water, *i.e.*, the axial water and water found in a second coordination sphere consisting of four positions on the faces of the pyramidal structure of the hydrated vanadyl ion (Figure 11). Furthermore there is evidence that $1/T_{2\text{pII}}$ contains appreciable contributions from dipole–dipole, scalar, and quadrupole coupling.

It would have been nice if the two kinds of loosely coordinated waters could have been studied separately in various chelate complexes, *e.g.*, by comparing the data on VO(NTA)^- and VO(PIDA), where only the loose coordination on the faces of the pyramid could possibly be of importance (Figure 6F), with those on $\text{VO(TIR)}_2{}^{6-}$ and $\text{VO(SSA)}_2{}^{4-}$, where one would expect to observe the effects of both kinds of labile waters (Figure 5B). Since we are looking for extremely small effects on the nuclear resonance, such experiments have to be done with concentrated solutions of the vanadyl complexes, which seem not to be stable over an extended period of time. Furthermore the viscosity in these concentrated solutions is greatly enhanced compared to that of pure water. Therefore it seems beyond the limits of the method to measure the small enhancement of the relaxation of O^{17} which might arise from a possible exchange of labile waters in solutions of the above-mentioned vanadyl complexes. The small effects shown in Figure 4 for VO(NTA)^-, VO(EDTA^{2-}, and $\text{VO(SSA)}_2{}^{4-}$ are at about the limit of the experimental accuracy and cannot be taken to establish axial or second-coordination-sphere relaxation. Such relaxation may be appreciably diminished in these complexes through an increase in the rate of water exchange.

Chemical shift measurements appeared to give more reliable data. No measurable shift was observed in the solutions of complexes of the types in Figures 5B and 6F. This indicates that the hydration in the second coordination sphere of these complexes differs appreciably from that in the second coordination sphere of the hydrated vanadyl ion. It therefore appears rather unlikely that one might be able to deduce more information about the coordination of the labile waters in the hydrated vanadyl ion from further studies of vanadyl chelate complexes.

Proton Exchange from the Equatorial Positions.—From the curve-fitting process in Figure 13 we find for τ_{MI} at 25° a value of $n \times 1.15 \times 10^{-5}$ sec, where n is the number of water molecules coordinated to positions of type I. Since the proton exchange from anyone of the coordination sites cannot be slower than the corresponding water exchange, we can immediately exclude the possibility that τ_{MI} in Figure 13 corresponds to exchange from the axial position or from the second coordination sphere. Experiments with solutions of VO(EDTA)^{2-} showed that the transverse proton nuclear relaxation in the bulk water is not affected by the presence of this complex. This is consistent with the assumption that a possible protonation of the vanadyl oxygen is not an important relaxation mechanism in nonacidified solutions. It follows that τ_{MI} in Figure 13 corresponds to the protons of the equatorial waters, as has been anticipated previously,[4] and the proton exchange from these positions can be characterized by $k(25°) = 2.2 \times 10^4\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 7.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -13$ eu, and $A/h = 1.6 \times 10^6$ cps. As was pointed out previously,[3,34] these values clearly indicate that the proton exchange from the equatorial positions is not controlled by the rate of the water exchange (Table II) but by a hydrolysis mechanism.

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(34) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

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Synthesis and Resolution of Heterochelate Metal Complexes of Chromium(III) and Cobalt(III) with the Ligands 2,2′-Bipyridine, 1,10-Phenanthroline, and Oxalate Ion

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New heterochelate complex cations $\text{Cr(ox)(bipy)}_2{}^+$, $\text{Cr(ox)(phen)}_2{}^+$, $\text{Co(ox)(bipy)}_2{}^+$, and $\text{Co(ox)(phen)}_2{}^+$ (ox = oxalate ion, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been prepared as their chloride, perchlorate, or iodide salts and resolved by means of optically active $\text{Cr(ox)}_2\text{phen}^-$. The anionic complexes $\text{Co(ox)}_2\text{bipy}^-$ and $\text{Co(ox)}_2\text{phen}^-$ have also been obtained in combination with either Ba^{2+} or $\text{Co(ox)(phen)}_2{}^+$, respectively. All of the optically active cations have been found to racemize in solution and in addition the cobalt(III) complexes were markedly photosensitive.

Introduction

Systematic changes in the nature of the ligands together with changes in the over-all charge of a complex are pertinent in many studies of coordination compounds. The present work was undertaken to provide an interrelated series of optically active chromium(III) and cobalt(III) complexes with the ligands 2,2′-bipyr-

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idine (bipy), 1,10-phenanthroline (phen), and oxalate (ox) for use in racemization and ligand-exchange experiments. Earlier papers[2] have described studies on the anions $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ while the tris(oxalato) species with both metals have been extensively investigated.[3] Russian workers[4] have reported the complex $[Co(ox)(phen)_2]Cl \cdot 4H_2O$ prepared from the dichlorobis(1,10-phenanthroline)cobalt(III) complex, but it was characterized only by analysis. In this paper we report methods of synthesis for $Cr(ox)(bipy)_2^+$, $Cr(ox)(phen)_2^+$, $Co(ox)(bipy)_2^+$, $Co(ox)(phen)_2^+$, $[Co(ox)(phen)_2][Co(ox)_2phen]$, and $Co(ox)_2bipy^-$, together with a general method of resolution for the above cations. The new compounds have been characterized by various chemical and physical methods.

Experimental Section

Materials.—$[CrCl_2(\text{bipy or phen})_2]Cl \cdot 2H_2O$ was prepared by the literature method.[5] Potassium tris(oxalato)cobaltate(III) trihydrate was obtained by the method in ref 6. Potassium bis(oxalato)-1,10-phenanthrolinechromate(III) tetrahydrate was prepared and resolved as described previously.[2a] All other reagents were commercial products used without further purification.

Methods.—In the resolutions to follow, all rotations refer to the sodium D line unless otherwise stated. For the chromium complexes the rotations were measured using a Perkin-Elmer 141 automatic polarimeter. For the cobalt complexes rotations were measured using a conventional Schmidt and Haensch polarimeter.

Chromium(III) Complexes. Oxalatobis(2,2′-bipyridine or 1,10-phenanthroline)chromium(III) Chloride Tetrahydrate, $[CrC_2O_4(C_{10}H_8N_2)_2]Cl \cdot 4H_2O$ or $[CrC_2O_4(C_{12}H_8N_2)_2]Cl \cdot 4H_2O$.—Note that for these preparations quantities labeled (a) refer to the 2,2′-bipyridine complex and those labeled (b) refer to the 1,10-phenanthroline complex. $[CrCl_2(\text{bipy or phen})_2]Cl \cdot 2H_2O$ ((a) 5.7 g, 0.011 mol; (b) 3.7 g, 0.007 mol) was added to a solution of potassium oxalate ((a) 2.1 g, 0.011 mol; (b) 1.3 g, 0.007 mol) in water ((a) 12 ml; (b) 18 ml) at the boiling point. The solution was heated with stirring for (a) 4 min and (b) 1 min and the color changed to a deep red. Water (110 ml) was added and the solution was heated and then filtered hot to remove a small quantity of red-brown solid. Potassium iodide (8 g) in water (15 ml) was added to the hot filtrate to give a yellow-orange solid. The reaction mixture was cooled in ice, and the yellow product was filtered off at the pump and washed with cold 90% ethanol and then acetone. The yields were: (a) 4.2 g, 62%; (b) 4.0 g, 92%. *Anal.* Calcd for $C_{22}H_{21}N_4O_{6.5}ICr$: C, 42.1; H, 3.0; N, 8.7; I, 20.3. Found: C, 42.3; H, 3.4; N, 9.0; I, 20.3. Calcd for $C_{26}H_{20}N_4O_6ICr$: C, 46.8; H, 2.8; N, 8.4; I, 18.8. Found: C, 47.1; H, 3.0; N, 8.4; I, 19.1. The iodide salts were converted to the corresponding chlorides by metathetical reactions with hot (50°) suspensions of freshly prepared silver chloride. The silver iodide was filtered off and the filtrates were evaporated on the steam bath to give orange crystals which were recrystallized from water. *Anal.* Calcd for $C_{22}H_{24}N_4O_8ClCr$: C, 47.2; H, 4.3; N, 10.0; Cl, 6.3. Found: C, 47.0; H, 4.3; N, 10.1; Cl, 6.2. Calcd for $C_{26}H_{24}N_4O_8ClCr$: C, 51.4; H, 4.0; N, 9.2; Cl, 5.8. Found: C, 51.2; H, 3.9; N, 9.1; Cl, 5.7.

Resolution of (±)-Oxalatobis(1,10-phenanthroline)chromium(III) Chloride Tetrahydrate.—(±)-$[Cr(ox)(phen)_2]Cl \cdot 4H_2O$ (2.3 g, 0.0039 mol) was dissolved in water (280 ml) and cooled to 3°. (+)-$K[Cr(ox)_2phen] \cdot 3H_2O$ (1 g, 0.002 mol) in cold water (36 ml) was added to precipitate a pink diastereoisomer. The mixture was cooled in ice and the product was filtered off and washed with ice water and then ethanol and acetone. The yield was 1.9 g. *Anal.* Calcd for $C_{42}H_{30}N_6O_{15}Cr_2$: C, 52.4; H, 3.1; N, 8.7. Found: C, 52.1; H, 3.2; N, 8.7. The cold filtrate was passed through an ion-exchange column (20 × 1.5 cm Dowex I-X, chloride form) to remove a small amount of the resolving agent and the eluate solution was reduced in volume by freeze-drying. Two fractions of $[Cr(ox)(phen)_2]Cl \cdot 4H_2O$ were isolated in this manner by filtering off the crystals which separated. The least soluble and least active fraction (0.24 g) gave $[\alpha]_D$ +33 for a 0.13% solution in a 10-cm tube while the most soluble fraction (0.4 g) gave $[\alpha]_D$ −562 and $[\alpha]_{5461}$ −854. Only the least soluble fraction was obtained free from potassium chloride. *Anal.* Calcd for $C_{26}H_{24}N_4O_8ClCr$: C, 51.4; H, 4.0; N, 9.2; Cl, 5.8. Found: C, 50.6; H, 3.8; N, 9.1; Cl, 5.7.

(+)-Oxalatobis(1,10-phenanthroline)chromium(III) Perchlorate–2.5-Water.—The pink diastereoisomer (1.4 g) was made into a mull with water (5 ml) and then treated with 10 *M* perchloric acid (10 ml) in which it dissolved and then almost immediately gave an orange solid. The product was filtered off and washed with cold perchloric acid (15 ml, 3 *M*) followed by acetone. The yield was 1 g. A 0.025% solution in a 40-cm tube gave $[\alpha]_D$ +855 and $[\alpha]_{5461}$ +1290. *Anal.* Calcd for $C_{26}H_{21}N_4O_{6.5}ClCr$: C, 48.4; H, 3.4; N, 8.7; Cl, 5.5. Found: C, 48.5; H, 3.6; N, 8.6; Cl, 5.7.

Resolution of (±)-Oxalatobis(2,2′-bipyridine)chromium(III) Chloride Tetrahydrate.—(±)-$[Cr(ox)(bipy)_2]Cl \cdot 4H_2O$ (2.9 g, 5.17×10^{-3} mol) was dissolved in water (220 ml) and cooled to 2°. (+)-$K[Cr(ox)_2phen] \cdot 4H_2O$ (1.3 g, 2.62×10^{-3} mol) in cold water (44 ml) was added gradually to precipitate a pink diastereoisomer. The mixture was cooled in ice and filtered off to be washed with ice-cold water, ethanol, and then acetone. The filtrate was reserved for the isolation of the other enantiomer. The yield was 2.5 g. A 0.02% solution in a 10-cm tube gave $[\alpha]_D$ +480 and $[\alpha]_{5461}$ −196. *Anal.* Calcd for $C_{38}H_{32}N_6O_{16}Cr_2$: C, 48.9; H, 3.5; N, 9.0. Found: C, 48.7; H, 3.7; N, 9.0. The diastereoisomer (0.4 g) was shaken mechanically with a suspension of Dowex I-X exchange resin (*ca.* 5 g, chloride form) in water (20 ml) for a period of 15 min. The resin was filtered off and washed with water (20 ml). Potassium hexafluorophosphate (2 g) in water (20 ml) was added to the filtrate to give an orange crystalline precipitate. The product was filtered from the cold solution and washed with cold ethanol (85%), ethanol, and then ether. The yield was 0.12 g. A 0.01% solution in a 10-cm tube gave $[\alpha]_D$ +361 and $[\alpha]_{5461}$ +611. *Anal.* Calcd for $C_{22}H_{16}F_6N_4O_5PCr$: C, 39.6; H, 2.96. Found: C, 39.4; H, 2.75.

The other optical isomer present in the filtrate from the diastereoisomer could be isolated by the addition of potassium hexafluorophosphate (2 g). Alternatively the cold filtrate was passed through an anion exchanger (Dowex I-X, chloride form) to remove a small amount of the resolving agent and the solution was then freeze-dried. A number of fractions were isolated during the freeze-drying and, although contaminated with potassium chloride, were nevertheless suitable for use in racemization studies. The most soluble fraction gave $[\alpha]_D$ −261 and $[\alpha]_{5461}$ −440 for a 0.05% solution in a 10-cm tube.

Cobalt(III) Complexes.—Since the new complexes are photosensitive, it is necessary to avoid exposure of reaction vessels to direct sunlight. The following preparations were carried out in diffuse artificial lighting.

Oxalatobis(2,2′-bipyridine)cobalt(III) Iodide Monohydrate, $[CoC_2O_4(C_{10}H_8N_2)_2]I \cdot H_2O$.—2,2′-Bipyridine (2.5 g, 1.6×10^{-2} mol) was dissolved in hot aqueous ethanol (75 ml, 20% v/v) and a solution of potassium tris(oxalato)cobaltate(III) trihydrate (5 g, 1.01×10^{-2} mol) in water (50 ml) was then added. The reaction mixture was heated rapidly to the boiling point and refluxed for 4 min. During this time the green color of the solution changed to a deep red, and some orange solid[7] (*ca.* 0.5 g) precipitated and was filtered off. Potassium iodide (20 g) was added to the filtrate to precipitate orange-yellow crystals. The

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[2] (a) J. A. Broomhead, *Australian J. Chem.*, **15**, 228 (1962); (b) J. A. Broomhead, *J. Inorg. Nucl. Chem.*, **27**, 2049 (1965).

[3] K. Krisnamurty and G. Harris, *Chem. Rev.*, **61**, 213 (1961).

[4] A. V. Ablov and D. M. Palade, *Russ. J. Inorg. Chem.*, **7**, 1304 (1962).

[5] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[6] J. C. Bailar and E. M. Jones, *Inorg. Syn.*, **1**, 35 (1939).

mixture was cooled in an ice bath and the product was filtered off at the pump. It was washed in turn with ice water (three times), ethanol (three times), and then acetone. The yield was 4.1 g [70% based upon potassium tris(oxalato)cobaltate(III)]. *Anal.* Calcd for $C_{22}H_{18}N_4O_5ICo$: C, 43.7; H, 3.0; N, 9.3. Found: C, 43.7; H, 3.1; N, 9.2. The iodide was converted to the more soluble chloride by metathesis with silver chloride, and samples of the chloride and the bromide salts were isolated by conventional methods. *Anal.* Calcd for $C_{22}H_{24}N_4O_8ClCo$, $[CoC_2O_4(C_{10}H_8N_2)_2]Cl\cdot 4H_2O$: C, 46.6; H, 4.3; N, 9.9. Found: C, 46.0; H, 4.3; N, 9.8. Calcd for $C_{22}H_{18}N_4O_5BrCo$, $[CoC_2O_4(C_{10}H_8N_2)_2]Br\cdot H_2O$: C, 47.4; H, 3.3; N, 10.1. Found: C, 47.5; H, 3.5; N, 10.2.

Oxalatobis(1,10-phenanthroline)cobalt(III) Iodide Monohydrate, $[CoC_2O_4(C_{12}H_8N_2)_2]I\cdot H_2O$.—1,10-Phenanthroline (0.5 g, 2.7×10^{-3} mol) was dissolved in aqueous ethanol (15 ml, 33% v/v) and added to a solution of potassium tris(oxalato)cobaltate(III) trihydrate (0.81 g, 1.6×10^{-3} mol) in water (9 ml). The green solution was heated to 95° for 6 min, and the color changed to a deep red. Water (15 ml) was then added and the hot reaction mixture was filtered to remove a salmon pink solid[7] (0.3 g). Potassium iodide (6 g) in water (6 ml) was added to the filtrate to give pale orange crystals which were filtered off at the pump. The product was washed with ice water (three 10-ml portions), ethanol (three 10-ml portions), and then acetone. The yield was 0.6 g (55% based upon potassium tris(oxalato)cobaltate(III). *Anal.* Calcd for $C_{26}H_{18}N_4O_5CoI$: C, 47.8; H, 2.8; N, 8.6. Found: C, 47.5; H, 2.4; N, 8.6. Metathesis with silver chloride enabled conversion of the iodide to the more soluble chloride form $[CoC_2O_4(C_{12}H_8N_2)_2]Cl\cdot 4H_2O$. *Anal.* Calcd for $C_{26}H_{24}N_4O_8ClCo$: C, 50.8; H, 3.90; N, 9.1; Cl (ionic), 5.8. Found: C, 50.8; H, 3.90; N, 9.0; Cl (ionic), 5.7.

Oxalatobis(2,2′-bipyridine)cobalt(III) Bis(oxalato)-2,2′-bipyridinecobaltate(III) Tetrahydrate and Oxalatobis(1,10-phenanthroline)cobalt(III) Bis(oxalato)-1,10-phenanthrolinecobaltate(III) Trihydrate, $[CoC_2O_4(C_{10}H_8N_2)_2][Co(C_2O_4)_2C_{10}H_8N_2]\cdot 4H_2O$ and $[CoC_2O_4(C_{12}H_8N_2)_2][Co(C_2O_4)_2C_{12}H_8N_2]\cdot 3H_2O$.—The isolation of these mauve double-complex compounds followed the same methods as have been described for the cationic complexes until the stage in which potassium iodide was to be added. Instead of this addition the purple-red solutions were cooled in an ice bath and in both cases mauve, needlelike crystals were deposited. These were filtered off and washed with cold water and then acetone. From 0.47 g of 2,2′-bipyridine 0.48 g of mauve solid was obtained; 0.6 g of 1,10-phenanthroline gave 0.2 g of mauve product. *Anal.* Calcd for $C_{36}H_{32}N_6O_{16}Co_2$: C, 46.8; H, 4.5; N, 9.1. Found: C, 47.1; H, 3.6; N, 9.1. Calcd for $C_{42}H_{30}N_6O_{15}Co_2$: C, 51.6; H, 3.1; N, 8.6. Found: C, 51.5; H, 2.8; N, 8.7.

Barium Bis(oxalato)-2,2′-bipyridinecobaltate(III) Pentahydrate, $Ba[Co(C_2O_4)_2C_{10}H_8N_2]_2\cdot 5H_2O$.—Oxalatobis(2,2′-bipyridine)cobalt(III) bis(oxalato)-2,2′-bipyridinecobaltate(III) tetrahydrate (0.48 g) was dissolved in water (60 ml) at the boiling point and potassium iodide (5 g) was added. The solution was then cooled in an ice bath and gave 0.2 g of the orange-yellow oxalatobis(2,2′-bipyridine)cobalt(III) iodide monohydrate. This was filtered off and barium acetate (4 g) was added to the cerise filtrate. A purple solid was deposited and filtered off; it was washed with water, ethanol, and then acetone. The compound was recrystallized from hot water, but some decomposition occurred. The yield was 0.03 g. *Anal.* Calcd for $C_{28}H_{26}N_4O_{21}Co_2Ba$: C, 33.4; H, 2.6; N, 5.6. Found: C, 33.4; H, 2.4; N, 5.7.

An analogous procedure starting with oxalatobis(1,10-phenanthroline)cobalt(III) bis(oxalato)-1,10-phenanthrolinecobaltate(III) trihydrate (0.2 g) gave only oxalatobis(1,10-phenanthroline)cobalt(III) iodide monohydrate (0.1 g). *Anal.* Found: C, 48.1; H, 2.9; N, 8.3. The addition of barium acetate to the cerise mother liquor resulted in solids of indefinite composition.

(+)-Oxalatobis(2,2′-bipyridine)cobalt(III) Perchlorate Sesquihydrate, $[CoC_2O_4(C_{10}H_8N_2)_2]ClO_4\cdot 1.5H_2O$.—Oxalatobis(2,2′-bipyridine)cobalt(III) iodide monohydrate (0.62 g, 10^{-3} mol) was converted to the more soluble chloride form by shaking for 5 min with a suspension of ion-exchange resin (*ca.* 5 g of Dowex I-X) in water (10 ml). The resin was filtered off and washed with water (10 ml), and the filtrate and washings were then cooled thoroughly in an ice bath.

(−)-Potassium bis(oxalato)-1,10-phenanthrolinechromate(III) tetrahydrate (0.23 g, 0.5×10^{-3} mol) was dissolved in water (10 ml) at 2° and converted to the sodium salt by means of a column of ion-exchange resin. (Dowex 50-WX, 10 × 1.5 cm). The column temperature was first reduced to 5° by washing in ice water. The (−)-sodium bis(oxalato)-1,10-phenanthrolinechromate(III) solution eluted from the column with the aid of a further 20 ml of ice water was passed directly into the cold solution of racemic oxalatobis(2,2′-bipyridine)cobalt(III) chloride. The pink diastereoisomer was precipitated almost immediately. The mixture was allowed to stand at 2° for 10 min and then the solid was filtered off at the pump. It was washed with ice water (two 10-ml portions), ethanol (two 10-ml portions), and then acetone. The yield was 0.48 g. *Anal.* Calcd for $C_{38}H_{34}N_6O_{17}CoCr$: C, 47.7; H, 3.6; N, 8.8. Found: C, 47.8; H, 3.6; N, 9.0. Sodium perchlorate (20 g) was added to the above filtrate and crystallization was induced by scratching with a glass rod. The pink product was cooled in ice and filtered off. It was washed with cold, saturated sodium perchlorate solution, then ethanol (two 10-ml portions), and ether (two 10-ml portions). The yield was 0.29 g. *Anal.* Calcd for $C_{22}H_{19}N_4O_{9.5}ClCo$: C, 45.1; H, 3.3; N, 9.6. Found: C, 45.4; H, 3.3; N, 9.6. A 0.059% solution in aqueous acetone (10% w/v) gave $[\alpha]_D$ +285.

(−)-Oxalatobis(2,2′-bipyridine)cobalt(III) Perchlorate Hemihydrate.—The above diastereoisomer was suspended in water (10 ml) containing a Dowex I-X chloride-form anion exchanger (*ca.* 5 g) and shaken vigorously at room temperature for a period of 5 min. The resin was removed by filtration and washed with water (10 ml). Sodium perchlorate (20 g) was added to the filtrate which was cooled in ice and scratched to induce crystallization. The (−) product (0.19 g) was filtered off and washed as was the (+) isomer. *Anal.* Calcd for $C_{22}H_{17}N_4O_{8.5}ClCo$: C, 46.5; H, 3.0; N, 9.9. Found: C, 46.5; H, 3.2; N, 9.7.

(+)-Oxalatobis(1,10-phenanthroline)cobalt(III) Perchlorate Pentahydrate, $[CoC_2O_4(C_{12}H_8N_2)_2]ClO_4\cdot 5H_2O$.—A solution of oxalatobis(1,10-phenanthroline)cobalt(III) chloride was prepared from the corresponding iodide (0.66 g, 10^{-3} mol) by shaking with freshly precipitated silver chloride in water (10 ml) at 55° for *ca.* 5 min. The mixture was filtered at this temperature and the residue washed with water (10 ml). The filtrate was then treated with a solution of (−)-sodium bis(oxalato)-1,10-phenanthrolinechromate(III) prepared from the potassium salt (0.23 g) by a technique identical with that described above for the bipyridine counterpart. The very insoluble pink diastereoisomer was precipitated and after standing in an ice bath for 10 min was filtered off at the pump and washed with ice water, ethanol, and then acetone. The yield was 0.39 g. *Anal.* Calcd for $C_{42}H_{32}N_6O_{16}CoCr$: C, 51.1; H, 3.3; N, 8.5. Found: C, 51.4; H, 3.2; N, 8.7. Sodium perchlorate (15 g) was added to the above aqueous filtrate and the solution was cooled in ice and scratched with a glass rod. The pink product was filtered off and washed with saturated aqueous sodium perchlorate (10 ml), ethanol (10 ml), and then ether. The yield was 0.13 g. *Anal.* Calcd for $C_{26}H_{26}N_4O_{13}ClCo$: C, 44.8; H, 3.8; N, 8.0. Found: C, 44.9; H, 3.3; N, 7.9. A 0.076% solution in aqueous acetone (10% w/v) gave α_D +0.57 and $[\alpha]_D$ +750.

Physical Measurements.—Infrared spectra were recorded for Nujol or hexachlorobutadiene mulls in the range 4000–650 cm^{-1} using a Unicam SP200G or Perkin-Elmer 457 spectrophotometer and in the range 500–200 cm^{-1} using a Grubb-Parsons DM 4 instrument. Visible and ultraviolet spectra were obtained with Cary Model 14 and Beckman DK 2A spectrophotometers.

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[7] These products were washed with water and dried 2 hr in a vacuum desiccator. The orange product from the bipyridine reaction analyzed for 53.7% C, 2.9% H, and 8.9% N, while the salmon-colored phenanthroline reaction product analyzed for 50.8% C, 2.7% H, and 12.8% N.

Conductivity measurements were made at 25° using a Phillips GM249 direct-reading conductivity bridge.

Results and Discussion

The singularity of the $Cr(ox)_2phen^-$ ion as a resolving agent in this work is noteworthy as also is the need to carry out the procedures below room temperature. Attempts to effect resolutions using optically active anions such as bis(oxalato)ethylenediaminecobaltate(III), bis(malonato)ethylenediaminecobaltate(III), antimony (+)-tartrate, arsenyl (+)-tartrate, and (+)-tartrate itself at room temperatures gave only precipitates containing the racemic cationic complexes. Evidently there is a reversal here of the relative solubilities such that the required diastereoisomers are only less soluble than the partially racemic salts below about 10°.

Justification of the formulas assigned to the new heterochelate compounds is based on the following evidence. Direct anion analysis by means of cation-exchange resins helps to differentiate complexes of the type $[MC_2O_4(AA)_2]X \cdot nH_2O$ (M = Cr(III) or Co(III), AA = 2,2′-bipyridine or 1,10-phenanthroline, X = halide ion, $n \geq 1$) from $[MX(H_2O)(AA)_2]C_2O_4 \cdot (n-1)H_2O$ or $[MXOH(AA)_2]HC_2O_4 \cdot (n-1)H_2O$. The formulations $[MOHHC_2O_4(AA)_2]X \cdot (n-1)H_2O$ may be eliminated on the basis of conductometric titration experiments which were found to give decreases in resistance parallel to that expected for the addition of alkali to a 1:1 electrolyte solution. Addition of 1 equiv of alkali should produce almost no change in the conductance for a complex containing one acidic proton. The double complexes $[CoC_2O_4(AA)_2][Co(C_2O_4)_2(AA)] \cdot nH_2O$ (n = 3, 4) are distinguished from $[CoC_2O_4(AA)_2]_3[Co(C_2O_4)_3] \cdot nH_2O$ and $[Co(AA)_3][Co(C_2O_4)_3] \cdot nH_2O$ by their reactions when treated in solution with potassium iodide followed by barium acetate to yield $[CoC_2O_4(AA)_2]I \cdot H_2O$ and cerise solutions. When AA is phenanthroline, $Ba[Co(C_2O_4)_2phen] \cdot 5H_2O$ is isolated (see Experimental Section).

The new compounds are 1:1 electrolytes (Table I) when compared with conductance data for similar complexes taken from the literature.[8,9] The lower conductivities generally found for heterochelate metal–oxalato complexes in water have been discussed elsewhere in terms of hydrogen-bonding effects.[9] The infrared spectra (Table II) are consistent with the presence of coordinated oxalate and lattice water. Further, there are no C=O bands above 1720 cm^{-1}, whereas monodentate oxalate gives a C=O stretching band at 1757 cm^{-1}.[10]

TABLE I

CONDUCTIVITY DATA FOR Cr(III) AND Co(III) HETEROCHELATE COMPLEXES AT 25°

Compound	Λ,[a] ohm^{-1} cm^2 mole^{-1}
$[Cr(ox)(bipy)_2]Cl \cdot 4H_2O$	104
$[Cr(ox)(bipy)_2]I \cdot 2.5H_2O$	109
$[Cr(ox)(phen)_2]Cl \cdot 4H_2O$	89, 75[b]
$[Cr(ox)(phen)_2]I \cdot 2.5H_2O$	88
$[Co(ox)(phen)_2]Cl \cdot 4H_2O$	92
$[Co(ox)(phen)_2]I \cdot H_2O$	92
$[Co(ox)(bipy)_2]Cl \cdot 4H_2O$	90
$[Co(ox)(bipy)_2]I \cdot H_2O$	102
$[Co(phen)_3]Cl_3 \cdot 6H_2O$	366[c]

[a] 10^{-3} M aqueous solution unless otherwise stated. [b] 10^{-3} M in nitromethane for which A^+X^- electrolytes give Λ 80–100: C. M. Harris and T. N. Lockyer, *J. Chem. Soc.*, 3083 (1959). [c] B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959).

TABLE II

CHARACTERISTIC COORDINATED OXALATE AND LATTICE WATER INFRARED DATA (CM^{-1})

Compound	ν_{as}(C=O)	Lattice water
$[Cr(ox)(phen)_2]Cl \cdot 4H_2O$[a]	1711, 1672	3490, 3340
$[Cr(ox)(bipy)_2]Cl \cdot 4H_2O$[a]	1718, 1680	3520, 3370
$K[Cr(ox)_2phen] \cdot 3H_2O$[a]	1713, 1690, 1670	3480
$K[Cr(ox)_2bipy] \cdot 3H_2O$[a]	1720, 1704, 1680	3540
$[Co(ox)(phen)_2]I \cdot H_2O$[b]	1710, 1678	3420
$[Co(ox)(bipy)_2]I \cdot H_2O$[b]	1710, 1680	3520, 3380
$Ba[Co(ox)_2bipy]_2 \cdot 5H_2O$[b]	1720, 1680	3500
$[CoHC_2O_4(NH_3)_5]Br_2$[c]	1757, 1672	. . .

[a] Hexachlorobutadiene mulls. [b] Nujol mulls. [c] Reference 10.

Gouy balance measurements on the cobalt(III) compounds show them to be diamagnetic, and these complexes are all photosensitive. Aqueous solutions of $[Co(ox)(AA)_2]Cl$ exposed to sunlight very rapidly precipitate orange-yellow solids which have the same X-ray powder patterns as the orange materials isolated during the syntheses of the cations (see Experimental Section). Photochemical reactions are also evident in the solid state. For example, red $[Co(ox)(phen)_2]Cl \cdot 4H_2O$ becomes yellow when exposed to direct sunlight for 5 min. It is likely that cobalt(II) species are produced since the magnetic force on a sample of $[Co(ox)(phen)_2]I \cdot H_2O$ after a 2-hr exposure to ultraviolet radiation increases by a factor of 5, indicating the formation of paramagnetic species by irradiation. It is of interest that when the syntheses of the cationic cobalt(III) complexes are performed in the dark, smaller quantities (66% of those quoted in the Experimental Section) of the above orange cobalt(II) materials are obtained. Therefore, they must originate in the main from thermal reactions, probably involving cobalt(II) species arising from the reduction and dissociation of the tris(oxalato)cobaltate(III) anion. The ready sensitivity of the new complexes to light is perhaps not surprising in view of the presence of the conjugated π-bonding ligands, a reducible metal such as Co(III), and an oxidizable ligand such as $C_2O_4^{2-}$. Despite the photosensitivity, the complexes are sufficiently stable to permit measurement of their visible and ultraviolet absorption spectra. All of the new complexes show the intense ultraviolet absorption characteristic of the heteroaromatic ligands present. The visible spectra for solutions of $Cr(ox)(bipy)_2^+$, $Co(ox)(phen)_2^+$, and $Co(ox)_2bipy^-$ are given in Figure 1 and typify the visible spectra of the other phenanthroline and bipyridine chromium(III) and cobalt(III) complexes described here. Complete spectral data are included in Table III. The successive replacement of the weaker field

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(8) H. S. King, *J. Chem. Soc.*, 1912 (1948).

(9) J. A. Broomhead and L. Kane-Maguire, *ibid.*, *A*, 546 (1967).

(10) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, **79**, 4904 (1957).

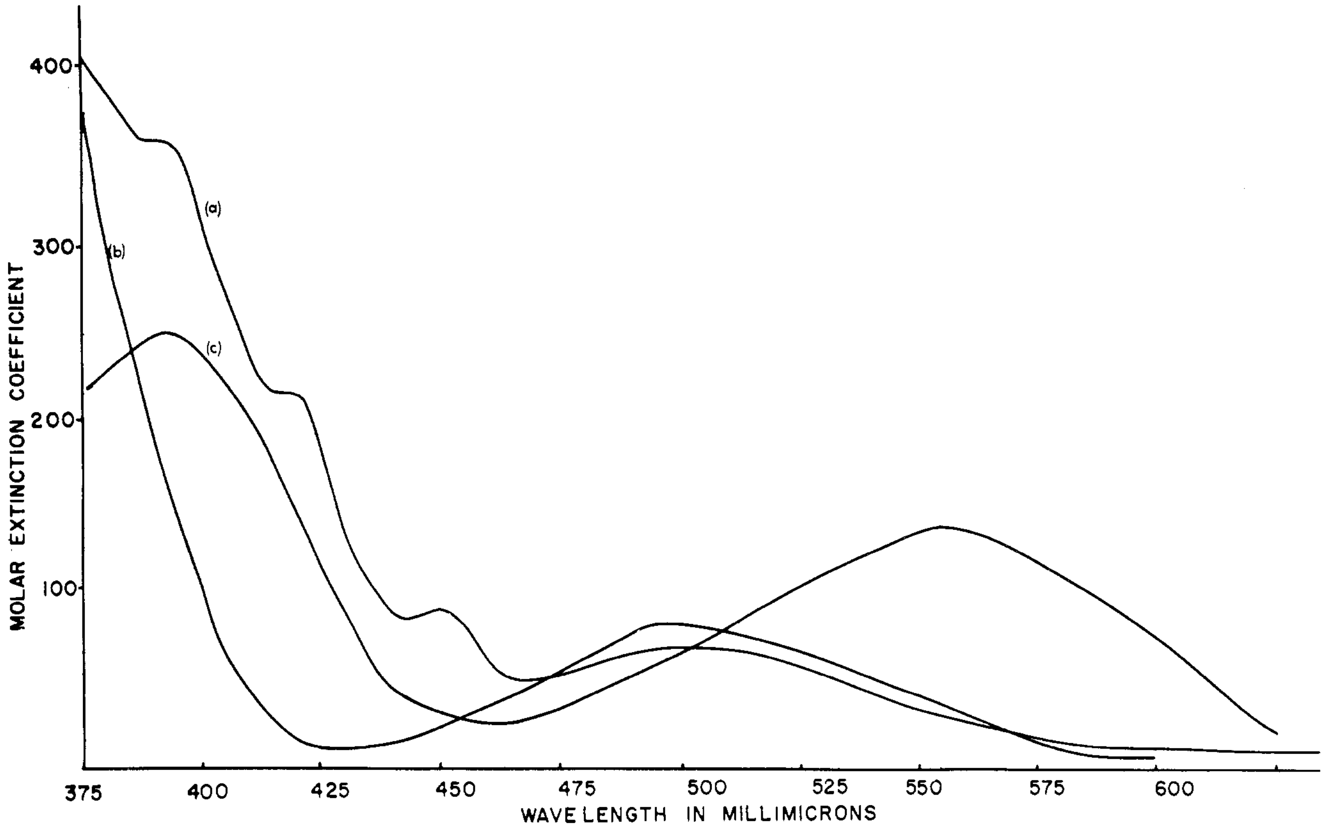

Figure 1.—Typical absorption spectra for aqueous solutions of: (a) $[Cr(ox)(bipy)_2]Cl \cdot 4H_2O$; (b) $[Co(ox)(phen)_2]Cl \cdot 4H_2O$; (c) $K[Co(ox)_2bipy]$.

Table III

Visible Absorption Maxima (mμ) for Cr(III) and Co(III) Complexes in Aqueous Solutions[a]

Compound	mμ	
$K_3[Cr(ox)_3] \cdot 3H_2O$[b]	420 (97)	570 (75)
$K[Cr(ox)_2phen] \cdot 4H_2O$[c]	397 (133)	543 (77)
$K[Cr(ox)_2bipy] \cdot 3H_2O$[c]	392 (178)	535 (86)
$[Cr(ox)(phen)_2]Cl \cdot 4H_2O$	351 (1810), 420 (126) sh	502 (62)
$[Cr(ox)(bipy)_2]Cl \cdot 4H_2O$	392 (364) sh, 417 (220) sh, 447 (90) sh	510 (60)
$[Cr(phen)_3](ClO_4)_3 \cdot 2H_2O$		426 (384)
$K_3[Co(ox)_3] \cdot 3H_2O$[b]	420 (220)	605 (170)
$K[Co(ox)_2bipy]$[d]	390 (252)	555 (145)
$[Co(ox)(phen)_2]Cl \cdot 4H_2O$		495 (80)
$[Co(ox)(bipy)_2]Cl \cdot 4H_2O$		498 (88)
$[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$		470 (42)

[a] ε values (M^{-1}) in parentheses; sh = shoulder. [b] A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958). [c] See ref 2a; T. Bürer, *Helv. Chim. Acta*, **46**, 242 (1963). [d] Prepared in solution from $Ba[Co(ox)_2bipy]_2 \cdot 5H_2O$ and potassium sulfate.

oxalate ligand by the stronger field heteroaromatic base is well illustrated for both metals by the progressive shift of the d–d absorption maxima to shorter wavelengths. Although the symmetry is no longer cubic, the main features of the spectrum of $Cr(ox)_3^{3-}$ are maintained, particularly for $Cr(ox)_2phen^-$ and $Cr(ox)_2bipy^-$. However, there is evidence of "intensity stealing" for the shorter wavelength absorptions of these anions. Assignment of the first two long-wavelength bands in $Cr(ox)_2phen^-$ at 18,400 and 25,200 cm^{-1} to the spin-allowed $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ transitions and use of the Tanabe–Sugano energy diagram having Racah parameter ratios C/B of 4.5 gives a value of the Racah parameter B of 657 cm^{-1} and $10Dq$ equal to 18,400 cm^{-1}.[11] Using the rule of average ligand field environment and the literature value[12] of $10Dq$ for $Cr(phen)_3^{3+}$ of 23,500 cm^{-1}, the predicted $10Dq$ value for $Cr(ox)_2phen^-$ is, however, 19,500 cm^{-1}. A similar spectral assignment for the two lowest energy bands in the spectrum of $Cr(ox)(phen)_2^+$ leads to a value of B = 432 cm^{-1} and $10Dq$ = 20,300 cm^{-1}. Here the average environment rule predicts a $10Dq$ value of 21,500 cm^{-1} so that in neither case is the rule satisfactory. When successive differences in $10Dq$ values are considered, failure of the average environment approach is particularly evident.[13] For the series $Cr(ox)_3^{3-}$, $Cr(ox)_2phen^-$, $Cr(ox)(phen)_2^+$, and $Cr(phen)_3^{3+}$ equal 2000-cm^{-1} increments in $10Dq$ are predicted, whereas the actual increments are 900, 1900, and 3200 cm^{-1}, respectively. This failure is probably related in part to the π-acceptor properties of the heteroaromatic ligands present.

For the cobalt(III) complex cations, only one d–d band is observed, other structure being completely obscured by the intense charge-transfer absorption. Again, using the approximation of cubic symmetry,

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[11] B. N. Figgis, "Introduction to Ligand Fields," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 163 ff.

[12] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. T. Hunt, *Inorg. Chem.*, **5**, 1397 (1966).

[13] The authors wish to thank a referee for constructive criticism of this aspect.

the long-wavelength bands are assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition. The spectrum of $Co(ox)_3^{3-}$ has been reported with d–d bands at 16,500 and 23,800 cm^{-1}. From the Tanabe–Sugano diagrams,[11] B is calculated as 532 cm^{-1} and $10Dq$ is 17,600 cm^{-1} for this complex. From the literature,[12] an estimate of $10Dq$ for $Co(phen)_3^{3+}$ of 21,250 cm^{-1} leads to a predicted $10Dq$ value in $Co(ox)(phen)_2^+$ of 20,000 cm^{-1} compared with the observed value of 20,200 cm^{-1}. The satisfactory agreement here, using the simple average ligand field rule, may perhaps be fortuitous, though Figure 1 shows that there is better separation of the d–d band from the charge-transfer region than is found for the chromium complexes. The visible spectrum of $Co(ox)_2phen^-$ could not be obtained owing to the low solubility of $[Co(ox)(phen)_2][Co(ox)_2phen]$ and the decomposition that accompanied various metathesis attempts. A similar treatment to that given above has not been applied to the bipyridine complexes for which spectral data on the tris(bipyridine)cobalt(III) ions are lacking.

All of the optically active complexes described in this work are observed to racemize in neutral aqueous solution. $(+)$-$Cr(ox)(bipy)_2^+$ and $(+)$-$Cr(ox)(phen)_2^+$ racemize at very similar rates in water and are decomposed in 0.1 M alkali. In 1 M HCl at 25° $Cr(ox)(phen)_2^+$ racemizes with a half-life of 385 min to be compared with a half-life of 14 min for $Cr(ox)_2phen^-$ under the same conditions. The corresponding cobalt(III) complex, $Co(ox)(phen)_2^+$, racemizes very slowly in water (half-life is approximately 10 days at 40°), and the optical inactivation is accelerated by light and also by organic solvents. The last-mentioned cobalt complex does not racemize in 1 M hydrochloric acid. Detailed studies of the mechanisms of racemization and ligand exchange in these complexes will be published subsequently.

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Circular Dichroism of Some Ethylenediaminetriacetate Complexes of Cobalt(III)[1]

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The preparation and resolution of the series of complexes $Co(MEDTA)X^-$ and $Co(YOH)X^-$ are reported, where MEDTA is the anion of N-methylethylenediamine-N,N′,N′-triacetic acid, YOH is the anion of N-hydroxyethylethylenediamine-N,N′,N′-triacetic acid, and X^- is Br^-, Cl^- or NO_2^-. The absorption spectra and circular dichroism (CD) curves for these complexes are compared with those for the related series of complexes $Co(EDTA)X^{2-}$. The CD splitting patterns are similar for complexes containing the same monodentate ligand, but significant variations are observed in the intensities of some CD bands, particularly for the NO_2^- complexes. The great similarities of the CD curves for $Co(MEDTA)X^-$, $Co(YOH)X^-$, and $Co(EDTA)X^{2-}$ ($X^- = Br^-$ or Cl^-) indicate that the free acetate group in $Co(EDTA)X^{2-}$ does not make a significant contribution to the optical activity of the complex.

Introduction

Circular dichroism (CD) curves have been reported for cobalt(III) complexes containing EDTA acting as a hexadentate[2] or as a pentadentate[3] ligand. The pentadentate EDTA complexes studied previously have the general formula $Co(EDTA)X^{2-}$, where X^- is Br^-, Cl^-, or NO_2^-. The circular dichroism splitting patterns for these complexes were used to relate their absolute configurations to those of $Co(EDTA)^-$. In the present work CD data were obtained for similar complexes with two related pentadentate ligands: N-hydroxyethylethylenediaminetriacetic acid (YOH) and N-methylethylenediaminetriacetic acid (MEDTA). The CD splitting patterns for these complexes are like those reported for the corresponding EDTA complexes so the assignments of configuration made previously hold for these cases also.

Significant variations were found in the intensities of some circular dichroism bands within series of corresponding complexes with differing pentadentate ligands. Such a variation allows the observation of a band in the CD curve of $Co(EDTA)Cl^{2-}$ in 0.1 M hydrochloric acid which is completely hidden in the CD curves of the other chloro complexes. Also one CD peak in the curve for $Co(MEDTA)NO_2^-$ is observed as a shoulder in the curves of the other nitro complexes. These observations illustrate the importance of studying series of similar complexes when using CD data for obtaining stereochemical information.

For all of the complexes studied two relatively unstrained geometrical isomers are possible; the X group may be *trans* to either a nitrogen or an oxygen atom. The existence of at least two geometrical isomers has been invoked to interpret kinetic data for the bromo complexes with EDTA and YOH. Previous studies[3,4] and the present work with the optical isomers of these complexes, however, have found no evidence for geo-

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(1) This work was supported by a research grant (GM 10829-09) from the Division of General Medical Studies, Public Health Service.

(2) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(3) R. A. Haines and B. E. Douglas, *ibid.*, **4**, 452 (1965).

(4) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).