

Improvement of Optical Purity of Metal Tris-(1,10-phenanthroline) Chelates by Use of Adsorption on a Colloidal Clay

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Summary When the clay-metal adducts are filtered through a membrane filter from a solution containing sodium montmorillonite (3.3×10^{-4} M cation exchange sites), 3.4×10^{-4} M $(+)_546$ -[Ni(phen)₃][ClO₄]₂, and 1.7×10^{-4} M $(-)_546$ -[Ni(phen)₃][ClO₄]₂, the filtrate contains 1.2×10^{-4} M $(+)_546$ -[Ni(phen)₃][ClO₄]₂ and 0.2×10^{-4} M $(-)_546$ -[Ni(phen)₃][ClO₄]₂ (phen = 1,10-phenanthroline); this improvement in optical purity results from the adsorption of the racemic metal chelate on the clay surface.

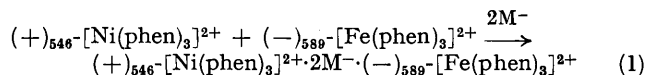
SEVERAL investigations have been reported which show that clay preferentially adsorbs, or catalyses the reactions of, only one of the optical isomers of biologically important compounds.¹⁻³ The underlying mechanism for such selectivity is difficult to understand, particularly because clay itself is optically inactive. In the present study, we report the improvement of the optical purity of a metal chelate by use of adsorption on the surface of a colloidal clay. The method is based on the fact that a metal chelate tends to bind with the cation-exchange sites of clay as the racemic-body rather than a single enantiomer.

The optical active tris-(1,10-phenanthroline)nickel(II) perchlorate {denoted by $(+)_546$ - or $(-)_546$ -[Ni(phen)₃][ClO₄]₂} and racemic tris-(1,10-phenanthroline)iron(II) perchlorate {[Fe(phen)₃][ClO₄]₂} were synthesized by the reported procedures,⁴ and identified by electronic and optical rotatory dispersion (o.r.d.) spectroscopy. Sodium montmorillonite (Na⁺M⁻; 87 mg), from Kunimine Co. Ind. (Japan), was dispersed in 100 ml of distilled water. The resultant solution contained 1.0×10^{-3} M of cation-exchange sites. From electric birefringence measurements, the radius of the colloidal particles ranged from 0.2 to 2 μm.⁵ Accordingly, no clay particle passed through a membrane filter with a maximum radius for passage of 0.1 μm (Toyo, Japan, TM-5).

The extent of binding of the metal chelate was first determined as a function of added Na⁺M⁻ from the decrease in concentration of the chelate after passing the solution through the membrane. For all experiments with $(+)_546$ - and racemic-[Ni(phen)₃][ClO₄]₂, the binding isotherm could be approximated by a Langmuir-type equation. The concentration of Na⁺M⁻ at which half the initial nickel chelate (2×10^{-4} M) was bound to the clay was determined to be 2.8×10^{-4} , 2.8×10^{-4} , and 1.6×10^{-4} M, for $(+)_546$ -

$(-)_546$ -, and racemic-[Ni(phen)₃][ClO₄]₂, respectively. Since the exchange capacity for the racemic mixture is almost exactly double that for either enantiomer alone, it appears likely that any site already occupied by a given enantiomer can further bind a molecule of the other enantiomer. This racemic adsorption was verified by the following experiments: 3.3×10^{-4} M Na⁺M⁻ was added to a solution of 3.4×10^{-4} M $(+)_546$ -[Ni(phen)₃][ClO₄]₂ and 1.7×10^{-4} M $(-)_546$ -[Ni(phen)₃][ClO₄]₂. On passage through the membrane filter, the clay-metal chelate adduct was eliminated from the bulk solution. The filtrate contained 1.2×10^{-4} M $(+)_546$ -[Ni(phen)₃][ClO₄]₂ and 0.2×10^{-4} M $(-)_546$ -[Ni(phen)₃][ClO₄]₂. During this procedure, the ratio of the more abundant [$(+)_546$] to the less abundant isomer [$(-)_546$] increased 3-fold as result of the predominant adsorption of the racemic-body. It was also confirmed that no optical activity was generated by adsorption on the clay from racemic solutions.

If similar racemic adsorption takes place even between enantiomers of different kinds of metal chelate, the optical resolution of the racemic-body of one kind is possible at the expense of the enantiomer of another kind. The following experiment verifies this expectation: 2.9×10^{-4} M Na⁺M⁻ was added to a solution of 2.7×10^{-4} M $(+)_546$ -[Ni(phen)₃][ClO₄]₂ and 2.2×10^{-4} M racemic [Fe(phen)₃][ClO₄]₂ and the solution was filtered through a membrane filter. From the o.r.d. and electronic spectra, the filtrate contained 1.4×10^{-4} M $(+)_546$ -[Ni(phen)₃]²⁺, 0.6×10^{-4} M $(+)_589$ -[Fe(phen)₃]²⁺, and no $(-)_589$ -[Fe(phen)₃]²⁺. In other words, most of the nickel chelate was eliminated as a 'pseudo' racemic-body with an enantiomer of the iron chelate according to equation (1),† which results in the preponderance of



$(+)_589$ -[Fe(phen)₃]²⁺ in the bulk medium. When $(-)_546$ -[Ni(phen)₃][ClO₄]₂ was used instead of $(+)_546$ -[Ni(phen)₃][ClO₄]₂, the other isomer, $(-)_589$ -[Fe(phen)₃]²⁺, remained in solution. For the method to work satisfactorily, there must be an excess of the adsorbed species; ideally the amount of clay should be exactly that required totally to remove the enantiomer present in lower concentration.

† In this equation, two cation sites are assumed to be occupied by a pair of (+)- and (-)-enantiomers. This is deduced from results for the binding of the iron chelates (details will be published elsewhere).

The same principle is expected to hold for the adsorption of a metal-amino-acid chelate where the molecular asymmetry lies in the amino-acid ligands. It might give one explanation as to how a single enantiomeric form of amino-

acids, the L-form, has been continuously accumulated on a global scale.

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