TABLE I

	$CH_3OP(O)(CF_3)_2$	$CH_3OP(CF_3)_2$	$CH_3P(O)(CF_3)_2$	$CH_3P(CF_3)_2$
$\delta(^1H)$, ppm	−3.72	−3.47	−1.80	−1.20
J_{HP}, cps	11.1	13.0	15.6	4.6
$J_{H\cdots F}$, cps	"0.5"	. . .	0.83	. . .
$\delta(^{19}F)$, ppm	73.3	66.2	72.4	66.9
J_{FP}, cps	120	85.4	99	75
$J_{F\cdots H}$, cps	0.37	0.46	0.78	. . .
$\delta(^{31}P)$, ppm	−2.5	−94.8	. . .	5.76
J_{PF}, cps	120	86	. . .	76
J_{PH}, cps	10.8	12.7	. . .	?

septet. The relation of these J values to variously placed oxygen is interesting, especially since such coupling could not be resolved for $CH_3P(CF_3)_2$.

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The Use of the (+)- or (−)-Tris(ethylenediamine)cobalt(III) Cation as a Resolving Agent for Some Complex Anions[1]

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The tris(oxalato) complexes of chromium(III) and cobalt(III) were first resolved by the use of strychnine salts.[4] Until recently Werner's method was probably the best way of obtaining the optical antipodes of these complexes; however, in 1956 Dwyer and Sargeson[5] demonstrated that the (+)-tris(1,10-phenanthroline)-nickel(II) cation could be utilized to resolve the tris(oxalato) complexes of Co(III), Cr(III), and Rh(III). The method of Dwyer and Sargeson avoids the difficulties of working with extremely toxic resolving agents.

This investigation was initiated to determine if the (+)- or (−)-tris(ethylenediamine)cobalt(III) cation could be utilized to resolve racemic complexes of ionic charge 3−. This cation can be prepared economically in quantity; the reagent has a good solubility in water thus avoiding the use of mixed solvents; and the diastereoisomer isomer formed is not of a "mixed type" and hence should have a lower water solubility than the double complex obtained by use of the tris(1,10-phenanthroline)nickel(II) ion.

Experimental Section

Preparation of Complexes.—The (+)- or (−)-tris(ethylenediamine)cobalt(III) iodide was prepared according to standard methods.[6] Potassium (±)-tris(oxalato)cobaltate(III) trihydrate was prepared by literature methods.[7] Potassium (±)-tris(oxalato)chromate(III) trihydrate was prepared by the method given by Palmer.[8] Potassium (±)-tris(oxalato)rhodate(III) hydrate was prepared by the method of Werner,[9] starting with the water-soluble rhodium(III) chloride trihydrate.

Resolution of the (±)-Tris(oxalato)chromate(III) Ion.—A solution of 1.6 g (0.0025 mol) of (−)-tris(ethylenediamine)-cobalt(III) iodide in 40 ml of water at 15° was quickly added to a stirred solution of 2.2 g (0.005 mol) of potassium (±)-tris(oxalato)chromate(III) trihydrate in 40 ml of water at 15°. The reaction mixture was stirred for 1 min before the brownish tan precipitate of $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$ was collected by filtration. The filtration was carried out in such a fashion that the filtrate was run directly into about 400 ml of cold acetone. The precipitated $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$ was washed with acetone and air dried. The diastereoisomer was obtained in 95% yield (1.3 g). *Anal.* Calcd for $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$: C, 26.0; H, 4.3; N, 15.1. Found: C, 26.2; H, 4.4; N, 14.8.

The filtrate obtained from the collection of $[Co(en)_3][Cr(C_2O_4)_3]$ was stirred for 2–3 min to coagulate the precipitated $(+)$-$K_3[Cr(C_2O_4)_3]\cdot H_2O$. The precipitate was collected by filtration, washed with acetone, and air dried. The product was obtained in 44% yield (0.5 g). A 0.02% solution gave $[\alpha]_D$ +1550–1600°.

The following method was utilized to obtain the (−) form of the active anion in the form of the potassium salt from the diastereoisomer. The entire sample of the double complex was placed in a mortar in an ice bath and 5–10 ml of ice water was added along with 5–7 g of solid potassium iodide. This mixture was ground for 3–5 min at 5–10°. During the grinding the mixture turned brownish yellow owing to the precipitation of $(-)$-$[Co(en)_3]I_3$. The pasty reaction mixture was filtered and the blue-green filtrate was run directly into 100 ml of cold, stirred acetone. The acetone solution was stirred for 3 min to coagulate the precipitate before the product was collected by filtration. To remove the excess potassium iodide from the product, the collected material was crushed to a powder and slurried three times with 100-ml portions of 95% alcohol for 3 min each. The product was collected, washed with acetone, and air dried. This procedure gave 44% (0.5 g) of $(-)K_3[Cr(C_2O_4)_3]\cdot H_2O$. A 0.02% solution gave $[\alpha]_D$ −1680°.

Resolution of the (±)-Tris(oxalato)cobaltate(III) Ion.—The method was the same as that utilized for the resolution of the corresponding chromium(III) complex except that the initial water volumes were reduced to 20 ml each. This procedure gave the double complex in 98% yield (1.4 g) and the optical antipode obtained directly from the acetone solution after the removal of the diastereoisomer weighed 1.0 g (82%). The following specific rotations were found for the antipode obtained from the acetone solution: $[\alpha]_{5461}$ −1425° for a 0.04% solution and $[\alpha]_D$ −1750° for a 0.02% solution. This product was dissolved in water and reprecipitated by the addition of alcohol and the rotation was redetermined. This material gave $[\alpha]_D$ −1850°. Further recrystallization did not raise the angle of rotation.

The double complex $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$ had a very low solubility in water and prolonged grinding with solid potassium iodide in cold water was necessary to cleave this material. The $(+)_{5461}K_3[Co(C_2O_4)_3]$ was obtained in poor yield (30%) and in a low degree of optical purity, $[\alpha]_{5461}$ +1030° for a 0.04% solution and $[\alpha]_D$ +1200° for a 0.02% solution.

Resolution of the (±)-Tris(oxalato)rhodate(III) Ion.—The

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[2] National Science Foundation Research Participant.

[3] National Science Foundation Undergraduate Research Participant.

[4] A. Werner, *Ber.*, **45**, 3061 (1912).

[5] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **60**, 1331 (1956).

[6] J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Syn.*, **6**, 183 (1960).

[7] J. C. Bailar, Jr., and E. M. Jones, *ibid.*, **1**, 35 (1939).

[8] W. G. Palmer, "Experimental Inorganic Chemistry," 1st ed, Cambridge University Press, Cambridge, England, 1954, p 386.

[9] A. Werner and J. Poupardin, *Ber.*, **47**, 1955 (1914).

procedure was the same as that utilized for the corresponding Co(III) complex. As in the case of Cr(III), both antipodes were isolated. When the double complex was cleaved with potassium iodide, $(-)_{5461}K_3[Rh(C_2O_4)_3]$ was obtained. The specific rotations were $[\alpha]_D$ 0° and $[\alpha]_{5461}$ −66° for a 0.1% solution. This material was dissolved in the minimum amount of cold water, the solution was filtered, and sufficient 95% alcohol was added just to induce precipitation. The cloudy solution was cooled in ice for 15 min before the product was collected by filtration, washed with acetone, and air dried. The specific rotations were $[\alpha]_D$ 0° and $[\alpha]_{5461}$ − 74° for a 0.1% solution. Further recrystallization did not raise the angle of rotation.

Instrumentation.—Optical rotations were determined either on a Bendix-Ericson U.K. Ltd. Type 143 A ETL-NPL automatic polarimeter or on a Durrum-Jasco ORD/UV-5 optical rotatory dispersion recorder.

Discussion

The (+)- or (−)-tris(ethylenediamine)cobalt(III) ion can be used as a resolving agent for the rapid resolution of the tris(oxalato) complexes of Cr(III), Co(III), and Rh(III). When $(-)Co(en)_3{}^{3+}$ is used to effect the resolution, the least soluble diastereoisomters formed are $(-)[Co(en)_3](-)[Cr(C_2O_4)_3]$, $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$, and $(-)[Co(en)_3](-)_{5461}[Rh(C_2O_4)_3]$.

The solubility rule of Werner[10,11] when applied to these diastereoisomers indicated that $(-)Cr(C_2O_4)_3{}^{3-}$, $(+)_{5461}Co(C_2O_4)_3{}^{3-}$, and $(-)_{5461}Rh(C_2O_4)_3{}^{3-}$ all have the same configuration. This is in agreement with the optical rotatory dispersion data which indicate all of the anions in the least soluble diastereoisomers to have the same configuration. The absolute configurations of the anions in the diasterioisomer are L when compared to $D\text{-}Co(en)_3{}^{3+}$.

A comparison of the results using the $(-)Co(en)_3{}^{3+}$ ion as the resolving agent for the tris(oxalato) complexes of Cr(III), Co(III), and Rh(III) with those obtained by other investigators with other resolving agents is shown in Table I.

Table I

Complex anion	$[\alpha]_D$, deg	
	Lit.	This work
$Cr(C_2O_4)_3{}^{3-}$	±1640[a]	+1550–1600, −1680[b]
$Co(C_2O_4)_3{}^{3-}$	±4050[a,c]	
	±1940[d,e]	−1850, +1875[e]
	±1375[a,f]	−1425[f]
$Rh(C_2O_4)_3{}^{3-}$	±85[a]	−74[g]
	0[h]	0

[a] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **60**, 1331 (1956). [b] A 0.02% solution at room temperature. [c] A 0.016% solution at 20°. [d] G. B. Kauffman, L. T. Takahashi, and N. Sugisaka, *Inorg. Syn.*, **8**, 207 (1966). [e] A 0.032% solution at 5°; see discussion. [f] A 0.04% solution at 20° and λ 5461 Å. [g] A 0.1% solution at room temperature at λ 5461 Å. [h] A. Werner, *Ber.*, **45**, 1229 (1912).

In the case of $(-)[Co(en)_3](+)_{5461}[Co(C_2O_4)_3]$ the double complex was so insoluble in water that the diastereoisomer could not be conveniently cleaved by grinding with a saturated solution of potassium iodide. If both antipodes of the anion are desired, the best way to obtain them is to carry out two separate resolutions using $(+)Co(en)_3{}^{3+}$ and $(-)Co(en)_3{}^{3+}$ as the resolving agents and isolate the desired optical form from the filtrate after removal of the diastereoisomer.

It is not necessary to resort to this method in the case of the Cr(III) and Rh(III) complexes since the diastereoisomer can be rather easily cleaved by grinding with potassium iodide.

The (+)- or $(-)Co(en)_3{}^{3+}$ ion can be used to resolve the $(\pm)Co(C_2O_4)_3{}^{3-}$ ion, and the separation using (+)- or $(-)Co(en)_3{}^{3+}$ would appear to be equal to that obtained by the use of the $(+)Ni(phen)_3{}^{2+}$ ion as the resolving agent.

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Amine–Borane Hydrolysis at Bridgehead Nitrogen

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In a previous study,[1] it was suggested that the acid-catalyzed hydrolysis of BH_3 adducts of a series of alkyl, aryl, and heterocyclic amines proceeded by a rate-determining electrophilic displacement of BH_3 from nitrogen by the proton of a general acid, followed by rapid hydrolysis of the borane fragment. A comparable mechanism has been suggested by Ryschkewitsch for the acid hydrolysis of methylamine–boranes.[2,3] No implications have been made as to the geometry of transition states for such displacements, although models of transition states for electrophilic substitution at saturated carbon, based on numerous reactions of aliphatic substrates, are described in the literature.[4–6]

In relation to this question, we chose to study the rates of hydrolysis of triethylamine–borane and quinuclidine–borane in aqueous dioxane in the region 25–60°. Since electronic inductive effects should be quite similar for these substrates, it was felt that a comparison of rates should provide an indication of the effect of the rigidity of nitrogen at the bridgehead position on the ease of formation of the activated complex. The similarity in rate, as well as enthalpy and entropy of activation for these substrates (Table I), strongly suggests

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