Contribution from the Department of Chemistry,
Faculty of Science, Hokkaido University, Sapporo 060, Japan

Racemic Adsorption of Dicyanobis(1,10-phenanthroline)iron(II) on Colloidally Dispersed Sodium Montmorillonite

AKIHIKO YAMAGISHI

Adsorption of $Fe(phen)_2(CN)_2$ (phen ≡ 1,10-phenanthroline) on colloidally dispersed sodium montmorillonite has been compared between the racemic and enantiomeric solutions of the metal complex. Binding capacity of a clay is almost 2 times larger for the racemic solution than for the enantiomeric one. It indicates that any site already occupied by a given enantiomer can further accept the binding of an opposite enantiomer. The tendency for racemic adsorption has been utilized to improve the optical purity of a solution as well as to resolve racemic $Fe(phen)_2(CN)_2$ at the expense of enantiomeric $[Ni(phen)_3]^{2+}$.

Binding of an inorganic metal ion with a clay usually occurs within the amount of the cation-exchange capacity (CEC). A certain metal complex is, however, adsorbed on a clay in excess of CEC.[1,2] It is believed that a screening of the electrostatic charge by the complex cation permits the penetration of more of the complex cation into the interlamellar space. Studying the adsorption of an optically active metal complex, we recently revealed that the stereospecific regulation was operative in forming such a superstructure.[3,4] For example, when an enantiomer of $[Fe(phen)_3]^{2+}$ (phen ≡ 1,10-phenanthroline) or $[Ni(phen)_3]^{2+}$ was adsorbed by colloidally dispersed sodium montmorillonite, the complex occupied two cation-exchange sites per chelate to neutralize its dipositive charge. On the other hand, the maximum amount of adsorbed complex was doubled when the complex was added as a racemic mixture. In the latter case, the extra charge was neutralized by the binding of an anion. Thus any site already occupied by a given enantiomer can further accept the binding of a different enantiomer.

In the present work, the above racemic adsorption has been observed also, when a central Fe^{II} ion is coordinated with two bulky and two small ligands. The investigated complexes were $Fe(phen)_2(CN)_2$, $[Fe(phen)_2(CN)_2]^+$, and $Fe(bpy)_2(CN)_2$ (bpy ≡ 2,2'-bipyridyl). Although the binding strength of a clay is dependent on the kinds of metal complexes, the binding capacity is always higher for racemic mixtures than for the corresponding enantiomers. From equilibrium and kinetic studies, it has been concluded that such a preference for racemic adsorption is realized by stereoregular stacking due to the van der Waals interaction between the bulky ligands.

Experimental Section

Λ-$Fe(phen)_2(CN)_2$ was prepared by adding KCN into a Δ-$[Fe(phen)_3](ClO_4)_2$ solution at 0 °C.[5] Δ-$Fe(phen)_2(CN)_2$ was synthesized similarly from Λ-$[Fe(phen)_3](Sb-d\text{-}tart)_2$. The molecular rotation at 490 nm was found to be $[M]_{490} = 4.0 \times 10^4$ and -4.1×10^4 for Λ- and Δ-$Fe(phen)_2(CN)_2$, respectively. Optically active $[Fe(phen)_2(CN)_2]^+$ was obtained by oxidizing $Fe(phen)_2(CN)_2$ with concentrated HNO_3;[6] $[M]_{395} = 2.8 \times 10^4$ and -2.9×10^4 for Λ- and Δ-$[Fe(phen)_2(CN)_2]^+$, respectively. Δ-$Fe(bpy)_2(CN)_2$ was prepared from Λ-$[Fe(bpy)_3](Sb-d\text{-}tart)_2$; $[M]_{500} = -3.5 \times 10^4$. Sodium montmorillonite (Na^+M^-) was purchased from Kunimine Ind. Co. (Japan) (Kunipia-G). An 87-mg quantity of Na^+M^- was dispersed in 100 mL of distilled water. The resultant solution contained 10^{-3} M of cation-exchange site.[7]

Electronic spectra were recorded on a Hitachi EPS-3T spectrophotometer at 20 °C. Optical rotatory dispersion (ORD) was measured with a JEOL Model ORD/UV-5 ORD spectrophotometer at room temperature. The transient electric dichroism was measured at 20 °C by use of a high-electric-field pulse of a temperature-jump apparatus.[8] The details of the instruments were described elsewhere.[9] X-ray diffraction lines were measured with a Toshiba XC-40H X-ray diffraction apparatus at room temperature. The rate of adsorption was followed at 20 °C with a stopped-flow apparatus, a Union Giken RA 1300 stopped-flow spectrophotometer.[10] A membrane filter had a maximum passage of 0.45 μm (Toyo (Japan) TM-2).

Results

Binding Equilibria. When sodium montmorillonite (Na^+M^-) was added to a solution of $Fe(phen)_2(CN)_2$, the solution was pale pink. Since the radius of a colloidal particle of a clay was less than 2 μm,[3] the absorption spectrum of a solution was measured without serious interference of light scattering. Figure 1 shows such a spectrum when the clay-to-metal chelate ratio was varied at constant $Fe(phen)_2(CN)_2$ concentration. The results were interpreted in terms of the binding equilibrium

$$n Fe(phen)_2(CN)_2 + M^- \rightleftharpoons [Fe(phen)_2(CN)_2]_n \cdot M^- \quad (1)$$
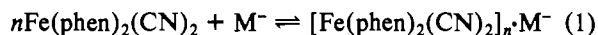
where n denotes the number of metal chelates adsorbed on one cation-exchange site. If there were no cooperativity operative among the bound metal chelates, the simple mass-action law held for reaction 1 would be

$$K_b = \frac{[\text{bound metal chelate}]}{[\text{free metal chelate}] \times n[\text{free clay site}]} \quad (2)$$

where [free clay site] was measured in terms of cation-exchange sites. With use of the absorbance increase at 530 nm in Figure 1, the degree of binding (X) defined by

$$X = [\text{bound metal chelate}]/[\text{total metal chelate}]$$

was expressed by

$$X = \Delta A_{530}/(\Delta A_{530})_\infty \quad (3)$$

where ΔA_{530} and $(\Delta A_{530})_\infty$ were the increases of absorbance at the given and infinite clay-to-metal chelate ratios, respectively. Equation 2 was rearranged into a linear form as

$$Y = \alpha - \beta X \quad (2')$$

with $Y = [\text{total } Na^+M^-]([\text{bound metal chelate}]^{-1} - [\text{total metal chelate}]^{-1})$, $\alpha = (1/n)(1 + K_b^{-1}[\text{total metal chelate}]^{-1})$, and $\beta = 1/n$. In Figure 2, Y was plotted against X for both the enantiomeric and the racemic solutions of $Fe(phen)_2(CN)_2$.

In a comparison of the results for Λ-, Δ-, and *rac*-$Fe(phen)_2(CN)_2$, the following points were noteworthy: (i) For the racemic solution, Y decreases almost linearly with X as predicted from eq 2'. n and K_d were found to be 1.75 and 4.1

(1) Berkheiser, V. E.; Mortland, M. M. *Clays Clay Miner.* **1977**, *25*, 105.
(2) Swartzen-Allen, S. L.; Matijevic, E. *J. Colloid Interface Sci.* **1975**, *50*, 143.
(3) Yamagishi, A.; Soma, M. *J. Chem. Soc., Chem. Commun.* **1981**, 539.
(4) Yamagishi, A.; Soma, M. *J. Am. Chem. Soc.* **1981**, *103*, 4640.
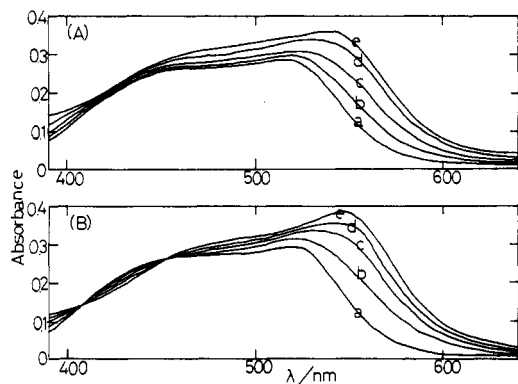(5) Archer, R. D.; Suydam, L. J.; Dollberg, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 6837.
(6) Shilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.
(7) Yamagishi, A.; Soma, M. *J. Phys. Chem.* **1981**, *85*, 3090.

(8) Yamagishi, A. *J. Phys. Chem.* **1976**, *80*, 1271.
(9) Yamagishi, A. *Biopolymers* **1981**, *20*, 201.
(10) Yamagishi, A.; Sakamoto, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2152.

Figure 1. Electronic spectra of a solution containing Fe(phen)$_2$(CN)$_2$ and sodium montmorillonite: (A) Λ-Fe(phen)$_2$(CN)$_2$ (6.8 × 10^{-5} M) and [Na$^+$M$^-$]/[Fe(phen)$_2$(CN)$_2$] = (a) 0, (b) 0.25, (c) 0.60, (d) 0.98, (e) 2.34; (B) rac-Fe(phen)$_2$(CN)$_2$ (7.0 × 10^{-5} M) and [Na$^+$M$^-$]/ [Fe(phen)$_2$(CN)$_2$] = (a) 0, (b) 0.23, (c) 0.46, (d) 0.69, (e) 1.10.
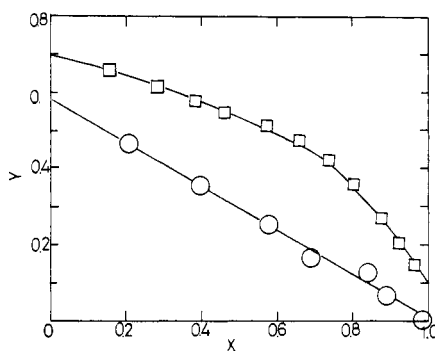
Figure 2. Plot of Y against X according to eq 2': (□) Λ-Fe-(phen)$_2$(CN)$_2$ + Na$^+$M$^-$; (○) rac-Fe(phen)$_2$(CN)$_2$ + Na$^+$M$^-$.

× 10^5 M^{-1}, respectively. (ii) On the other hand, the bindings from the enantiomeric solutions give the curved Y–X plots. From the initial slope ($X \ll 1$), n and K_d were found to be 1.3 and 3.1 × 10^4 M^{-1}, respectively, while from the final slope ($X \approx 1$), n and K_d were 0.74 and 1.3 × 10^5 M^{-1}, respectively. (iii) There was no meaningful difference in n and K_d between the Λ and Δ enantiomers.

The obtained n for the racemic solution was about 2 times larger than the value for the enantiomeric solution. Thus the results have demonstrated that Fe(phen)$_2$(CN)$_2$ tends to be adsorbed by a colloidal clay as a racemic pair rather than as a single enantiomer. This tendency is in accord with the adsorption of [Fe(phen)$_3$]$^{2+}$ and [Ni(phen)$_3$]$^{2+}$, for which n was found to be 1 and 0.5 for the racemic and enantiomeric solutions, respectively.[3,4]

Similar measurements were performed for other iron complexes like Fe(bpy)$_2$(CN)$_2$ and [Fe(phen)$_2$(CN)$_2$]$^+$. The equilibrium results of these complexes are summarized in Table I.

Electric Dichroism Measurements. The orientation of adsorbed Fe(phen)$_2$(CN)$_2$ was determined by transient electric dichroism measurements. Under the electric field pulse, a colloidal flake of montmorillonite was aligned in the direction of the electric field ($\vec{E}$).[11] Accompanying this orientational motion, a bound chelate directed its transition moment ($\vec{\mu}$) at some definite angle with respect to $\vec{E}$. The amplitude of the dichroism induced by such an alignment gave a value for the angle (ψ) between $\vec{E}$ and $\vec{\mu}$.

A solution of 5 × 10^{-6} M Fe(phen)$_2$(CN)$_2$ and 1.0 × 10^{-5} M Na$^+$M$^-$ showed the transient transmittance change, when the electric field pulse was applied at 34–62 kV cm^{-1} with the

(11) Shah, M. J.; Thompson, D. C.; Hart, C. M. *J. Phys. Chem.* **1963**, *67*, 1170.

Table I. Binding Equilibria of Iron Complexes with Colloidally Dispersed Sodium Montmorillonite at 20 °C

complex		n^a	K_b/M^{-1} ^{b}
Fe(phen)$_2$(CN)$_2$	racemic	1.75	4.1 × 10^5
	enantiomeric	1.33–0.74	(0.31–1.3) × 10^5
[Fe(phen)$_2$(CN)$_2$]$^+$	racemic	0.90^c	>10^6 ^{c}
	enantiomeric	0.55^c	>10^6 ^{c}
Fe(bpy)$_2$(CN)$_2$	racemic	2.2	1.8 × 10^6
	enantiomeric	1	~10^5

^{a} Number of adsorbed metal chelates per cation-exchange site. ^{b} Binding constant of eq 1. ^{c} n and K_b were obtained from the decrease of free metal complex by centrifuging a solution.

half-life time of about 400 μs. The amplitude of the signal depended on the angle (θ) between $\vec{E}$ and the polarization of incident light as

$$\Delta A / A = (\rho/6)(1 + 3 \cos 2\theta) \qquad (4)$$

where $\Delta A/A$ denoted the relative absorbance change under the electric field. Equation 4 agreed with the theoretical expression for $\Delta A/A$ when the buildup of orientational dichroism was monitored by linearly polarized light. ρ in eq 4 was reduced linear dichroism defined by

$$\rho = (\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon \qquad (5)$$

with ϵ = isotropic molar extinction coefficient at $\vec{E}$ = 0, $\epsilon_{\parallel}$ = molar extinction coefficient at θ = 0°, and $\epsilon_{\perp}$ = molar extinction coefficient at θ = 90°.

The electronic absorption at 400–600 nm for Fe(phen)$_2$-(CN)$_2$ may arise from the charge-transfer transition from Fe^{II} to phenanthroline ligands.[12] Accordingly $\vec{\mu}$ has the two components $\vec{\mu}_1$ and $\vec{\mu}_2$ along the straight lines connecting Fe^{II} with the short axes of two phenanthroline ligands. Any combination of $\vec{\mu} = a\vec{\mu}_1 + b\vec{\mu}_2$ (a, b = constants) can be the observed transition moment if the excited states of the transition concerned are doubly degenerate. Within this approximation, the vector, $\vec{\mu}$, lies in a plane made by $\vec{\mu}_1$ and $\vec{\mu}_2$, directing its arrow from Fe^{II}. In this case, ρ is expressed by

$$\rho = -\tfrac{3}{8}(1 - 3 \cos 2\psi)(\Phi(\vec{E})) \qquad (6)$$

where ψ denotes the angle between $\vec{E}$ and the plane spanned by $\vec{\mu}_1$, $\vec{\mu}_2$ and $\Phi(\vec{E})$, the orientation function at $\vec{E}$. $\Phi(\vec{E})$ represents the degree of orientation of a clay flake and takes a value from 0 to 1.

For a solution of Na$^+$M$^-$ and racemic Fe(phen)$_2$(CN)$_2$, ρ was found to be +0.45 at $\vec{E}$ = 34 kV cm^{-1}. ρ increased only 5% when $\vec{E}$ was raised from 34 to 62 kV cm^{-1}, indicating that a clay flake oriented almost completely. With the insertion of ρ = +0.45 and $\Phi(\vec{E})$ = 1 in eq 6, ψ was calculated to be 21°. For a solution of Na$^+$M$^-$ and Λ-Fe(phen)$_2$(CN)$_2$, ρ was found to be +0.40 at $\vec{E}$ = 34 kV cm^{-1}, leading to ψ = 23°. Thus in both racemic and enantiomeric cases, Fe(phen)$_2$(CN)$_2$ had its transition moment roughly parallel with $\vec{E}$. Since a clay flake is aligned with its surface parallel with $\vec{E}$,[11] the above results imply that the transition moment is parallel with a clay surface itself. The results are similar for [Fe(phen)$_3$]$^{2+}$, in which the iron chelate directed its C_3 axis perpendicular to a clay surface.[13]

Adsorption Kinetics. The rate of adsorption of Fe-(phen)$_2$(CN)$_2$ was followed by mixing a solution of the metal chelate with a Na$^+$M$^-$ solution. The progress of reaction was monitored by the absorbance increase at 530 nm when Fe-(phen)$_2$(CN)$_2$ was bound with a clay (Figure 1). The following three runs were studied. (i) Na$^+$M$^-$ was mixed with racemic

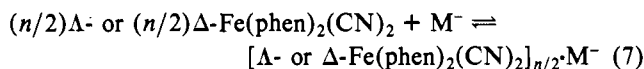(12) Cf.: McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.
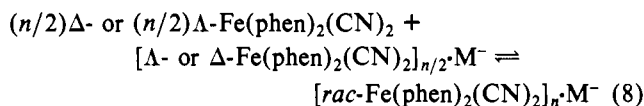
(13) Yamagishi, A. *J. Phys. Chem.*, in press.
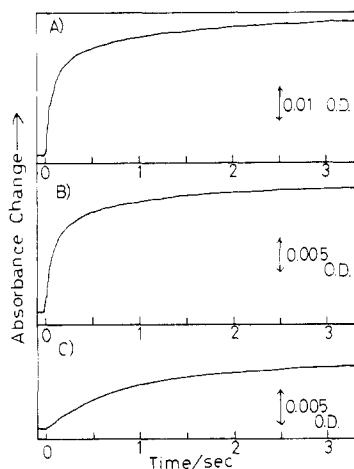
Figure 3. Transient change of absorbance at 530 nm, when two solutions were mixed in a stopped-flow apparatus: (A) *rac*-Fe-(phen)$_2$(CN)$_2$ (3.6 × 10^{-5} M) + Na$^+$M$^-$ (3.6 × 10^{-5} M); (B) Λ-Fe(phen)(CN)$_2$ (3.6 × 10^{-5} M) + Na$^+$M$^-$ (3.6 × 10^{-5} M); (C) Λ-Fe(phen)$_2$(CN)$_2$ (1.8 × 10^{-5} M)–Na$^+$M$^-$ (1.8 × 10^{-5} M) + Δ-Fe(phen)$_2$(CN)$_2$ (1.8 × 10^{-5} M)–Na$^+$M$^-$ (1.8 × 10^{-5} M).

Fe(phen)$_2$(CN)$_2$ (racemic adsorption). (ii) Na$^+$M$^-$ was mixed with Λ-Fe(phen)$_2$(CN)$_2$ (enantiomeric adsorption). And finally, (iii) a solution of Na$^+$M$^-$ and Λ-Fe(phen)$_2$(CN)$_2$ was mixed with a solution of Na$^+$M$^-$ and Δ-Fe(phen)$_2$(CN)$_2$ (buildup of racemic adsorbate layer from the different enantiomeric solutions).

In a comparison of the results in Figure 3, it was concluded that the signal due to run (i) was roughly the overlap of the signals due to runs (ii) and (iii). The absorbance change due to run (ii) was almost complete at 0.5 s after mixing, at which stage the absorbance change due to run (iii) only attained about 50% of the total change. These results implied that the racemic adsorption took place by way of the succeeding steps of enantiomeric and racemic adsorptions

$$(n/2)\Lambda\text{- or } (n/2)\Delta\text{-Fe(phen)}_2(\text{CN})_2 + \text{M}^- \rightleftharpoons$$
$$[\Lambda\text{- or } \Delta\text{-Fe(phen)}_2(\text{CN})_2]_{n/2}\cdot\text{M}^- \quad (7)$$

followed by

$$(n/2)\Delta\text{- or } (n/2)\Lambda\text{-Fe(phen)}_2(\text{CN})_2 +$$
$$[\Lambda\text{- or } \Delta\text{-Fe(phen)}_2(\text{CN})_2]_{n/2}\cdot\text{M}^- \rightleftharpoons$$
$$[rac\text{-Fe(phen)}_2(\text{CN})_2]_n\cdot\text{M}^- \quad (8)$$

If the above adsorption mechanisms hold even between different kinds of enantiomers, a clay surface already occupied by an enantiomer of one kind will be stereoselective toward the adsorption of an enantiomer of another kind. This expectation was ascertained by measuring the adsorption rates of Λ- or Δ-Fe(phen)$_2$(CN)$_2$ on such a surface already occupied by Δ-[Ni(phen)$_3$]$^{2+}$. As is given in Table II, the adsorption rate of Δ-Fe(phen)$_2$(CN)$_2$ was 0.6 times slower than that of Λ-Fe(phen)$_2$(CN)$_2$. In other words, a surface modified by Δ-[Ni(phen)$_2$]$^{2+}$ became stereoselective toward the adsorption of Fe(phen)$_2$(CN)$_2$. The same surface, however, can no longer recognize the chirality of Fe(bpy)$_2$(CN)$_2$ (runs 3 and 4 in Table II), indicating that there exists a rigorous steric regulation for racemic pairing.

X-ray Diffraction Measurements. Sodium montmorillonite has a lamellar structure of 2:1 SiO$_2$–Al$_2$O$_3$ sheets.[14] The basal spacing of the neighboring sheets in a clay–metal chelate adduct was determined by X-ray diffraction measurements. A 2:1 solution of Fe(phen)$_2$(CN)$_2$ and Na$^+$M$^-$ was filtered through a membrane filter. The resultant precipitates were

(14) Cowley, J. M.; Goswami, A. *Acta Crystallogr.* **1961**, *14*, 1071.

Table II. Initial Rates of Absorbance Change at 530 nm (V_{530}) When Solutions I and II Were Mixed in a Stopped-Flow Apparatus

run	soln I	soln II[b]	V_{530}[a]
1	Λ-Fe(phen)$_2$(CN)$_2$ (4.0 × 10^{-5} M)	Na$^+$M$^-$ (4.0 × 10^{-5} M) + Δ-[Ni(phen)$_3$]$^{2+}$ (8.0 × 10^{-5} M)	0.28
2	Δ-Fe(phen)$_2$(CN)$_2$ (4.0 × 10^{-5} M)	Na$^+$M$^-$ (4.0 × 10^{-5} M) + Δ-[Ni(phen)$_3$]$^{2+}$ (8.0 × 10^{-5} M)	0.16
3	Δ-Fe(bpy)$_2$(CN)$_2$ (6.7 × 10^{-5} M)	Na$^+$M$^-$ (4.0 × 10^{-5} M) + Δ-[Ni(phen)$_3$]$^{2+}$ (8.0 × 10^{-5} M)	0.45
4	Δ-Fe(bpy)$_2$(CN)$_2$ (6.7 × 10^{-5} M)	Na$^+$M$^-$ (4.0 × 10^{-5} M) + Λ-[Ni(phen)$_3$]$^{2+}$ (8.0 × 10^{-5} M)	0.44

^{a} V_{530} indicates the adsorption rate of Fe(phen)$_2$(CN)$_2$ on the clay and was measured in terms of optical density change per second. ^{b} Λ-[Ni(phen)$_3$]$^{2+}$ was added as the bis(antimonous *d*-tartrate) salt, and Δ-[Ni(phen)$_3$]$^{2+}$ was added as the perchlorate salt.

Table III. Improvement of the Optical Purity of the Fe(phen)$_2$(CN)$_2$ Solution

	init concn/ 10^{-5} M		final concn/ 10^{-5} M^a		% optical purity^b	
run	Λ isomer	Δ isomer	Λ isomer	Δ isomer	before	after
1	4.1	1.8	1.8	0.0	70	100
2	5.7	1.8	3.3	0.0	76	100
3	8.2	1.8	4.8	0.4	82	92
4	1.7	4.2	0.5	2.0	71	80
5	1.7	5.6	0.9	2.8	76	85
6	1.7	7.0	0.4	4.3	80	92

^{a} The concentrations of Λ and Δ isomers in a supernatant when the initial solution was centrifuged after the addition of 3.7 × 10^{-5} M Na$^+$M$^-$. ^{b} The percentage of excess isomer in a solution before or after elimination of a clay–metal chelate adduct.

dried over silica gel for 2 days. At that stage, a clay–*rac*-Fe(phen)$_2$(CN)$_2$ adduct was a deep red film, while a clay–Λ-Fe(phen)$_2$(CN)$_2$ adduct was reddish brown. The basal spacing (*d*) was calculated from the (001) diffraction line at the smallest angle (θ):

$$d = 1.54(2 \sin \theta)^{-1} \text{ Å} \quad (9)$$

d was determined to be 23.6 and 18.2 Å for clay–*rac*-Fe-(phen)$_2$(CN)$_2$ and clay–Λ-Fe(phen)$_2$(CN)$_2$ films, respectively. By subtraction of the thickness of 2:1 SiO$_2$–Al$_2$O$_3$ (9.0 Å) from *d*, the height of interlamellar space was obtained to be 14.6 and 9.2 Å for racemic and enantiomeric adducts, respectively. The latter value was almost identical with the height of Fe-(phen)$_2$(CN)$_2$ with their $\bar{\mu}_1$ and $\bar{\mu}_2$ parallel with a clay surface (~9 Å). On the other hand, the layer of *rac*-Fe(phen)$_2$(CN)$_2$ in an interlamellar space was about 5.5 Å higher than Fe-(phen)$_2$(CN)$_2$ itself. Thus in a combination of these data with the stopped-flow results (eq 7 and 8), it is suspected that the racemic layer is composed of such a double layer as is the overlap of Λ and Δ enantiomeric layers.

Improvement of Optical Purity and Optical Resolution. The optical purity of a Fe(phen)$_2$(CN)$_2$ solution was improved by use of the preference for racemic adsorption as below. An appropriate amount of Na$^+$M$^-$ was added to a solution containing Λ-Fe(phen)$_2$(CN)$_2$ in excess over Δ-Fe(phen)$_2$(CN)$_2$. The adduct of clay–metal complex was eliminated by centrifuging the solution. By means of measurements of the absorbance and ORD of a supernatant, the amount of Λ- and Δ-Fe(phen)$_2$(CN)$_2$ in the bulk solution was determined. The results are given in Table III. It was confirmed that the optical purity of a solution was enhanced due to the elimination of racemic mixture from the solution. The same conclusions
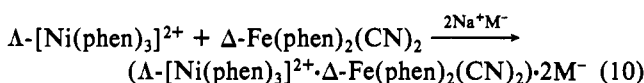
Table IV. Optical Resolution of Racemic $Fe(phen)_2(CN)_2$ at the Expense of Λ-$[Ni(phen)_3](ClO_4)_2$[a]

	initial soln		final soln[b]		
run	$Fe(phen)_2(CN)_2/$ 10^{-4} M	Λ-$[Ni(phen)_3]^{2+}/$ 10^{-4} M	Λ-$Fe(phen)_2(CN)_2/$ 10^{-4} M	Δ-$Fe(phen)_2(CN)_2/$ 10^{-4} M	Λ-$[Ni(phen)_3]^{2+}/$ 10^{-4} M
1	1.8	1.3	0.85	0.35	0.80
2	1.8	1.0	0.90	0.40	0.50
3	1.8	0.70	0.90	0.40	0.25
4	1.8	0.40	0.80	0.50	0.0
5[c]	7.0	10.0	0.50	0.50	0.0

[a] The solvent contained 10–30% methanol for all runs. [b] The concentrations in a supernatant when the initial solution was centrifuged after addition of 1.0×10^{-4} M Na^+M^- to it. [c] A solid of Δ-$[Ni(phen)_3]^{2+}$-montmorillonite was added to a $Fe(phen)_2(CN)_2$ solution.

were derived for a solution containing the Δ isomer as an excess enantiomer.

Next it was shown that the racemic adsorption of Fe-(phen)₂(CN)₂ with $[Ni(phen)_3]^{2+}$ led to the resolution of Fe(phen)₂(CN)₂. Na^+M^- was added to a solution of *rac*-Fe(phen)₂(CN)₂ and Λ-$[Ni(phen)_3](ClO_4)_2$. The solution was centrifuged, and the ORD and electronic spectra were measured for a supernatant. The results are given in Table IV. Evidently, the supernatant contained Λ-Fe(phen)₂(CN)₂ as an excess enantiomer. This arose from the formation of "pseudo" racemic pairs on a clay surface:
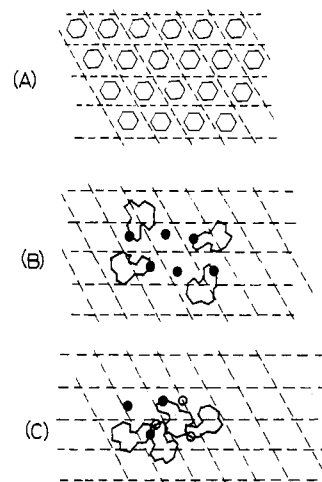
$$\Lambda\text{-}[Ni(phen)_3]^{2+} + \Delta\text{-}Fe(phen)_2(CN)_2 \xrightarrow{2Na^+M^-}$$

$$(\Lambda\text{-}[Ni(phen)_3]^{2+}\cdot\Delta\text{-}Fe(phen)_2(CN)_2)\cdot2M^- \quad (10)$$

It should be noted that the addition of solid Δ-$[Ni(phen)_3]^{2+}$·$2M^-$ into a racemic solution of Fe(phen)₂(CN)₂ did not resolve Fe(phen)₂(CN)₂, although most of the Fe(phen)₂(CN)₂ was adsorbed on the solid (run 5 in Table IV). The results indicated that the column chromatographic resolution of Fe(phen)₂(CN)₂ on a Δ-$[Ni(phen)_3]^{2+}$·$2M^-$ column was impossible.[15]

Solubility of Fe(phen)₂(CN)₂. By visual observation, it was noted that the racemic mixture precipitated when Λ- and Δ-Fe(phen)₂(CN)₂ were mixed at low temperature. Thus the solubility of Fe(phen)₂(CN)₂ was determined in the temperature range of 4–25 °C. An aqueous suspension of Fe-(phen)₂(CN)₂ was incubated at constant temperature for 6 h. The racemization of an enantiomer was negligible under these conditions.[5] After the suspension was centrifuged, the concentration in the supernatant was determined from its optical density of the electronic spectrum. Since both racemic and enantiomeric solutions gave identical spectra, the same molar extinction coefficient was used for a dissolved chelate (ϵ 5.1×10^4 at 267 nm and 4.1×10^3 at 510 nm). At 15 °C, the solubility was 7.0×10^{-5} or 7.9×10^{-4} M for *rac*- or Λ-Fe(phen)₂(CN)₂, respectively. From the dependence of the solubility on temperature (4–25 °C), the enthalpy change of solvation was determined to be $-\Delta H = 3.9 \pm 0.5$ or 1.1 ± 0.3 kcal mol⁻¹ for *rac*- or Λ-Fe(phen)₂(CN)₂, respectively. The above solubility data imply that Fe(phen)₂(CN)₂ tends to form a racemic crystal even in the absence of a clay.

Discussion

A montmorillonite layer consists of triple sheets of SiO_2–Al_2O_3–SiO_2.[14] When an outer silicate sheet is overviewed, the surface is filled with hexagonal holes, each of which is surrounded by six SiO_4^{4-} tetrahedrons (Figure 4A). A cation-exchange site is usually generated by replacing an Al^{3+} ion with a Mg^{2+} ion. From the stated elemental composition of the present clay sample,[16] about three hexagonal holes are allotted to one cation-exchange site.

(15) Fe(phen)₂(CN)₂ was recovered neither by water nor by methanol when it was placed on a Δ-$[Ni(phen)_3]^{2+}$–montmorillonite column.
(16) 58.0% SiO_2, 21.9% Al_2O_3, 1.9% Fe_2O_3, 3.4% MgO, and 3.0% Na_2O.

Figure 4. (A) Ideal surface of a silicate sheet. A hexagon denotes the hexagonal hole surrounded by six SiO_4^{4-} tetrahedrons. (B) Schematic drawing for the enantiomeric adsorption of Fe(phen)₂(CN)₂. ● denotes the three bottoms of two 1,10-phenanthroline ligands and one CN^- in Λ-Fe(phen)₂(CN)₂. (C) Schematic drawing for the racemic adsorption of Fe(phen)₂(CN)₂. O denotes the three bottoms of two 1,10-phenanthroline ligands and one CN^- in Δ-Fe(phen)₂(CN)₂.

For the enantiomeric adsorption of Fe(phen)₂(CN)₂, one metal chelate occupies one cation-exchange site approximately (Table I). When Fe(phen)₂(CN)₂ is placed with its $\vec{\mu}_1$ and $\vec{\mu}_2$ parallel with the surface, the bottoms of two phenanthroline molecules and CN^- almost fit into the three hexagonal holes (Figure 4B). Thus the enantiomeric adsorption at $n = 1$ corresponds to the saturated coverage of the surface by Fe-(phen)₂(CN)₂. Contrary to this, the maximum amount of adsorbed complex is almost doubled for racemic adsorption ($n \approx 1.75$ from Table I). Thus a pair of Λ and Δ isomers should be located over three hexagonal holes. Such a high degree of stacking seems to be impossible, as long as the whole adsorbates are in contact with the surface. However, the racemic pair achieves the stacking of $n = 1.5$, if the neighboring two phenanthroline ligands are overlapped closely (Figure 4C). n can be even higher if either component of the racemic pair is displaced upward from the surface. As a result, a double layer of racemic adsorbates may attain the observed degree of stacking ($n \approx 1.75$). The situations are consistent with the X-ray diffraction data ($d = 23.6$ Å). An important point is that the enantiomeric pairing cannot attain a stacking higher than $n = 1$ because the neighboring phenanthroline ligands interfere with each other. Thus it is concluded that the racemic stacking is realized by the highest stacking of phenanthroline ligands in which the van der Waals interaction between the large aromatic rings may be responsible.

On the basis of the above considerations, it is reasonable to expect that $[Fe(phen)_2(CN)_2]^+$ and Fe(bpy)₂(CN)₂ are also adsorbed racemically since these complexes have two bulky planar ligands. On the other hand, a complex with no bulky ligand like $[Co(en)_3]^{3+}$ (en ≡ ethylenediamine) will show no

tendency for racemic adsorption. In fact, both enantiomeric and racemic [Co(en)₃]³⁺ are adsorbed, occupying three cation-exchange sites per chelate.[17]

The resolution of Fe(phen)₂(CN)₂ at the expense of Λ-[Ni(phen)₃]²⁺ (Table IV) shows promise for the use of a clay as a material for optical resolution. Although column chromatography was impossible in the present systems, other chiral complexes like Co(acac)₃ (acac ≡ acetylacetonato) are actually resolved on a Δ-[Ni(phen)₃]²⁺–montmorillonite column.[18,19]

(17) This was ascertained by measuring the decrease of [Co(en)₃]³⁺ after centrifuging a clay–metal complex solution.

(18) Yamagishi, A. *J. Chem. Soc., Chem. Commun.* **1981,** 1168.
(19) Yamagishi, A.; Ohnishi, R.; Soma, M. *Chem. Lett.* **1982,** 85.

Properties of Copper(II) Hydride Formed in the Reaction of Aquacopper(I) Ions with Hydrogen Atoms. A Pulse Radiolytic Study[1]

W. A. MULAC[2a] and DAN MEYERSTEIN*[2a,b]

The spectrum of Cu–H⁺(aq), formed via Cu⁺ + H → Cu–H⁺(aq) in aqueous solutions, is reported. In neutral solutions it decomposes via Cu–H⁺(aq) + H₂O → Cu²⁺(aq) + H₂ + OH⁻(aq) with a rate of 4×10^3 s⁻¹. The properties of Cu–H⁺(aq) are discussed and compared with those of similar Cu^{II}–R compounds.

The formation of CuH⁺(aq) ions as intermediates in catalytic reductions by hydrogen in the presence of copper(II) ions was proposed long ago.[3] The mechanism of formation of CuH⁺(aq) was suggested to be
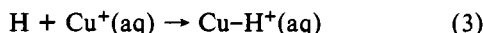
$$Cu^{2+}(aq) + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu\text{–}H^+(aq) + H_3O^+(aq) \tag{1}$$
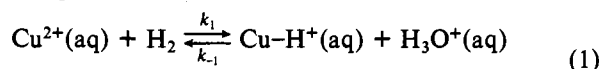
$$k_1 = 9.5 \times 10^{-5} \text{ M}^{-1}\text{ s}^{-1} \text{ at 110 °C}$$

where this reaction is followed, in the absence of other oxidants, by[3]

$$Cu\text{–}H^+(aq) + Cu^{2+}(aq) \rightarrow 2Cu^+(aq) + H_3O^+(aq) \tag{2}$$
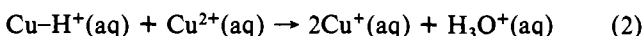
We decided to try to study, using the pulse radiolytic technique, the properties of Cu–H⁺(aq) by following the reaction

$$H + Cu^+(aq) \rightarrow Cu\text{–}H^+(aq) \tag{3}$$

in parallel to the reactions

$$\cdot RH + Cu^+(aq) \rightarrow Cu\text{–}RH^+(aq) \tag{4}$$
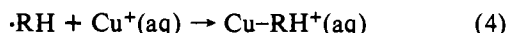
which were recently observed.[4–7] Some of the latter reactions were suggested to be equilibrium processes.[4,5]

Recently, Ferraudi reported the observation of CuHCl₃²⁻ formed via an analogous mechanism in the photolysis of CuCl₃²⁻.[8] HCuCl₃²⁻, HCuCl₂⁻, HCu₂Cl₃⁻, or similar complexes have also been shown to be intermediates in the production of hydrogen from the UV photolysis of chlorocuprate(I) ions.[8b] It is of interest to compare the properties of Cu–H⁺(aq) with those of CuHCl₃²⁻.

Experimental Section

Deaerated solutions containing $(2\text{–}10) \times 10^{-4}$ M CuSO₄ at pH 3.2–6.0 were irradiated by short pulses from the electron linear accelerator at Argonne National Laboratory. The solutions were irradiated in Suprasil cells which were contained in specially designed high-pressure cells.[9] After deaeration the solutions were always saturated with hydrogen, usually at 100 atm pressure, and for blank experiments, at atmospheric pressure. No observable reaction between Cu²⁺ and H₂ occurs under these conditions at room temperatures within several hours.

The spectra of the transients were recorded with use of the streak camera;[10] i.e., the total spectrum was recorded at desired times with application of a single pulse. The kinetics of reaction were followed with the regular photomultiplier setup.[11]

Dosimetry was carried out by measuring the yield of (NCS)₂⁻· at 475 nm formed by identical pulses in the same cells containing N₂O-saturated solutions of 1×10^{-3} M NaNCS.[11]

Results and Discussion

The radiolysis of water or dilute aqueous solutions may be summed up by[12]

$$H_2O \rightarrow e_{aq}^-, H, OH, H_2O_2, H_2, H_3O^+(aq), OH^-(aq) \tag{5}$$
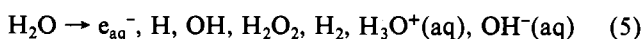
where the yields, G, of these primary products are $G_{e_{aq}^-} = 2.65$, $G_H = 0.60$, $G_{OH} = 2.65$, $G_{H_2O_2} = 0.75$, $G_{H_2} = 0.45$, $G_{H_3O^+} = 3.65$, and $G_{OH^-(aq)} = 1.00$ in units of molecules per 100 eV absorbed in the solution.[12]

(1) Work performed in part under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.
(2) (a) Argonne National Laboratory. (b) Nuclear Research Centre—Negev and Ben Gurion University of the Negev (address correspondence to Ben Gurion University of the Negev).
(3) Halpern, J.; MacGregor, E. R.; Peters, E. *J. Phys. Chem.* **1956,** *60,* 1455.
(4) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1977,** 934; *J. Chem. Soc., Faraday Trans. 1* **1980,** *76,* 1838.
(5) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978,** *74,* 697.
(6) Ferraudi, G. *Inorg. Chem.* **1978,** *17,* 2506.
(7) Das, S.; Johnson, G. R. A. *J. Chem. Soc., Faraday Trans. 1* **1980,** *76,* 1779.
(8) (a) Ferraudi, G. *Inorg. Chem.* **1978,** *17,* 1370. (b) Stevenson, K. L.; Kaehr, D. M.; Davis, D. D.; Davis, C. R. *Ibid.* **1980,** *19,* 781.

(9) Michael, B. D.; Hart, E. J. *J. Phys. Chem.* **1970,** *74,* 2878.
(10) Schmidt, K. H.; Gordon, S.; Mulac, W. A. *Rev. Sci. Instrum.* **1976,** *47,* 356.
(11) Gordon, S.; Mulac, W. A.; Schmidt, K. H.; Sjoblom, R. K.; Sullivan, J. S. *Inorg. Chem.* **1978,** *17,* 294.
(12) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.