Auger Electron Spectroscopic Evidence for the Racemic Adsorption of Tris(1,10-phenanthroline)iron(II) on Sodium Montmorillonite

Akihiko Yamagishi,[a] Ken-ichi Tanaka,[b] and Isamu Toyoshima[c]

[a] *Department of Chemistry, Faculty of Science,* [b] *Department of Chemistry, Faculty of Engineering, and* [c] *Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan*

Auger electron spectroscopy is used to prove that enantiomeric $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) is adsorbed as dipositive $Fe(phen)_3^{2+}$ on a montmorillonite, while racemic $Fe(phen)_3^{2+}$ is adsorbed as a monopositive ion-pair with an external anion or $Fe(phen)_3^{2+}\cdot X^-$ with X = antimonyl (+)-tartrate in the present case.

The adsorption on colloidally dispersed sodium montmorillonite of $Fe(phen)_3^{2+}$ or $Ni(phen)_3^{2+}$ (phen = 1,10-phenanthroline) from their enantiomeric and racemic solutions have been compared.[1,2] From the adsorption isotherm it was shown that enantiomeric $Fe(phen)_3^{2+}$ occupies two cation-exchange sites per one chelate while the maximum amount of adsorption was twice this when the same chelate was adsorbed from a racemic solution,[1] indicating that the sites already occupied by a given enantiomer can further accept the same amount of the opposite enantiomer. Similar conclusions were obtained for the adsorption of $Ni(phen)_3^{2+}$.[2]

If this is the case, adsorption from a racemic solution should charge a clay surface positively, because $Fe(phen)_3^{2+}$ or $Ni(phen)_3^{2+}$ is adsorbed in an excess over the cation-exchange capacity. Therefore, the adduct in the solid state may include an external anion to neutralize the charge. The existence of such an external anion would provide proof for the above racemic adsorption.

Table 1. Relative abundances of elements in a clay–metal chelate adduct.

Experimental results[a]

| Sample | Elements[b] | | | |
	Sb	Fe	C	N
(A)	none	1.0	40	4.5
(B)	1.2	1.0	41	4.2

Calculated results[c]

| Sample | Elements | | | |
	Sb	Fe	C	N
(A)	0	1	36	6
(B)	1	1	40	6

[a] The Fe abundance is normalized to unity. The values contained $\pm$ *ca.* 20% as relative error. [b] The A.e.s. transition and peak used for each element were the following; Sb (MNN, 455 eV); Fe ($L_2M_3M_5$, 625.5 eV); C (KLL, 275 eV); N (KLL, 385 eV). [c] The adsorbate is assumed to be $Fe(phen)_3^{2+}$ or $Fe(phen)_3^{2+}\cdot$[antimonyl (+)-tartrate]$^-$ for sample (A) or (B), respectively.

Auger electron spectroscopy was the most suitable method for determining the elemental compositions of the *ca.* 5 mg samples investigated. Sample (A) was a precipitate from a solution containing 2×10^{-6} mol of sodium montmorillonite and 1×10^{-6} mol of Λ-Fe(phen)$_3\cdot$bis[antimonyl (+)-tartrate] and sample (B) a precipitate from a solution containing 2×10^{-6} mol of sodium montmorillonite and 2×10^{-6} mol of racemized Fe(phen)$_3\cdot$bis[antimonyl (+)-tartrate]. The concentration of the clay was measured in terms of its cation-exchange capacity. Each sample was sucked over a membrane filter with a water jet and was dried until it separated as a thin film. An ESCA-3 (Vacuum Generator Scientific Ltd.) was used for the measurements. A sample was placed on a gold mesh spotwelded onto a nickel plate. Spectra were recorded with a 3 KeV electron source at 100 mA, scanning over a kinetic energy range of 1250 to 0 eV. The peak amplitudes were analysed using the relative elemental sensitivities given in the literature.[3]

The results are shown in Table 1 accompanied by the calculated values. Sb was found only in sample B, which is strong evidence for the inclusion of the antimonyl (+)-tartrate anion. The relative abundances of Sb, Fe, C, and N were calculated by assuming that sample (A) contained $Fe(phen)_3^{2+}$ as adsorbate, while sample (B) contained {Fe(phen)$_3\cdot$[antimonyl (+)-tartrate]}$^+$. The calculated results agreed well with the experimental ones within experimental error and provided direct proof that racemic $Fe(phen)_3^{2+}$ was adsorbed in an excess over the cation-exchange capacity. The stereospecific adsorption revealed here suggests that, in the layer of racemic adsorbates, (+)- and (−)-enantiomers are stacked in an alternating way. An important consequence of this would be that when the interlamellar space of a clay is modified by a chiral compound, discrimination may occur between penetrating molecules of opposing chirality, depending on the ease of racemic stacking.[4]

References

1 A. Yamagishi and M. Soma, *J. Am. Chem. Soc.*, 1981, **103**, 4640.

2 A. Yamagishi and M. Soma, *J. Chem. Soc., Chem. Commun.*, 1981, 539.

3 L. E. Davis, N. C. MacDonald, P. W. Palmbey, G. E. Riach, and R. E. Weber, 'Handbook of Auger Electron Spectroscopy' Phys. Electronics Div., Perkin-Elmer Corp., Minnesota, 1978.

4 A. Yamagishi, *J. Chem. Soc., Chem. Commun.*, 1981, 1128, 1168.