substitution which is followed by fast electron transfer or a reduction step which is followed by fast iron(I) substitution. A high value for the latter is of course reasonable since the substitution rate is very much dependent on charge (the value[19] for iron(III) is about 2×10^4 sec^{-1} and those for monovalent alkali metals[1] are about 10^9 sec^{-1}). It has thus been shown that, should the iron(I) complex exist in solution, it is nevertheless possible for substitution to involve iron(II).

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Resolution of the Oxalatobis(ethylenediamine)chromium(III) Ion

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The oxalatobis(ethylenediamine)chromium(III) ion was first resolved by Werner and Bosshart[2] by the method of preferential crystallization using *d*-$[Co(en)_2(C_2O_4)]Br$ as the seed material. Both Werner and Mathieu[3] found that this particular cation could not be resolved with salts a number of optically active acids.

In 1939 Bushra and Johnson[4] reported a method for obtaining one of the optical antipodes of this ion. These authors found that *d-cis*-dichlorobis(ethylenediamine)chromium(III) chloride reacted with a warm aqueous solution of ammonium oxalate without total racemization to produce some *d*-oxalatobis(ethylenediamine)chromium(III) chloride.

The present investigation was undertaken to find a direct method for the resolution which would avoid the use of substitution reactions on an optically active starting material and would also avoid the use of mixed solvents to precipitate the desired optical forms as used in the method of preferential crystallization.

Experimental Section

Synthesis of the Starting Materials.—Potassium *cis*-dioxalatodiaquochromate(III) dihydrate was prepared according to Werner.[5] *Anal.* Calcd for *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Cr, 15.34; $C_2O_4^{2-}$, 51.89. Found: Cr, 15.57; $C_2O_4^{2-}$, 51.67. The solid complex was heated on a steam bath with an excess of dry ethylenediamine for 10 min; the reaction is fairly rapid, and the progress of the reaction can be followed by the color change from gray to dark red. At the end of 10 min the reaction mixture was treated with two 50-ml portions of water and filtered to remove any unreacted starting materials. The dark red, water-insoluble precipitate which remained was washed with acetone and allowed to air dry. *Anal.* Calcd for $[Cr(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]\cdot 2H_2O$: Cr, 17.75; $C_2O_4^{2-}$, 45.2. Found: Cr, 17.74; $C_2O_4^{2-}$, 45.6. Oxalatobis(ethylenediamine)chromium(III) bromide monohydrate was prepared from the double complex, oxalatobis(ethylenediamine)chromium(III)bis(oxalato)ethylenediaminechromate(III) dihydrate, by grinding the material with an excess of concentrated hydrobromic acid and precipitating the desired product with alcohol. The crude product was collected by filtration, washed with alcohol then acetone followed by ether, and finally air dried. Purification of the complex was by recrystallization from water at 40°. *Anal.* Calcd for $[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; Br, 22.3. Found: Cr, 14.4; Br, 22.2.

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared as described by Dwyer, Gyarfas, and Mellor.[6] *Anal.* Calcd for $KCoC_{10}H_{16}N_2O_{10}$: Co, 13.96. Found: Co, 14.1.

Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was resolved into its optical antipodes as described by Dwyer and Garvan.[7] The optical rotations were in excellent agreement with the literature values. The *cis*-dinitrobis(ethylenediamine)cobalt(III) ion used in the resolution of the potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared as described by Holtzclaw, Sheetz, and McCarty.[8]

Resolution of the Oxalatobis(ethylenediamine)chromium(III) Ion.—A 400-mg (0.0011 mole) sample of the purified racemic complex was quickly dissolved in 12 ml of water at 40°, and 0.94 g (0.003 mole) of solid *l*-potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was added with constant stirring. The dark solution was quickly cooled to 25° and kept at this temperature for 10 min. Crystallization was induced by occasional stirring and scratching of the beaker during this time.

The crystals of oxalatobis(ethylenediamine)chromium(III) ethylenediaminetetraacetatocobaltate(III) monohydrate which had precipitated during this time were filtered off, and the filtrate was immediately cooled in ice. The crystals which had been collected were washed with cold 50–50 alcohol–water, cold alcohol, acetone, and ether and then were air dried. This procedure yielded 0.305 g (81% based on oxalatobis(ethylenediamine)chromium(III) bromide monohydrate) of reddish purple crystals. The specific rotations at the sodium D line and at 5461 A were +350 and −300° for a 0.01% solution. *Anal.* Calcd for *d*-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot H_2O$: C, 30.76; H, 4.80; N, 13.46. Found: C, 30.88; H, 4.94; N, 13.19. Recrystallization did not appear to raise the optical rotations by an appreciable amount.

The filtrate was kept in ice with stirring and scratching for 5 min after the contents had cooled to 0°. The precipitate was filtered off, washed with cold 50–50 alcohol–water, alcohol, acetone, and ether, and air dried. This procedure yielded 0.205 g (55% based on the racemic complex) of reddish purple crystals whose specific rotations at the sodium D line and 5461 A were +325 and −925° for a 0.01% solution. *Anal.* Calcd for *d*-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot 4H_2O$: C, 28.31; H, 5.31; N, 12.39. Found: C, 27.99; H, 4.97; N, 12.46.

Nearly all of the excess resolving agent could be recovered in an impure form by the addition of alcohol to the filtrate.

Removal of the resolving agent from the active complex was

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accomplished by grinding the disastereoisomers with cold, concentrated hydrobromic acid which contained a little water. A sample of d-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot H_2O$ which weighed 0.275 g (0.00044 mole) was ground at 0° with a solution which contained 0.75 ml of concentrated hydrobromic acid and 0.4 ml of water. After 10 min of grinding, the orange crystals of d-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$ were collected by filtration and washed with cold, concentrated hydrobromic acid until the filtrate turned from the deep purple of the cobalt complex to a pale orange. Any excess acid was removed by washing with cold alcohol, followed by acetone and ether. This procedure gave 0.141 g (71% based on the racemate) of a pale orange powder. The specific rotations of a 0.1% solution at the sodium D line and at 5461 A were +275 and +510°, respectively.

The d form was suspended in a small amount of ice-cold water and ground for 10 min to remove any racemate present. After two such treatments, the specific rotations of a 0.1% solution at the D line and 5461 A were constant at +310 and +600°, respectively. The yield of this isomer was 0.120 g (60% based on the racemate). *Anal.* Calcd for d-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; C, 20.12; Br, 22.3. Found: Cr, 14.9; C, 20.38; Br, 22.5.

The l diastereoisomer was treated as described above and gave 0.090 g (45% based on the racemic complex) of a pale orange powder. The specific rotations of a 0.1% solution at the D line and 5461 A were −305 and −625° after two grindings with cold water. *Anal.* Calcd for l-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; C, 20.12; Br, 22.3. Found: Cr, 14.7; C, 20.38; Br, 22.5.

The resolution works equally well using d-$K[CoC_{10}H_{12}N_2O_8]\cdot 2H_2O$ as the resolving agent. However, in this case, the fraction which precipitated at 25° contained the l isomer and the fraction obtained at 0° contained the d isomer.

Analytical Methods and Instrumentation.—Chromium was determined by oxidation to dichromate with hot perchloric acid followed by titration with a standard iron(II) solution to the ferroin end point. All microanalyses were performed by the Spang Micro Analytical Laboratory, Ann Arbor, Mich. Optical rotations were taken on a Bendix-Ericsson Type 143-A ETL-NPL automatic polarimeter. Appropriate glass filters were used to isolate the desired wavelengths, and all measurements were at room temperature. Syringe-type cells with 40-mm path lengths were used.

Discussion

A new method has been developed for the resolution of the oxalatobis(ethylenediamine)chromium(III) ion. The molar rotations are in agreement with those reported by Werner and Bosshart[2] (literature[2] values, $[M]_D$ +1129° and $[M]_L$ −1075°; this work $[M]_D$ +1110° and $[M]_L$ −1090°) and about 180° higher than the value given by Bushra and Johnson.[4]

Correspondence

A Solution to the Structural Dilemma of $Co_4(CO)_{12}$ Based on Valence Tautomerism and Steric Nonrigidity[1]

Sir:

The problem of the structure of tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, presents an interesting and significant challenge on the basis of the information available in the literature. Corradini[2] studied the structure of the crystalline substance using zonal data with the following results. (1) There is an approximately regular tetrahedron of cobalt atoms. (2) The molecules are disordered making it impossible, with the data available to him, to specify directly and conclusively the arrangement of the CO groups. (3) The most likely arrangement of CO groups *for the molecule in the crystal* is one in which one Co atom is bound to three terminal CO groups while the other three Co atoms are each bound to two terminal CO groups with the three edges between them being spanned by bridging CO groups. This structure possesses idealized C_{3v} symmetry.

The infrared spectrum measured in pentane solution under fairly high resolution[3] contained only four well-defined peaks in the terminal CO-stretching region and one in the bridging region, whereas the C_{3v} structure should have six and two bands in these regions, respectively. It was pointed out[3] that the discrepancy is surprising but that the spectrum is not *necessarily* inconsistent with Corradini's structure. It may be noted here, however, that the extent to which accidental degeneracies and/or extreme weakness of CO-stretching bands must be assumed in order to correlate the infrared data with the C_{3v} structure is disquieting.

More recently, Smith[4] showed that a structure containing the Co_4 tetrahedron with four bridging groups and two terminal groups on each Co atom so arranged as to give D_{2d} symmetry should have precisely the infrared spectrum observed in solution, and he therefore questioned the correctness of Corradini's structure. Quite recently, Corradini[5] has tested Smith's structure against his crystallographic data and considers that it is inadmissible *in the crystal*.

The purpose of this communication is to point out that Corradini's work and Smith's work are not necessarily incompatible and to suggest some ideas which can resolve the apparent inconsistency and which have some further implications.

As the very first step, it should be noted that the infrared data and the X-ray crystallographic data pertain to two different phases and that the structure does not have to be the same in both.[6]

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[1] The substance of this correspondence and explicitly the summary statements were part of a lecture presented on Feb 3, 1966, at the Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa.

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[5] P. Corradini, private communication.

[6] There are a great many examples of this variability of structure with phase throughout chemistry. Two which are particularly close to the present one are those of $Fe_3(CO)_{12}$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, both of which have infrared spectra in solution which are quite inconsistent with the structures of the molecules in the solid state and which thus indicate the presence of molecules with different structures in solution.