Total Resolution of the Hexakis(2-aminoethanethiolo)tricobalt(III) Cation by Ion-Exchange Chromatography[1]

Sir:

Numerous attempts to resolve optically active transition metal complexes into their antipodes by relatively rapid and simple chromatographic techniques have been reported.[2,3] In general, these procedures have resulted in partial resolution, with the notable exception of the resolution of mixed $[Co(en)_n(l\text{-pn})_{3-n}]^{3+}$ complexes on cellulose by Dwyer and co-workers.[4] We report the total resolution of the hexakis(2-aminoethanethiolo)tricobalt(III) cation (Figure 1) using cation-exchange cellulose.

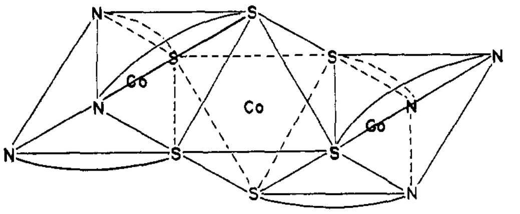

Figure 1. The hexakis(2-aminoethanethiolo)tricobalt(III) cation.

Hexakis(2-aminoethanethiolo)tricobalt(III) bromide was prepared by the method of Busch and Jicha.[5] Bio-Rad Cellex CM cation-exchange cellulose (26 g) was poured into a column 22 mm in diameter, according to the instructions of the supplier,[6] to give a bed about 38 cm in length. A saturated aqueous solution containing 0.5 g (0.57 mequiv) of $Co_3L_6Br_3$ was poured onto the column and equilibrated with water flowing about 3.5 ml/min. The complex was eluted with 0.1 *N* NaCl at approximately the same rate. The effluent was collected in 22-ml fractions, and the optical density and circular dichroism were determined at 540 mμ. The molecular rotation of $Co_3L_6Br_3$ was determined at 589 mμ.

Within experimental uncertainties, the first 110 ml of effluent displayed a constant $\Delta\epsilon$ at 540 mμ of -23.4; M_D (at 589 mμ) $-4020°$. This value corresponds closely with the $\Delta\epsilon$ (540 mμ) of $+23.7$, M_D (589 mμ) of $+3980°$, obtained from a sample of $[Co_3L_6]^{3+}$ resolved by fractional crystallization of the $(+)_{589}$-$[Co_3L_6]$-$(-)_{546}$-$[Co(EDTA)]_3$ diastereoisomer from water. In addition to the optical antipodes, the trinuclear $[Co_3L_6]^{3+}$ cation exists in an inactive *meso* form. This isomer dominates the later fractions of the effluent and has not been successfully separated from the more strongly adsorbed optical antipode, though the latter' comprised some 75% of the last fractions collected. The electronic properties of the hexakis(2-aminoethanethiolo)tricobalt(III) cation and related species will be discussed in detail elsewhere.

The remarkable success of our method may be due, in part, to the high charge density and high formula weight (634.6) of the $[Co_3L_6]^{3+}$ entity. We have, however, achieved some success in the resolution of N-alkyl-substituted N,N′-ethylenediaminediacetato-(ethylenediamine)cobalt(III) complexes related to [Co-(EDDA)(en)]$^+$.[7] These results will be reported elsewhere.

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[1] This work was supported by a research grant (GM10829-08) from the Division of General Medical Studies, Public Health Service; work performed at the University of Pittsburgh.

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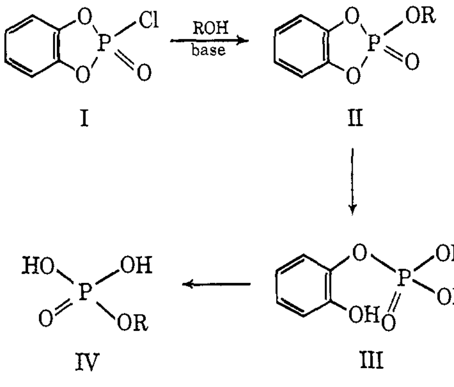
o-Phenylene Phosphorochloridate. A Convenient Phosphorylating Agent

Sir:

Reich's surprising claim[1] that phosphotriesters of type II undergo hydrolysis to give catechol and the corresponding monoesters IV has not been substantiated. Lora Tomayo and Calderón[2] treated a number of primary aliphatic alcohols with *o*-phenylene phosphorochloridate (I) in the presence of base and showed that the products (II) were readily hydrolyzed to the corresponding *o*-hydroxyphenyl phosphate esters (III). Calderón later reported[3] that hydrogenolysis of the latter diesters (III) in the presence of platinum oxide gave the required monoesters (IV) and cyclohexanol. However, Nagasawa[4] subsequently found no evidence for such platinum-catalyzed hydrogenolysis.



We now wish to report that when these *o*-hydroxyphenyl derivatives (III) are treated, in neutral aqueous buffer solution, with an excess of bromine water at room temperature they are rapidly converted into the corresponding monoesters (IV) in good yield. The possibility, which was suggested by the oxidative

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[1] W. S. Reich, *Nature*, **157**, 133 (1946).

[2] M. Lora Tomayo and J. Calderón, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **46B**, 475 (1950); *Chem. Abstr.*, **45**, 7046*e* (1951).

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