Stereoselective Adsorption on a Clay Surface modified by an Optically Active Nickel(II) Tris(1,10-phenanthroline) Chelate

By Akihiko Yamagishi

(*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo* 060, *Japan*)

Summary Adsorption of the optically active $(+)_{510}$-$[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) on a colloidal clay surface proceeds more rapidly when the surface is already occupied by the corresponding nickel chelate with the opposite chirality, $(-)_{546}$-$[Ni(phen)_3]^{2+}$, than when it is occupied by the different enantiomer, $(+)_{546}$-$[Ni(phen)_3]^{2+}$.

As was reported recently, the optically active tris(1,10-phenanthroline)nickel perchlorate isomers $\{(+)_{546}$- or $(-)_{546}$-$[Ni(phen)_3][ClO_4]_2\}$ are adsorbed racemically on the colloidal surface of sodium montmorillonite.[1] Any site already occupied by a given enantiomer can further bind a molecule of the other enantiomer. The present paper shows that such a preference for racemic pairing makes the clay surface stereoselective for adsorption of optically active configurational isomers of metal chelates.

The iron chelates used all exhibited a bathochromic shift when bound to a colloidal clay, and so the progress of adsorption could be monitored by the absorbance increase at 530 nm, after mixing two solutions under study in a stopped-flow apparatus (Union Giken RA-401.)[2] The mixing conditions are given in the Table and some of the observed absorbance *vs.* time plots are displayed in the

TABLE. Initial rates of absorbance change at 530 nm (V_{530}) due to adsorption on sodium montmorillonite.

Run	Solution 1 composition Complex	Conc./M	Solution 2[d]	V_{530}[e]
(i)	$(+)_{510}$-$[Fe(phen)_3]^{2+a}$	$4{\cdot}2 \times 10^{-5}$	A	0·87
(ii)	$(-)_{510}$-$[Fe(phen)_3]^{2+b}$	"	A	0·88
(iii)	$(+)_{510}$-$[Fe(phen)_3]^{2+a}$	$3{\cdot}6 \times 10^{-5}$	B	0·016
(iv)	"	"	C	0·004
(v)	$(-)_{450}$-$[Fe(phen)_2(CN)_2]$	$4{\cdot}0 \times 10^{-5}$	C	0·28
(vi)	"	"	B	0·16
(vii)	$(-)_{460}$-$[Fe(bipy)_2(CN)_2]^c$	$6{\cdot}7 \times 10^{-5}$	C	0·45
(viii)	"	"	B	0·44

[a] Counter-anion = antimonyl (+)-tartrate. [b] Counter-anion = antimonyl (—)-tartrate. [c] bipy = 2,2′-bipyridyl. [d] A: sodium montmorillonite ($4{\cdot}0 \times 10^{-5}$ M) alone; B: sodium montmorillonite ($4{\cdot}0 \times 10^{-5}$ M) + $(-)_{546}$-$[Ni(phen)_3]^{2+}$ ($8{\cdot}0 \times 10^{-5}$ M); C: as B, but with $(+)_{546}$-$[Ni(phen)_3]^{2+}$. [e] Measured as change in optical density per second.

Figure. For all runs, the transient increase in absorbance occurred in the time range 100 ms to 10 s. Concentrating our attention on the initial stage of adsorption, the rates were compared in terms of the initial rate of absorbance increase (denoted by V_{530}). V_{530} for run (i) represents the rate of enantiomeric adsorption of $(+)_{510}$-$[Fe(phen)_3]^{2+}$ on an empty surface. Comparing runs (i) and (ii), an empty surface exhibits no stereoselectivity. For the rest of the runs, the cation-exchange sites were already occupied completely by an enantiomer of $[Ni(phen)_3]^{2+}$.[1] Thus V_{530} represents the adsorption on the surface already containing either $(-)_{546}$- or $(+)_{546}$-$[Ni(phen)_3]^{2+}$. The large value (4·0) of the ratio V_{530}(iii)/V_{530}(iv) demonstrates the stereoselective character of the modified clay surfaces towards the adsorption of $(+)_{510}$-$[Fe(phen)_3]^{2+}$. Apparently this arises from the preference of $(+)_{510}$-$[Fe(phen)_3]^{2+}$ for racemic pairing with $(-)_{546}$-$[Ni(phen)_3]^{2+}$ rather than for the enantiomeric pairing with $(+)_{546}$-$[Ni(phen)_3]^{2+}$.

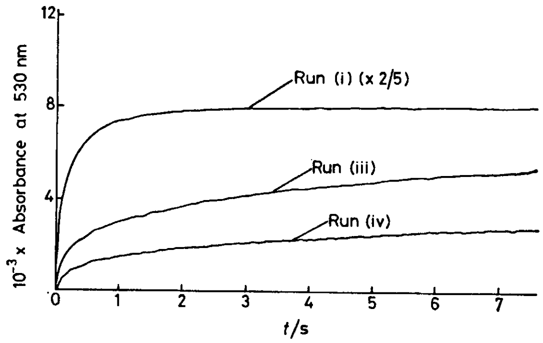

FIGURE. Examples of transient absorbance increases at 530 nm when the solutions 1 and 2 in the Table were mixed in a stopped-flow apparatus.

The value (1·8) of the ratio V_{530}(v)/V_{530}(vi) indicates that the modified surfaces still recognize the chirality of $(-)_{450}$-$[Fe(phen)_2(CN)_2]$, although the selectivity is less pronounced in comparison with $[Fe(phen)_3]^{2+}$. In the case of $(-)_{460}$-$[Fe(2,2'\text{-bipyridyl})_2(CN)_2]$, V_{530}(vii)/V_{530}(viii) was unity within experimental error, indicating that the modified surfaces can no longer recognize the chirality of this iron(II) chelate.

These facts indicate that the molecules must satisfy a rigorous steric requirement for racemic adsorption. This requirement probably arises from the necessity of stacking the chelates with bulky planar ligands in a narrow but well characterized interlayer space.

(*Received*, 9*th June* 1981; *Com.* 678.)

[1] A. Yamagishi and M. Soma, *J. Chem. Soc., Chem. Commun.*, 1981, 539.
[2] A. Yamagishi and M. Sakamoto, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2152.