(mercaptoethylimine)nickel(II) (1.85 and 1.86 A).[19] Undoubtedly, the nickel–nitrogen bonds in these compounds have double-bond character.

The accuracy of this structure determination was not sufficiently high to detect any structural changes in the pyridine molecule that could be attributed to coordination with the nickel atom.

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The computer programs used in this work were kindly provided by R. Shiono of the University of Pittsburgh. The refinement was carried out by a three-dimensional differential Fourier synthesis program written for the IBM 7070 computer (Technical Report No. 42. to the U. S. Public Health Service by R. Shiono). This program was adapted for use with the IBM 7072 computer at the University of Arizona.

(19) Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, **4**, 1726 (1965).

Electronic and Circular Dichroism Spectra of Polynuclear 2-Aminoethanethiol Complexes[1]

By GEORGE R. BRUBAKER and BODIE E. DOUGLAS

The cations hexakis(2-aminoethanethiolo)tricobalt(III) and hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II) have been prepared in *meso* and optically active forms. The electronic and circular dichroism (CD) spectra are reported for the optical isomers. Only the terminal cobalt(III) ions contribute to the visible CD spectrum of the heterometallic complex ion. This spectrum was subtracted from that for the tricobalt(III) complex to obtain the CD spectrum of the central cobalt. Opposite configurations about the central and terminal cobalt ions are assigned from the CD spectra.

Werner's verification of his octahedral stereochemical model for coordination compounds by resolving the completely inorganic complex $[Co((OH)_2(NH_3)_4Co)_3]^{6+}$ climaxed the preparation and resolution of numerous cobalt(III) complexes including several novel binuclear $[(en)_2Co\langle{}^X_Y\rangle Co(en)_2]^{n+}$ species. These binuclear complexes may be considered as combinations of two discrete monomeric compounds. If each of the latter is optically active, the binuclear product will exist in optically active and *meso* isomers.

Mathieu[2] examined Werner's $[(en)_2Co\langle{}^X_Y\rangle Co(en)_2]^{n+}$ binuclear complexes, concluding that the absolute configurations of the polynuclear complexes were inaccessible from either the ORD or CD measurements. Recently, Garbett and Gillard[3] have reexamined the optical properties of some of these compounds and their monomeric derivatives. By comparing the binuclear compound $[(en)_2(NH_3)Co(NH_2)-Co(NH_3)(en)_2]^{5+}$ with the products of its reaction with HCl, $[Co(en)_2NH_3Cl]^{2+}$ and $[Co(en)_2(NH_3)_2]^{3+}$, these authors established that the L configuration of the binuclear complex corresponds to the combination of two monomeric units of L configuration.

There has been little work reported on the optical properties of new polynuclear complexes since Werner's

classic work of 1915. Indeed, even the completely inorganic complex prepared by Werner is, by that author's account, too unstable to lend itself easily to more detailed study. We are reporting the results of an examination of the electronic spectra, circular dichroism, and optical rotatory dispersion of hexakis-(2-aminoethanethiolo)tricobalt(III) bromide (Figure 1), the synthesis of which was first reported by Busch and Jicha.[4]

Experimental Section

Commercially available salts and solvents of CP grade or better were used without further purification.

Preparation of Hexakis(2-aminoethanethiolo)tricobalt(III) Bromide, $[Co(Co(H_2NCH_2CH_2S)_3)_2]Br_3$.—The procedures given by Busch and Jicha[4] were employed, giving identical products by either route. *Anal.* Calcd for $[Co_3(H_2NCH_2CH_2S)_6]Br_3$: C, 16.50; H, 4.58; N, 10.60; Br, 27.45. Found: C, 16.37; H, 4.40; N, 9.77; Br, 27.20.

Resolution of the Hexakis(2-aminoethanethiolo)tricobalt(III) Cation, $[Co_3(H_2NCH_2CH_2S)_6]^{3+}$.—Three grams of silver antimony *d*-tartrate (0.0075 mole) suspended in 100 ml of water was added to a solution of 8.4 g (0.01 mole) of hexakis(2-aminoethanethiolo)tricobalt(III) bromide in 500 ml of water at 65°. The solution was heated with stirring for 0.5 hr and then filtered to remove the silver bromide. The filtrate was concentrated to about 300 ml, whereupon the mixed *meso*- and (−)-hexakis(2-aminoethanethiolo)tricobalt(III) antimonyl tartrates (the sign of the major CD peak in the low-energy absorption band is given) began to crystallize from the solution. Methanol (500 ml) was added and the mixture allowed to stand for several hours. The antimonyl tartrates were filtered and an excess of potassium iodide (10 g) was added to the filtrate to precipitate *meso*- and

(1) This work was supported by a research grant (GM-10829-08) from the Division of General Medical Studies, Public Health Service.

(2) J. P. Mathieu, *Bull. Soc. Chim. France*, **5**, 105 (1938).

(3) K. Garbett and R. D. Gillard, *Chem. Commun.*, 99 (1966).

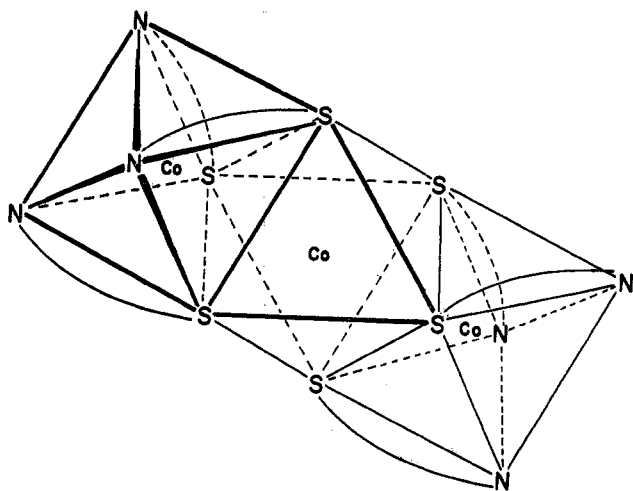(4) D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962).

Figure 1.—The structure of the $Co_3L_6^{3+}$ cation (L = 2-amino-ethanethiol).

(+)-hexakis(2-aminoethanethiolo)tricobalt(III) iodide. The iodide salts thus formed were collected on a filter and the (+) isomer was extracted from the less soluble *meso* form with 300 ml of hot methanol. Solid (+)-hexakis(2-aminoethanethiolo)tricobalt-(III) iodide was recovered from the methanol solution by evaporating the solution nearly to dryness. The circular dichroism of the product remained constant (23.7 at 545 mμ) through several recrystallizations. The resolution was reproduced without difficulty, and on several different scales. The antimonyl tartrates of the (−) and *meso* isomers were converted to the iodide salts with an excess (10 g) of potassium iodide. The (−) isomer was extracted from the *meso* form with 300 ml of methanol and crystallized by evaporating the methanolic solution nearly to dryness. The circular dichroism of this isomer remained constant (−23.8 at 545 mμ) through several recrystallizations. The hexakis(2-aminoethanethiolo)tricobalt(III) cation has also been completely resolved in this laboratory using ion-exchange chromatography.[5]

Preparation of Hexakis(2-aminoethanethiolo)dicobalt(III)-zinc(II)tetrakis(2-aminoethanethiolo)trizinc(II) Perchlorate, [Zn-$Co_2(H_2NCH_2CH_2S)_6$][$Zn_3(H_2NCH_2S)_4$](ClO_4)$_4$.—Five grams of anhydrous zinc chloride was added to a suspension of 2.9 g (0.01 mole) of tris(2-aminoethanethiolo)cobalt(III) in 150 ml of water containing 10 g of sodium perchlorate. The solution was stirred at room temperature for 1 hr. Crystalline hexakis(2-amino-ethanethiolo)dicobalt(III)zinc(II)tetrakis(2-aminoethanethiolo)-trizinc(II) perchlorate was filtered from the solution containing excess sodium perchlorate and the more soluble hexakis(2-amino-ethanethiolo)tricobalt(III) salt. Purification was accomplished by reprecipitation of the crude product from a solution of 15 g of sodium perchlorate in 200 ml of water. *Anal.* Calcd for Zn_4-$Co_2(H_2NCH_2CH_2S)_{10}(ClO_4)_4$: C, 15.70; H, 3.95; Cl, 10.85. Found: C, 15.42, 15.48; H, 4.54, 4.31; Cl, 10.37, 9.68.

Resolution of Hexakis(2-aminoethanethiolo)dicobalt(III)zinc-(II)tetrakis(2-aminoethanethiolo)trizinc(II) Perchlorate, [Zn-$Co_2(H_2NCH_2CH_2S)_6$][$Zn_3(H_2NCH_2CH_2S)_4$](ClO_4)$_4$. — Hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II)tetrakis(2-aminoethane-thiolo)trizinc(II) perchlorate (0.84 g, 10^{-3} mole) was dissolved in 150 ml of water to which 0.67 g (2 × 10^{-3} mole) of potassium antimonyl *d*-tartrate dissolved in 20 ml of water was added. The solution was concentrated to about 150 ml under a stream of dry air. The (+) and some of the *meso* isomer separated as antimonyl tartrates and were removed from the solution by filtration. An excess of sodium perchlorate was added to the filtrate to precipitate the (−) isomer and the remaining *meso* form from solution. This precipitate was collected on a filter and the (−) isomer was extracted from the less soluble *meso* isomer with technical (about 8% water) acetone. The acetone

(5) G. R. Brubaker, J. I. Legg, and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 3446 (1966).

solution thus obtained was added to a solution of 10 g of sodium perchlorate in 25 ml of water, and the acetone was evaporated under a stream of dry air to precipitate the (−) isomer (Δε −23.8 at 577 mμ). The resolution is easily reproduced on any scale; repeated recrystallizations do not affect the magnitude of the CD. The antimonyl tartrate salts of the (+) and *meso* isomers were converted to the perchlorates by treating a suspension of the antimonyl tartrates in 50 ml of water with 5 g of sodium perchlorate. This solution initially contains none of the tetrakis(2-aminoethanethiolo)trizinc(II) cation which is found in the product. Its formation accompanies the decomposition of hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II) in neutral aqueous solutions to give some hexakis(2-aminoethanethiolo)-tricobalt(III). The crystallization of the perchlorates from this solution is slow and is always accompanied by the formation of some of the tricobalt complex. The (+) isomer was extracted from the *meso* isomer as described above for the (−) isomer. The intensity of the CD band at 577 mμ remained constant at 23.8 through two recrystallizations.

Physical Measurements. Absorption spectra were obtained using a Cary Model 14 recording spectrophotometer. Solution measurements were obtained for about 10^{-4} M solutions in matched 10-mm cells. Diffuse transmission spectra were obtained using solid samples suspended in mineral oil which was spotted on filter paper.

Circular dichroism spectra were obtained using a Roussel-Jouan Dichrograph in the region from 650–300 mμ and a Jasco ORD-UV 5 recording spectropolarimeter equipped with a circular dichroism attachment in the region 300–250 mμ.

Optical rotatory dispersion curves were obtained using a Jasco ORD-UV 5 recording spectropolarimeter.

Molecular weights were determined with a Mechrolab Model 301A vapor pressure osmometer calibrated with sodium tetraphenylborate for acetone solutions at 37°.

Results and Discussion

The resolutions of the hexakis(2-aminoethanethiolo)-tricobalt(III) and hexakis(2-aminoethanethiolo)dico-balt(III)zinc(II) cations are among the few original resolutions of polynuclear complexes since Werner's classic work of 1915. Each of these entities contains six asymmetric sulfur atoms. The hexakis(2-amino-ethanethiolo)dicobalt(III)zinc(II) cation is a unique heterometallic complex containing both dissymmetric cobalt and dissymmetric zinc ions. The metal ions occupy sites of different symmetries, terminal (C_3) and bridged (D_{3d} or D_3, in the *meso* and optically active isomers, respectively). Through the device of substituting a zinc ion for one of the chromophores in the tricobalt complex, it has been possible to assign circular dichroism maxima to transitions appropriate to each site in these polynuclear complexes.

Hexakis(2-aminoethanethiolo)tricobalt(III) bromide was prepared by the method of Busch and Jicha.[4] The molecular weight of the tetraphenylborate salt was determined in acetone (calcd 1591, found 1570) to supplement the data obtained by those authors to confirm the trinuclear formulation.

Through an extension of the preparative route devised for the tricobalt complex, the heterometallic compound hexakis(2-aminoethanethiolo)dicobalt(III)zinc-(II)tetrakis(2-aminoethanethiolo)trizinc(II) perchlorate was prepared.

Both of these compounds were resolved by precipitation of a diastereoisomer formed with the antimonyl tartrate anion. This resolving agent does not, how-

ever, discriminate against the *meso* isomer which must be removed from each enantiomer by fractional recrystallization.

Hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II) slowly decomposes in neutral aqueous solutions at room temperature to produce the stable [hexakis(2-aminoethanethiolo)tricobalt(III)]³⁺ complex ion. It is relatively stable in acid solutions and rapidly and completely decomposed to tris(2-aminoethanethiolo)cobalt(III) in aqueous base. The product isolated as the perchlorate salt contains the tetrakis(2-aminoethanethiolo)trizinc(II) cation, the existence of which has been verified by Busch and Root.[6] The observation that [hexakis(2-aminoethanethiolo)tricobalt(III)]³⁺ is also formed in the reaction of tris(2-aminoethanethiolo)cobalt(III) with excess zinc(II) suggests the following route to the stable products

$$18CoL_3 + 4Zn^{2+} \longrightarrow 3(ZnCo_2L_6Zn_3L_4)^{4+} + Co_3L_6$$
$$(L = \text{2-aminoethanethiol})$$
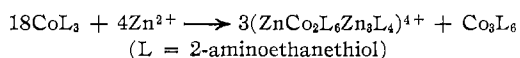
We believe that the uniform stoichiometry observed is a consequence of the crystal parameters, which may also contribute to the marked differences in the solubility of the *meso* and optically active isomers.

Our observations have shown the *meso* isomer to dominate the reaction yields, comprising about 80% of the product. A statistical distribution of racemic tris(2-aminoethanethiolo)cobalt(III) among the isomers of [hexakis(2-aminoethanethiolo)tricobalt(III)]³⁺, for example, would require the formation of only 50% of the *meso* isomer. An examination of molecular models revealed that the interaction between nonbonded protons across the bridged metal ion is significantly greater in the racemic than in the *meso* complex. Though our models do not show the difference, one might also expect the threefold axis to be somewhat longer in the former than in the latter, an effect which may account for the differences in the solubilities of the active and *meso* isomers.

Electronic spectra, circular dichroism spectra, and optical rotatory dispersion curves were obtained for each compound (Figures 2 and 3, Table I). Subtraction of the curves obtained for the heterometallic complex from those obtained for the tricobalt complex gave hypothetical spectra such as might be expected for the bridged cobalt(III) ion in, for example, the hypothetical heterometallic complex hexakis(2-aminoethanethiolo)dizinc(II)cobalt(III) (Figure 4). The assumption that substitution of a zinc(II) ion for the cobalt(III) ion in the bridging site will not greatly alter the electronic structure of the complex is justified by the appearance of intense bands above 28,000 cm⁻¹ in the CD spectra of each of these compounds at virtually the same energies, indicating that the ligands do not readily distinguish between the bridging ions. Hidaka,[7] in his discussion of some dithiooxalic acid complexes, has ascribed transitions in this region to charge-transfer phenomena.

The region of absorption due to d–d transitions may

(6) D. H. Busch and C. A. Root, private communication.
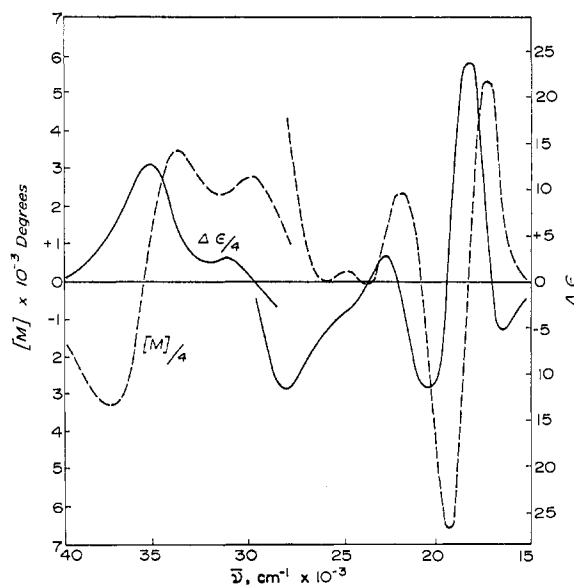(7) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1724 (1964).

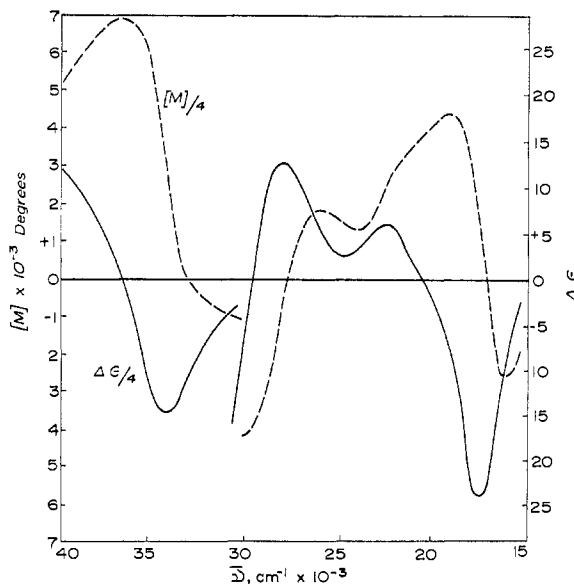Figure 2.—The CD (———) and ORD (– – – –) curves for (+)-hexakis(2-aminoethanethiolo)tricobalt(III) bromide.

Figure 3.—The CD (———) and ORD (– – – –) curves for (−)-hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II)tetrakis-(2-aminoethanethiolo)trizinc(II) perchlorate.

be identified as the region of the first two bands for each of the curves in Figure 5. These bands are best resolved for the dicobalt–zinc complex where the transitions are interpreted as $^1A_1$–$^1T_1$ at 17,690 cm⁻¹ and $^1A_1$–$^1T_2$ at 23,650 cm⁻¹ for the terminal [CoS₃N₃] groups. Assuming that the ligand transitions are essentially constant throughout the series, these cancel when the spectrum of the hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II) ion is subtracted from that of the hexakis(2-aminoethanethiolo)tricobalt(III) ion. The bands in the visible region are poorly resolved in the absorption spectrum of the tricobalt complex and there is serious overlap with the much more intense ultraviolet band at 30,960 cm⁻¹. For each of the three curves the band in the 22,000–23,000 cm⁻¹ region appears as a shoulder of the more intense ultra-

TABLE I

ABSORPTION SPECTRA AND CIRCULAR DICHROISM DATA FOR
2-AMINOMETHANETHIOL COBALT(III) COMPLEXES

Compound[a]	Absorption spectra $\bar{\nu}$, cm^{-1} × 10^{-3}	ϵ	Circular dichroism $\bar{\nu}$, cm^{-1} × 10^{-3}	$\Delta\epsilon$
CoL$_3$ (solid)	17.24			
	21.98			
	28.17			
(+)-Co$_3$L$_6$Br$_3$	18.31	2,140	16.50	−6.0
			18.35	23.7
	22.84	5,620	19.99	−11.6
			22.68	3.0
			(25.0)	−3
	28.82	18,190	28.39	−13.5
			31.00	8.0
	36.36	25,560	35.14	52.4
(−)-(ZnCo$_2$L$_6$Zn$_3$L$_4$)(ClO$_4$)$_4$	17.69	978	17.60	−23.8
	23.65	1,520	22.70	5.8
			28.10	12.6
	30.96	13,100	31.00	−16.4
	38.08	47,150	34.30	−59.2
Co(III) bridge	20.00	1,920	18.10	43.0
			20.50	−12.3
	22.85	2,480	(24.0)	−4.8
	28.40	7,200	28.10	−24.0
			(31.0)	25.6
			34.70	98.4

[a] L = 2-aminoethanethiol.
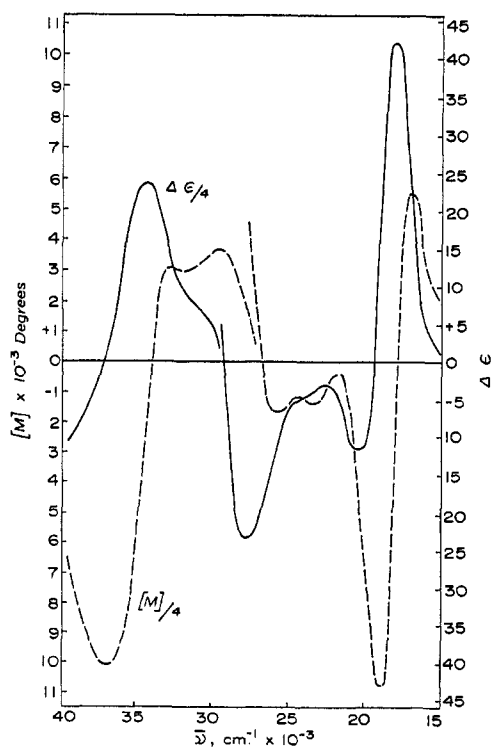
Figure 4.—The CD (———) and ORD (‑ ‑ ‑ ‑) curves for thio bridged cobalt(III).

Figure 5.—Electronic absorption spectra for hexakis(2-amino-ethanethiolo)tricobalt(III) bromide (———), hexakis(2-amino-ethanethiolo)dicobalt(III)zinc(II)tetrakis(2-aminoethanethiolo)-trizinc(II) perchlorate (‑ ‑ ‑ ‑), and thio-bridged cobalt(III) (· · · ·).

violet band so that the peak position cannot be located accurately. The steadily increasing absorption toward the ultraviolet region for the tricobalt complex causes the difference curve to be of little value. The CD spectra are much sharper giving a well-defined difference curve (Figure 4). The close correspondence between the signs and positions of the Cotton effects in the ORD
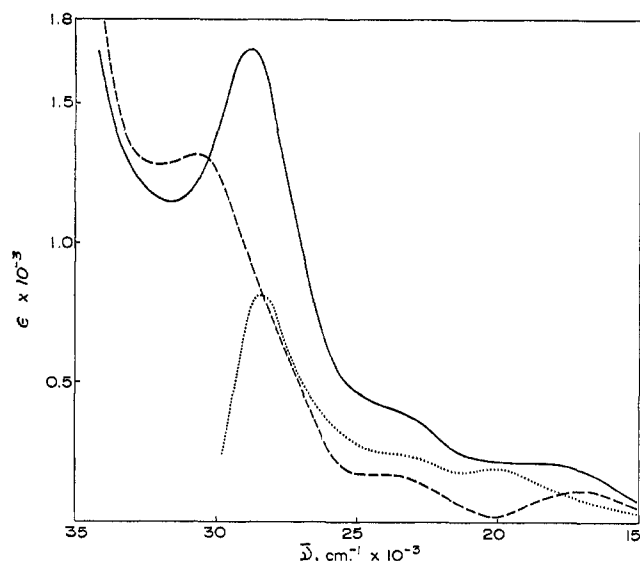
and CD difference spectra adds confidence in this approach.

The CD bands occurring at 17,600 cm^{-1} for the terminal cobalt ions in the heterometallic complex (Figure 3) and at 18,100 cm^{-1} for the bridging cobalt ion (difference spectrum, Figure 4) may be ascribed to the $^1A_1$–^1E_a transition in D$_3$ symmetry. This choice is dictated by the relative intensities of the two CD bands in the region of the first absorption band.[7,8] The CD band at 20,500 cm^{-1} ($\Delta\epsilon$ −12.3) for the bridging cobalt ion is assigned to $^1A_1$–$^1A_2$ (this transition is not resolved in the broad band occurring in the CD spectrum of the heterometallic complex, Figure 3). This assignment in the first band region reverses the trigonal splitting (E$_a$ is at higher energy here than A$_2$) reported[7,9] for [Co-(S$_2$C$_2$O$_2$)$_3$]$^{3-}$. However, the trigonal field requirements of the ligand are probably closer to that of ethylenediamine (where this same order is observed) than to that of S$_2$C$_2$O$_2$$^{2-}$. The band at 22,700 cm^{-1} ($\Delta\epsilon$ 5.8) for the terminal [CoS$_3$N$_3$] (Figure 3) and the shoulder (Figure 4) at about 24,000 cm^{-1} ($\Delta\epsilon$ −4.8) for the bridging [CoS$_6$] are assigned to $^1A_1$–^1E_b. Inflections in the ORD curves for these complexes have proved to be of considerable help in determining the energies, signs, and, indeed, the existence of some of the CD bands appearing as shoulders, as, for example, this 24,000 cm^{-1} band for the bridging cobalt ion. The CD bands occurring in the spectrum of each cobalt ion at about 28,000, 31,-000, and 35,000 cm^{-1} have been assigned to charge-transfer transitions. The spectrum of the tricobalt species may be interpreted as a composite of the spectra of the terminal and bridging cobalt ions.

From the energies of the visible absorption bands for the heterometallic complex one calculates the value

(8) T. Bürer, *Helv. Chim. Acta*, **46**, 2388 (1963).
(9) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

of the Racah parameter B to be 370 cm^{-1} (the band separation is 16B). This is very small compared to the values for typical complexes (505 cm^{-1} for [Co(en)$_3$]$^{3+}$) and is about 35% of that for the free ion, indicating that the interelectron repulsion of the d electrons is much reduced, presumably by covalency. Carlin and Canziani[10] calculated a value of 406 cm^{-1} for B for [Cr(S$_2$C$_2$O$_2$)$_3$]$^{3-}$ or about 45% of that for the free ion. Their spectral data indicate an even smaller value of B for [Co(S$_2$C$_2$O$_2$)$_3$]$^{3-}$ than that reported here.

The difference curve from the absorption spectra of the tricobalt and zinc bridged complexes is not considered to be sufficiently accurate as a facsimile spectrum of the bridging [CoS$_6$] group for the calculation of a B value. An approximate value of B calculated assuming a separation of 16B between the E$_a$ and E$_b$ peaks for [CoS$_6$] (difference spectrum, Figure 4) is also 370 cm^{-1}. This is only an estimate since some difference in the trigonal splitting for the two bands is expected and E$_b$ is located only as a shoulder. One would expect a smaller value of B for [CoS$_6$] than for [CoS$_3$N$_3$], but not as small as one would obtain from the difference absorption spectrum.

The most surprising feature of the spectra is that the ligand field bands for bridging [CoS$_6$] are at higher energy than those of terminal [CoS$_3$N$_3$]. This is the case for the absorption or the CD spectra. No explanation is offered although one notes that the ligands at the top of the spectrochemical series are strongly π bonding and unusual π-bonding interactions are expected in these trinuclear complexes.

At present, there is no evidence for direct metal–metal interactions. The charge-transfer CD peaks are remarkably constant for the charge-transfer region for all of the spectra. In Mathieu's study[2] of the CD and absorption spectra of some of Werner's binuclear oxygen and nitrogen bridged cobalt(III), complexes, he obtained data which may be interpreted solely on the basis of increasing ligand field strength of the bridging ligands. In the present case the π-bonding ability of the sulfur donors does not seem to contribute materially to metal–metal interactions.

The CD values reported here are among the highest observed in the visible region. Hidaka[7] has attributed the high intensities of the electronic and CD spectra of some dithiooxalic acid complexes to π bonding.

Absolute Configurations.—In the crystal field model, the optical activity of the bridged metal ion may be

(10) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).

ascribed to the octahedral array of six equivalent asymmetric sulfur atoms which surround it. A model in which the bridged ion is considered the central atom of a bis-tridentate complex will better accommodate the trigonal splitting observed in the CD spectra. The optically active terminal cobalt ions constrain one of the two available σ orbitals of each sulfur atom. The ethylene rings assure that this is the same orbital for each sulfur atom, and that the remaining σ orbital has the opposite configuration. These effects are, of course, cancelled when two tris(2-aminoethanethiolo)-cobalt(III) entities of opposite configuration combine with a bridging ion to form the *meso* isomer. In Figure 6, this effect is illustrated for a single chelate ring.
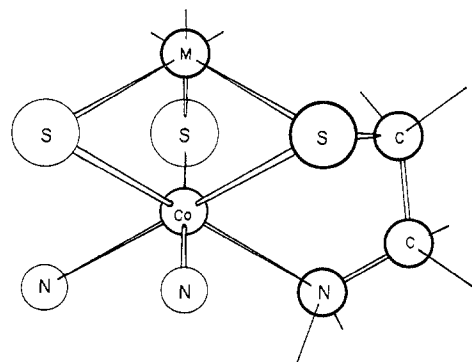

Figure 6.—The conformation of chelate rings about a terminal cobalt ion.

The fact that the configuration of the bridged ion is determined by that of the terminal complexes has been demonstrated by quantitatively degrading the heterometallic complex to tris(2-aminoethanethiolo)cobalt(III) with aqueous ammonia, followed by the regeneration of the optically active heterometallic complex with zinc chloride and the optically active tricobalt complex with hexaamminecobalt(III) chloride. It is gratifying to note that the heterometallic complex was regenerated with more than 97% retention of configuration.

Absolute configurations have been assigned by comparison of the sign of the CD bands assigned to ^{1}A$_1$–^{1}E$_a$ with that of the [Co(en)$_3$]$^{3+}$ ion. On this basis, the configuration of the terminal tris(2-aminoethanethiolo)cobalt(III) entities may be designated Λ (C$_2$) or Δ (C$_3$), and that of the bridged cobalt ion Δ (C$_2$) or Λ (C$_3$). The assignments of opposite configurations are further supported by the enantiomeric relationship between the charge-transfer bands attributed to each site.