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[CONTRIBUTION FROM THE DEPARTMENTS OF INORGANIC CHEMISTRY, THE AUSTRALIAN NATIONAL UNIVERSITY, AND THE UNIVERSITY OF ADELAIDE]

The Resolution of the Tris-(thio-oxalato)[1] Complexes of Co(III), Cr(III) and Rh(III)

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The tris-(thio-oxalato) complexes of Co(III), Cr(III) and Rh(III) have been separated into the optical isomers through the calcium *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salts. As anticipated from the similarity of the bonding of oxygen and sulfur to chromium, the complex with this metal racemized rapidly in solution and in the solid state. The Co(III) and Rh(III) complexes showed no significant loss of rotation in the solid state in several weeks nor in aqueous solution at 90° in 10 min. All were decomposed by light. Though the Fe(III) compound has the magnetic moment (2.35 B.M.) indicative of spin-pairing, attempts at resolution were fruitless.

In contrast with the trisoxalato metal complexes little investigation has been made of the analogous tristhio-oxalato complexes. From resolution[3] and racemization studies[4,5] and the rates of exchange[6] with oxalate ion the trisoxalato complexes fall into two roughly defined categories: those that are inert and easily resolved, (Co(III), Cr(III), Rh(III), Ir(III), and those that exchange rapidly and whose resolution has not been achieved[3] or is in dispute,[3] (Al, Ga, Fe(III), Ru(III), Mn(III)).

Because of the generally stronger bonding of sulfur to transition metals, which can be ascribed in part to double-bonding, enhanced optical stability might be anticipated in the tristhio-oxalato complexes of Co(III) and Fe(III), though not with Cr(III) because of the well known preference of this metal for oxygen. The Fe(III) complex, which might be expected to be spin-paired, is of particular interest since the reported resolution of the spin-free trisoxalato ion[7] has never been substantiated.

The bisthio-oxalato complexes with Ni(II) and Pd(II), and the tris complexes of Co(III) and Rh(III) have been described by Jones and Tasker.[8,9] A brownish purple iron(II) complex of indefinite composition was also isolated[9] as the anilinium salt (possibly a bis-complex).

In the present work the Cr(III) complex has been obtained by warming an aqueous mixture of potassium thio-oxalate and hexa-(urea)-chromium(III) chloride. The dark greenish brown potassium salt separated on the addition of calcium bromide. Because of the rather rapid hydrolysis of the thio-oxalate ion and slow reaction with simple hydrated chromium salts, poor yields result when these are employed in the synthesis. For the same reason efforts to prepare the tristhio-oxalatoiridates(III) and ruthenates(III) from potassium aquopentachloroiridate(III) and the corresponding ruthenium chloro complex were not successful. The case of replacement of the ammonia groups in hexamminecobalt(III) chloride by the thio-oxalate ion is surprising. All of the thio-oxalato complexes decomposed slowly in the dark and quite rapidly in the light. For satisfactory analytical results the analyses had to be done on very freshly prepared material.

The Fe(III) complex prepared from iron(III) nitrate and isolated as the dark purplish-brown potassium barium salt decomposed especially easily in the light. The rapid photoreduction of the trisoxalato-ferrate(III) ion is well known. The sparingly soluble tris-(ethylenediamine)-cobalt(III) trisdithio-oxalato-ferrate(III) salt was more stable. The moment of the latter substance (2.35 B.M.) showed that the Fe(III) anion was spin-paired.

Resolution of the Co(III), Rh(III) and Cr(III) complexes has been effected through the calcium *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salts, $[Ca(Co\ en_2\ (NO_2)_2][M(C_2O_2S_2)_3]$. The substitution of barium ion or magnesium ion for calcium ion allowed only a poor separation of the diastereoisomers because of unsuitable solubilities. Partial resolution could be effected by the use of active tris-(ethylenediamine)-cobalt(III) ion but the low solubility of both diastereoisomers is a disadvantage. Efforts to resolve the iron(III) complex were fruitless. This is due to its low stability with respect to reduction, and thence complete decomposition.

Unlike its trisoxalato analog the cobalt complex did not racemize appreciably in solution at 90° in 10 min. nor in the solid state over some weeks in the dark. The chromium compound lost its activity in ten hours in solution or in the solid state. Tristhio-oxalatorhodate(III) like the trisoxalato compound was optically stable.

Experimental

All rotations were measured at 20° in a 1 dm. tube.

***l*-Potassium Barium Tristhio-oxalatocobaltate(III) 5-Hydrate.**—Potassium thio-oxalate was prepared by the

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(1) The name thio-oxalato is used in *Chemical Abstracts.* A more precise name that defines the positions and number of the S atoms would be *sym*-dithio-oxalato.

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

(4) C. H. Johnson, *Trans. Faraday Soc.*, **31**, 1612 (1935).

(5) D. Beese and C. H. Johnson, *ibid.*, **31**, 1632 (1935).

(6) D. R. Stranks and R. G. Wilkins, *Chem. Revs.*, **57**, 743 (1957).

(7) W. Thomas, *J. Chem. Soc.*, 1140 (1921).

(8) H. O. Jones and H. S. Tasker, *ibid.*, 1904 (1909).

(9) H. O. Jones and H. S. Tasker, *ibid.*, 62 (1912).

method of Jones and Tasker[8] substituting *p*-thiocresol for thiophenol in the reaction with oxalyl chloride. The *dl*-cobalt complex was prepared in good yield by warming a mixture of hexammine-cobalt(III) chloride (2.7 g.) with potassium thio-oxalate (6 g.) in water (20 ml.) on the water-bath at 80° for 0.25 hr. After cooling, the small amounts of hexamminecobalt(III) tristhio-oxalatocobaltate(III) and cobalt(II) sulfide were removed, and calcium bromide (10 g.) added. The dark brown potassium calcium salt that separated was recrystallized from a small volume of hot water. This method of preparation is superior to that described previously[8] which involves aerial oxidation of the Co(II) complex and the formation of much cobalt(II) sulfide.

Anal. Calcd. for $KCa[Co(C_2O_2S_2)_3]\cdot 6H_2O$: C, 11.88; H, 2.00; S, 31.72; Co, 9.72. Found: C, 11.75; H, 3.09; S, 31.15; Co, 9.8.

The potassium calcium salt (1.14 g.) in water (15 ml.) at 40° was treated with *l-cis*-dinitrobis-(ethylenediamine)-cobalt(III) chloride[10] (0.3 g.) in water (15 ml.) at 40°. The diastereoisomer separated on cooling. Because of very low solubility of the diastereoisomer the active form of the complex cannot be obtained conveniently.

Anal. Calcd. for *l*-$[Co\ en_2(NO_2)_2]\cdot Ca\cdot$*d*-$[Co\ (C_2O_2S_2)_3]\cdot H_2O$: C, 16.04; H, 2.42; S, 25.70. Found: C, 16.12; H, 2.97; S, 25.5.

The filtrate from the above treated with barium bromide (2 g.) gave the dark brown crystalline *l*-potassium barium salt. Recrystallization was effected from warm water. A 0.02% aqueous solution gave $[\alpha]_{5893}\ -750^\circ$, $[\alpha]_{5780}\ -500^\circ$, $[\alpha]_{5461}\ +500^\circ$.

Anal. Calcd. for $KBa[Co(C_2O_2S_2)_3]\cdot 5H_2O$: C, 10.51; H, 1.47; S, 28.05. Found: C, 10.5; H, 1.5; S, 27.8.

***d*-Potassium Barium Tristhio-oxalatocobaltate(III) 5-Hydrate.**—This was obtained in the same manner as the *levo* isomer by using *d*-$[Co\ en_2(NO_2)_2]Cl$. A 0.02% solution gave $[\alpha]_{5893}\ +700^\circ$, $[\alpha]_{5780}\ +450^\circ$, $[\alpha]_{5461}\ -500^\circ$.

Anal. Found: C, 10.6; H, 1.6; S, 28.0.

***d*-Potassium Barium Tristhio-oxalatorhodate(III) 6-Hydrate.**—The large amounts of sulfur obtained in the previous method of preparation of the rhodium(III) complex[9] could be avoided by heating to 80° a mixture of rhodium chloride 1-hydrate (2.2 g., 1 mole) and potassium thio-oxalate (5.9 g., 2.9 moles in water (15 ml.) until the color became orange-yellow (0.25 hr.). On the addition of calcium bromide (8 g.) and cooling, yellow crystals of the potassium calcium salt separated. The salt was recrystallized from a small amount of hot water.

Anal. Calcd. for $KCa[Rh(C_2O_2S_2)_3]\cdot 4H_2O$: C, 11.72; H, 1.31; S, 31.32; Rh, 16.7. Found: C, 12.0; H, 1.8; S, 31.4; Rh, 16.74.

Resolution was effected in the same way as the cobalt complex above using the potassium calcium salt (1.22 g.) and *l*-$[Co\ en_2(NO_2)_2]Cl$ (0.2 g.).

Anal. Calcd. for *l*-$[Co\ en_2\ (NO_2)_2]Ca\cdot$*l*-$[Rh(C_2O_2S_2)_3]\cdot H_2O$: C, 15.16; H, 2.29; S, 24.28. Found: C, 15.35; H, 2.5; S, 24.36.

The filtrate remaining after the separation of the diastereoisomer was treated with barium bromide (2 g.) and the resulting yellow *d*-potassium barium salt recrystallized from a little hot water. A 0.1% aqueous solution gave $[\alpha]_{5893}\ +420^\circ$, $[\alpha]_{5780}\ +480^\circ$, $[\alpha]_{5461}\ +530^\circ$.

Anal. Calcd. for $KBa[Rh(C_2O_2S_2)_3]\cdot 6H_2O$: C, 9.64; H, 1.62; S, 25.72. Found: C, 9.62; H, 1.32; S, 25.55.

***l*-Potassium Barium Tristhio-oxalatorhodate(III) 6-Hydrate.**—The resolution was carried out as before using *d*-$[Co\ en_2(NO_2)_2]Cl$. A 0.1% aqueous solution gave $[\alpha]_{5893}\ -420^\circ$, $[\alpha]_{5780}\ -490^\circ$ $[\alpha]_{5461}\ -520^\circ$.

Anal. Found: C, 9.45; H, 1.6; S, 25.7.

***dl*-Potassium Calcium Tristhio-oxalatochromate(III) 6-Hydrate.**—Potassium thio-oxalate (6 g.) was added to a solution of hexa(urea)-chromium(III) chloride 3-hydrate (5.7 g.) in water (30 ml.) and the mixture heated at 80° until the successive precipitates of hexa(urea)-chromium(III) thio-oxalate and hexa(urea)-chromium(III) tristhio-oxalatochromate(III) had dissolved (0.3 hr.). After filtration, calcium bromide (10 g.) was added and the dark green potassium calcium salt separated on cooling. It was recrystallized from a small volume of hot water.

Anal. Calcd. for $KCa[Cr(C_2O_2S_2)_3]\cdot 6H_2O$: C, 12.01; H, 2.02; S, 32.08; Cr, 8.67. Found: C, 12.11; H, 2.67; S, 31.6; Cr, 8.8.

***l*-Tris-*trans*-dinitrobis-(ethylenediamine)-cobalt(III) Tristhiooxalatochromate(III) 2-Hydrate.**—Because of the rapid racemization of the complex chromium(III) anion and the higher solubility of the potassium barium salt, recourse was had to the sparingly soluble salt of the *trans*-$[Co\ en_2(NO_2)_2]^+$ cation for the isolation of the active forms. The *dl*-potassium calcium salt (1.2 g.) in water (25 ml.) at 10° when treated with *l*-$[Co\ en_2(NO_2)_2]Cl$ (0.3 g.) in water, (15 ml.), at 20° and then cooled in ice gave green crystals of the diastereoisomer.

Anal. Calcd. for *l*-$[Co\ en_2(NO_2)_2]Ca\cdot$*d*-$[Cr(C_2O_2S_2)_3]\cdot H_2O$: C, 16.19; H, 2.44; S, 25.94. Found: C, 16.25; H, 2.77; S, 25.24.

The ice cold filtrate from above on the addition of *trans*-$[Co\ en_2(NO_2)_2]Cl$ (2.0 g.) gave green plates of the *levo* form. A 0.025% aqueous solution gave $[\alpha]_{5893}\ -360^\circ$, $[\alpha]_{5780}\ -120^\circ$, $[\alpha]_{5461}\ +560^\circ$. All activity in the solid and the solution disappeared in ten hours.

Anal. Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]_3[Cr(C_2O_2S_2)_3]\cdot 2H_2O$: C, 17.13; H, 4.15; S, 15.24. Found: C, 17.14; H, 4.24; S, 15.28.

***d*-Tris-*trans*-dinitrobis-(ethylenediamine)-cobalt (III) Tristhio-oxalatochromate(III) 2-Hydrate.**—This was prepared in the same manner as the *l*-isomer by the use of *d*-$[Co\ en_2(NO_2)_2]Cl$. A 0.025% aqueous solution gave $[\alpha]_{5893}\ +400^\circ$, $[\alpha]_{5780}\ +200^\circ$, $[\alpha]_{5461}\ -600^\circ$.

Anal. Found: C, 17.39; H, 4.52; S, 15.38.

Potassium Barium Tristhio-oxalatoferrate(III) 4-Hydrate.—Iron(III) nitrate 10-hydrate (4.2 g.) in cold water (50 ml.) was treated with solid potassium thio-oxalate (6 g.), shaken to effect dissolution, and immediately filtered to remove iron(II) sulfide and sulfur. Barium bromide (5 g.) added to the dark purplish brown solution caused deposition of the dark potassium barium salt. The salt was recrystallized from a small volume of water at 60°. The magnetic moment, $\mu = 2.95$ B.M. (Gouy method) is a little high for one unpaired electron, but this is consistent with the presence of Fe(II) impurity as a result of some decomposition. The potassium calcium salt prepared in a similar manner, using calcium bromide, could not be obtained pure. Resolution experiments performed on the latter substance with active *cis*-dinitrobis-(ethylenediamine)-cobalt(III) chloride gave the usual diastereoisomer from ice cold solutions but no indication of activity in the mother liquor. The tris-(ethylenediamine)-cobalt(III) salt had a magnetic moment of 2.35 B.M.

Anal. Calcd. for $KBa[Fe(C_2O_2S_2)_3]\cdot 4H_2O$: C, 10.84; H, 1.21; S, 28.94. Found: C, 11.04; H, 1.52; S, 28.24. Calcd. for *l*-$[Co(C_2H_8N_2)_2(NO_2)_2]Ca[Fe(C_2O_2S_2)_3]\cdot 2H_2O$: C, 15.73; H, 2.64; S, 25.20. Found: C, 15.62; H, 2.66; S, 25.35. Calcd. for $[Co(C_2H_8N_2)_3][Fe(C_2O_2S_2)_3]\cdot 3H_2O$: C, 20.31; H, 4.25. Found: C, 20.41; H, 4.38.

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