. is at most 0.02 Å for each distance.

that organic additives like dioxane[21] diminish the Pfeiffer Effect of the present system greatly and the association constant estimated is 57 which is too great to be accounted for by the electrostatic attraction alone.[22] Furthermore, if the MeO group on the quinoline ring also participates in the hydrophobic interaction[23,24] with the phen chelate, stronger association with the complex anion is expected, and thus a much greater equilibrium shift induced by *d*-quinidinium (6′-methoxy-*d*-cinchoninium) ion than by *d*-cinchoninium ion may be rationalized.

In short, the association model shown in Fig. 3-a is constructed on the assumption that *d*-quinidinium cation recognizes the chirality of $[Cr(ox)_2(phen)]^-$ by interacting with the two chelate ligands, ox and phen, simultaneously through the hydrogen-bonding and hydrophobic stacking interactions, respectively. The simultaneous interactions with *d*-quinidinium cation come into play effectively when the complex anion has a Δ configuration, as seen in Fig. 3-a. The Λ-enantiomer cannot associate with *d*-quinidinium ion in such a way that the two interactions contribute simultaneously. In this way, the Δ-enantiomer is favored over the Λ-enantiomer, the former being thereby enriched at equilibrium in the presence of *d*-quinidinium ion.

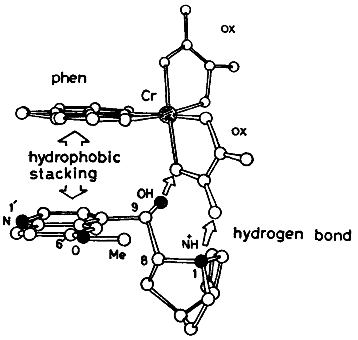


Fig. 3-a. Proposed model for stereoselective association between Δ-$[Cr(ox)_2(phen)]^-$ and *d*-quinidinium ions. The conformations of the latter are the same as those assumed in the solid state.

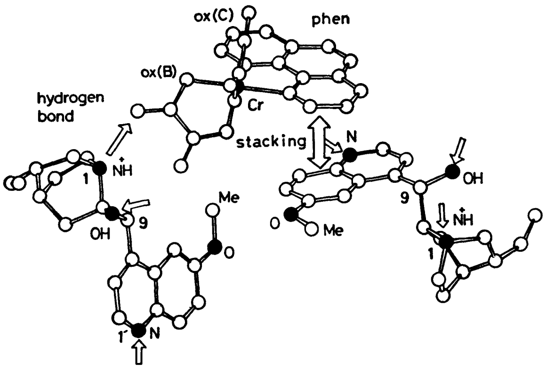


Fig. 3-b. Intermolecular interactions found in *d*-quinidinium Δ-$[Cr(ox)_2(phen)]\cdot H_2O$.

Now, turning to the intermolecular interactions found in the crystal structure of *d*-quinidinium Δ-$[Cr(ox)_2(phen)]\cdot H_2O$, one ox chelate(B) of the complex anion actually interacts with *d*-quinidinium cation through the hydrogen bond between the free carbonyl group and the H–N^+(1) proton, but the OH group on the C(9) atom is hydrogen-bonded not to the ox chelate but to the N(1′) atom of another *d*-quinidinium ion, thereby forming infinite chains of *d*-quinidinium cations. Furthermore, the phen ring of the complex anion is stacked with *d*-quinidinium cation, but the stacking is partial (Fig. 1) and is with the quinoline ring of another *d*-quinidinium ion hydrogen-bonded to another complex anion. The above-mentioned situations are easily visualized in Fig. 3-b, where a particular complex anion and two *d*-quinidinium cations interacting with it are projected along an appropriate axis.

It cannot be stated whether the intermolecular interactions found in the solid state persist also in solution. In fact, the metal complex anion interacts directly with two *d*-quinidinium cations simultaneously in the present crystal structure, while 1:1 association is dominant in solution.[2] Thus, the association modes in solution are not directly deduced from the crystal structure. However, the intermolecular interactions found in the solid state are often informative in discussing how the composite ions interact with each other in solution.[19]

As seen in Fig. 3-b, both the OH and N^+–H groups of *d*-quinidinium ion are associated with the intermolecular hydrogen bonds, and the quinolyl group is stacked, though partially, with the phen chelate in the present crystal structure. These observations imply that the complex and *d*-quinidinium ions are held together in solution also by both the hydrogen-bonding and hydrophobic stacking interactions. As a result, we suppose that the association modes shown in Fig. 3-a are fairly plausible and are probably responsible for the substantial equilibrium shift attained by the Pfeiffer Effect in water.

Finally, the MeO group on the quinoline ring is found not to participate at all in the interaction with the phen chelate in the solid state (Fig. 1). However, an appreciable up-field shift[23,24] has been observed in the pmr spectrum of the MeO group of *l*-quininium ion upon the addition of $[Co(ox)_2(phen)]^-$ in D_2O,[22] suggesting attractive interaction of the MeO group with the phen chelate of the complex anion in water. This observation supports the idea that the MeO group is also involved in the hydrophobic interaction with the phen part of the complex anion. Our proposed model allows the above interaction to work at least for the Δ-enantiomer and thus provides a possible interpretation to the fact that *d*-quinidinium and *l*-quininium cations induce a much greater equilibrium shift in $[Cr(ox)_2(phen)]^-$ than *d*-cinchoninium and *l*-cinchonidinium cations.

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