599. *Sulphitobis(ethylenediamine)cobalt(*III*) Complexes.*

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The following complexes have been prepared: *cis*-[Co en$_2$(SO$_3$)$_2$]Na; *trans*-[Co en$_2$(SO$_3$)$_2$]Na; [Co en$_2$SO$_3$,Cl]^0; [Co en$_2$SO$_3$,OH]^0; [Co en$_2$SO$_3$,NH$_3$]Cl; [Co en$_2$SO$_3$,OH$_2$]ClO$_4$; in these the sulphito-group is unidentate; complexes [Co en$_2$SO$_3$]X, where X = ClO$_4$, NO$_2$, I, or SCN, have also been prepared where the sulphito-group probably occupies two co-ordinate positions. Infrared and visible absorption spectra of the compounds have been measured.

Disulphito-complexes.—Although Riesenfeld [1] in 1923 and Klement [2] in 1926 had obtained compounds [Co en$_2$(SO$_3$)$_2$]Na, the configurations of these had not been determined. Two isomeric forms of the sodium disulphitobis(ethylenediamine)cobaltate(III) salt have been obtained in the present work, and the configurations have been assigned on the basis of visible and infrared spectral data.

The *cis*-isomer was obtained by reaction of an excess of sodium sulphite with *cis*- or *trans*-[Co en$_2$Cl$_2$]Cl. The infrared absorption spectrum of this compound showed two peaks in the CH$_2$ rocking region [3] and a band structure generally more complex than that of its isomer.

The *trans*-isomer was obtained from *trans*-[Co en$_2$NCS,OH$_2$]Br$_2$ by the action of an excess of sodium sulphite. This compound showed one sharp band in the CH$_2$ rocking region.

The visible absorption spectra supported these assignments.[4] The absorption maximum of the *cis*-isomer was at a lower wavelength and had a larger extinction coefficient ($\varepsilon_{\text{max.}}$ 406 at 431 mμ) than the *trans*-isomer ($\varepsilon_{\text{max.}}$ 313 at 440 mμ).

Monosulphito-complexes containing the Unidentate Sulphito-group.—The reaction of dilute aqueous sodium sulphite in the cold with *cis*- or *trans*-[Co en$_2$Cl$_2$]Cl produced a pink-brown compound of the empirical formula Co en$_2$SO$_3$,Cl,H$_2$O (I). The reactions of this product corresponded to a large extent to those described by Werner [5] for the compound formulated as [Co en$_2$SO$_3$]Cl,H$_2$O. Further examination showed that Werner's structure could not be correct. The general reactions may be correlated if it is assumed that the solid is [Co en$_2$SO$_3$,Cl]^0,H$_2$O which dissolves in water to give a solution of the salt [Co en$_2$SO$_3$,OH$_2$]Cl (II). The evidence may be summarised as follows:

(*a*) The solid (I) was dehydrated at 120°. The infrared spectrum of the anhydrous compound was little different from that of the original.

(*b*) The solid (I) dissolved in water to give a brown conducting solution (0·00169M), which had a molar conductivity of 111·3 ohm^{-1}, indicating that a 1 : 1 electrolyte was present.

(*c*) Chloride ions were precipitated quantitatively from the aqueous solution on the

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[1] Riesenfeld, *Z. anorg. Chem.*, 1923, **132**, 99.

[2] Klement, *Z. anorg. Chem.*, 1926, **150**, 117.

[3] (*a*) Morris and Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 1521; (*b*) Baldwin, *J.*, 1960, 4361.

[4] Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393; Basolo, Ballhausen, and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810.

[5] Werner, *Annalen*, 1912, **386**, 83.

addition of silver nitrate, without change in the visible absorption spectrum, *i.e.*, the complex species in solution was unaffected.

(*d*) The aqueous solution contained one equivalent of titratable hydrogen ion, which is consistent with the presence of an acidic aquo-group:

$$[\text{Co en}_2\text{SO}_3,\text{OH}_2]^+ + \text{OH}^- = [\text{Co en}_2\text{SO}_3,\text{OH}]^0 + \text{H}_2\text{O}$$

The hydroxosulphitobis(ethylenediamine)cobalt(III) compound has been isolated and is a non-electrolyte.

(*e*) The existence of the aquosulphitobis(ethylenediamine)cobalt(III) cation was confirmed by isolation of a yellow-brown, crystalline perchlorate that could not be dehydrated without change in character (solubility and colour; cf. p. 3127). The visible absorption spectrum of the perchlorate, $[\text{CO en}_2\text{SO}_3,\text{OH}_2]\text{ClO}_4$, was identical with that of the original compound (I) in solution.

(*f*) Concentrated hydrochloric acid converted the perchlorate into a pink solid whose infrared spectrum and analysis were identical with those of the original compound.

Addition of sodium thiocyanate to a solution of the chloro-compound (I) produced pale brown needles, $\text{Co en}_2\text{SO}_3,\text{NCS},2\text{H}_2\text{O}$. The infrared spectrum of this solid showed conclusively the presence of co-ordinated thiocyanate,[6] so the compound may be formulated $[\text{Co en}_2\text{SO}_2,\text{NCS}]2\text{H}_2\text{O}$. Its aqueous solution ($8{\cdot}6 \times 10^{-4}$M) had a molar conductivity of 33·5 ohm^{-1}, indicating rapid establishment of the aquation equilibrium:

$$[\text{Co en}_2\text{SO}_3,\text{NCS}]^0 + \text{H}_2\text{O} \rightleftharpoons [\text{Co en}_2\text{SO}_3,\text{OH}_2]^+ + \text{SCN}^-$$

In contrast to the aquation of the chlorosulphito-compound this reaction did not go to completion. The equilibrium was, however, displaced to the right by the addition of silver nitrate: silver thiocyanate was precipitated and the spectrum of the remaining solution was identical with that of $[\text{Co en}_2\text{SO}_3,\text{OH}_2]^+$ but different from that of the aquation equilibrium solution.

The compound $[\text{Co en}_2\text{SO}_3,\text{OH}]^0$, which was prepared by the reaction of hydroxide ion on $[\text{Co en}_2\text{SO}_3,\text{Cl}]^0$, behaved as a non-electrolyte in methanol solution, but an aqueous 0·002M-solution had a molar conductivity of 24 ohm^{-1}.

The salt $[\text{Co en}_2\text{SO}_3,\text{NH}_3]\text{Cl}$ was prepared by the action of dilute ammonia solution on the original compound (I). It behaved as a 1 : 1 electrolyte in water.

The maxima and minima of the visible and ultraviolet absorption spectra of various aqueous solutions are shown in Table 1. Beer's law was not obeyed in the ultraviolet region. It appeared that ion-pairing occurred. In the case of the "non-ionic" compounds the products of aquation might aggregate to form a species of the type $[\text{Co en}_2\text{SO}_3,\text{OH}_2]^+\text{NCS}^-$.

TABLE 1. *Wavelength* (mμ) *and molar extinction coefficients of absorption bands of unidentate sulphito-compounds in the region* 600—200 mμ.

Concn. (mmole l.$^{-1}$)	$\lambda_{\text{max.}}$	log $\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	log $\varepsilon_{\text{min.}}$	Concn. (mmole l.$^{-1}$)	$\lambda_{\text{max.}}$	log $\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$	log $\varepsilon_{\text{min.}}$
	$[\text{Co en}_2\text{SO}_3,\text{NH}_3]\text{Cl}$					$[\text{Co en}_2\text{SO}_3,\text{NCS}]$			
1·420	463	2·210	395	1·505	0·460	452	2·335	391	1·702
0·116	272	4·150	244	3·499	0·112	275	4·219	242	3·587
0·046	272	4·130	244	3·491		$[\text{Co en}_2\text{SO}_3,\text{OH}]$			
					0·715	460	2·380	401	1·764
					0·143	275	3·852	245	3·176

Isomeric forms of the compounds have not been isolated. The infrared spectra indicate that all the monosulphito-compounds have the *cis*-configuration. This evidence is not conclusive, and attempts to resolve the complex ions have not been successful.

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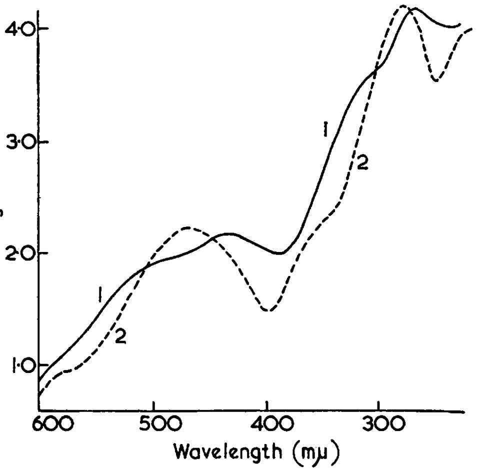
[6] Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412; Baldwin, *J.*, 1961, 471.

Monosulphito-compounds containing the Bidentate Sulphito-group.—A mixture of sodium sulphite and *trans*-[Co en_2Cl_2]Cl in a large excess of water was allowed to evaporate in the dark for about six weeks. Brown-red needles were obtained which had the same empirical formula as the compound (I), *viz.*, Co en_2SO_3,Cl,H_2O. The infrared spectrum of this compound was different from that of any of the complexes discussed above. The compound lost water at 120° without noticeable change in the infrared spectrum. It was soluble in water and behaved therein as a 1 : 1 electrolyte, showed the presence of chloride ions, and was not acidic. Molecular-weight determinations indicated that it was monomeric in aqueous solution.

Addition of sodium perchlorate to an aqueous solution of this compound produced brown-red needles of the composition [Co en_2SO_3]ClO_4, the visible absorption spectrum of which was identical with that of the chloride. Both these compounds must contain a chelated sulphito-group. The molecular-weight determinations on the chloride exclude the possibility of a dimeric cation containing sulphito-bridges.

Addition of aqueous sodium thiocyanate to a solution of the chloride gave brown-red crystals, the infrared spectrum of which showed the presence of thiocyanate ion. An iodide and a nitrite were also obtained. Addition of nitrite to the unidentate sulphito-compounds produced an immediate colour change to bright yellow,[5] owing to the formation of a nitrosulphito-compound [Co en_2SO_3,NO_2]^0 (which has been isolated). However, no colour change followed addition of nitrite to a solution of the compound [Co en_2SO_3]Cl; brown-red crystals were isolated on addition of methanol; these contained the nitrite ion, conductivity measurements indicated a 1 : 1 electrolyte, and there was no change in the conductivity or in the visible absorption of an aqueous solution during 2 days.

Visible absorption spectra of (1) [Co en_2SO_3]ClO_4 *and* (2) [Co en_2SO_3,OH_2]ClO_4.



The unidentate sulphito-compounds showed the yellow colour of the disulphito-anion on the addition of sodium sulphite. No colour change was produced when this reagent was added to a solution of the chloride [Co en_2SO_3]Cl, but the solution became yellow after prolonged boiling.

The visible absorption spectra of [Co en_2SO_3]ClO_4 and [Co en_2SO_3,OH_2]ClO_4 are shown in the figure.

Infrared Absorption Spectra.—The absorption bands due to the sulphito-group were determined by comparison of the spectra of the compounds containing the sulphite group with those of *cis*- and *trans*-[Co en_2Cl_2]Cl. The presence of the sulphito-group increased the intensity of the bands due to the deformation of the NH_2 group of the ethylenediamine. In order to distinguish between these intense NH_2 deformation bands and the bands due to vibration of the SO_3 group, the amine groups were deuterated. The bands assigned to the sulphito-group showed no shift. The bands due to the sulphito-group are shown in Tables 2 and 3.

TABLE 2. *Frequencies* (*cm.*$^{-1}$) *of bands due to the sulphito-group in acidosulphitobis-(ethylenediamine)cobalt*(III) *complexes.*

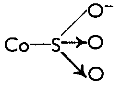
a	b	c	d	e	f
1095s	1068s	1099s	1112s	1117s	1117s
1018w	1020w	1089s	1079s	1075s	1062s
943vs	939vs	980vs	970vs	984vs	972vs
625s	630s	629s	637s	625s	625s

a = *cis*-$[Co\,en_2(SO_3)_2]Na$
b = *trans*-$[Co\,en_2(SO_3)_2]Na$
c = $[Co\,en_2SO_3,NCS]^0$
d = $[Co\,en_2SO_3,NH_3]Cl$
e = $[Co\,en_2SO_3,Cl]^0$
f = $[Co\,en_2SO_3,OH]^0$

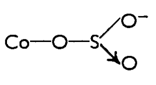
TABLE 3. *Frequencies* (*cm.*$^{-1}$) *of bands due to the sulphito-group in sulphitobis-(ethylenediamine)cobalt*(III) *complexes* $[Co\,en_2SO_3]X$.

X = Cl	1119s	1093s	1036vs	989vs	649m	625s
X = I	1119s	1070s	1042vs	983vs	649m	621m
X = SCN	1117s	1093s	1036vs	988vs	649m	621m

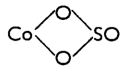
Discussion.—Two formulæ are possible for each of the uni- and bi-dentate sulphito-groups. The pyramidal sulphite ion has the symmetry C_{3v}, which would be effectively unchanged on co-ordination through sulphur (formula a). The number of observed infrared bands agrees with that expected from a group with this type of symmetry [7] and compares well with that found for the co-ordinated sulphato-group.



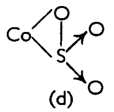
(a)



(b)



(c)



(d)

A cobalt–sulphur bond, which might involve $d\pi$–$d\pi$ bonding,[8] would also explain the marked lability of the unidentate sulphito-complexes. The withdrawal of electrons of the 3*d*-shell of the cobalt would allow attack, either by a water dipole or by an anion.[9] The kinetics of replacement reactions in these complexes is being investigated.

The bidentate sulphito-group may have structure (c) or (d). Structure (d) would involve a three-membered ring which might easily be ruptured. The sulphitobis(ethylenediamine)cobalt(II) compound, however, appears to be stable to water. There is no easy way of converting the bidentate sulphite into the unidentate and *vice versa*, so the bonding of the bidentate and of the unidentate group are probably different in type. It appears likely that the unidentate group is bound to cobalt through sulphur and that the chelate group is bound through two donor oxygen atoms.

EXPERIMENTAL

Visible absorption spectra were measured on a Unicam S.P. 500 spectrophotometer, 10 mm. silica cells being used.

Infrared spectra of solids were measured in Nujol (B.P. grade) mulls between sodium chloride plates, on a Grubb–Parsons G.S.2A double-beam recording spectrometer.

Conductivities were measured with a Philips AC bridge. The cell (constant 1·39) was fitted with bright platinum electrodes.

Chlorosulphitobisethylenediaminecobalt(III) *Monohydrate.*—*trans*-$[Co\,en_2Cl]Cl$ was dissolved in the least volume of water at 30°. The required amount of sodium sulphite, in the least volume of water, was added. On gentle heating, red-brown crystals appeared. The mixture was cooled

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[7] Nakamoto, Fujita, Tanaka, and Koboyashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[8] Craig, Maccol, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**.
[9] Ašperger and Ingold, *J.*, 1956, 2862.

and filtered. The crystalline *monohydrate* was washed with methanol and ether (Found: C, 15·2; H, 5·4; S, 9·6; Cl, 10·7. $C_4H_{18}ClCoN_4O_4S$ requires C, 15·35; H, 5·8; S, 10·0; Cl, 11·0%). Drying at 120° for 2 hr. gave the anhydrous *compound* (Found: C, 15·7; H, 5·1; S, 10·7, 11·1. $C_4H_{16}ClCoN_4O_3S$ requires C, 16·3; H, 5·4; S, 10·85%). Concentrated hydrochloric acid converted the following compounds into the same chlorosulphitobisethylenediamine-cobalt(III) complex: *cis*-[Co $en_2(SO_3)_2$]Na, *trans*-[Co $en_2(SO_3)_2$]Na, [Co en_2SO_3,NH_3]Cl, and [Co en_2SO_3,OH].

Thiocyanatosulphitobisethylenediaminecobalt(III).—(i) The salt[5] *trans*-[Co en_2NCS,OH_2]Br_2 was dissolved in the least volume of water, and sodium sulphite (required amount) was added. The mixture was heated to the b. p. and placed in the dark overnight. Dark brown needles of the *dihydrate* were filtered off and washed with methanol and ether (Found: C, 17·2; H, 5·7; N, 19·3. $C_5H_{20}CoN_5O_5S_2$ requires C, 17·0; H, 5·7; N, 19·8%).

(ii) The chloride,[5] *cis*-[Co en_2NCS,Cl]Cl was dissolved in the least amount of water, and sodium sulphite (required amount) was added. On warming, pale brown needles appeared. The infrared spectrum of this compound was identical with that of the compound prepared as in (i).

(iii) The chlorosulphitobisethylenediaminecobalt(III) complex was dissolved in water, and a saturated solution of sodium thiocyanate was added. On the addition of acetone pale brown crystals appeared; they were filtered off and washed with acetone. Their infrared spectrum was identical with those of the compounds obtained by methods (i) and (ii). These needles are the *trihydrate* (Found: C, 16·3; H, 5·5. $C_4H_{22}CoN_5O_6S_2$ requires C, 16·2; H, 5·9%). The compound is partially ionised in water: $\Lambda = 33{\cdot}5$ ohm^{-1} for a $8{\cdot}6 \times 10^{-4}$M-solution at 25°.

Aquosulphitobisethylenediaminecobalt(III) *Perchlorate*.—The *perchlorate* [Co en_2SO_3,OH_2]ClO_4 was prepared by the action of aqueous sodium perchlorate on the complex [Co en_2SO_3Cl]^0. Yellow brown crystals were obtained after a few minutes and were filtered off and washed with ethanol and ether (Found: C, 12·8; H, 5·05. $C_4H_{18}ClCoN_4O_8S$ requires C, 12·8; H, 4·8%). The compound became red at 120° and was then insoluble in water and organic solvents. However, on being left in contact with water it gradually dissolved. The colour of the solution was yellow-brown and the visible absorption spectrum showed the presence of the [Co en_2SO_3,OH_2]$^+$ ion. Analysis of the red *compound* showed that it contained one molecule of water less than [Co en_2SO_3,OH_2]ClO_4. The infrared spectrum was clearly different from those containing the chelated sulphito-group. It is possible that a dimerisation or polymerisation occurred, giving compounds which involve bridging sulphito-groups of the type $R_5Co–S(O_2)–O–CoR_5$ (Found: C, 13·2; H, 5·0. $C_4H_{16}ClCoN_4O_7S$ requires C, 13·35; H, 4·5%).

Aminosulphitobisethylenediaminecobalt(III) *Chloride*.—Sufficient 2N-ammonia was added to the compound [Co en_2SO_3,Cl]^0 to form a solution. The mixture was gently boiled for a few minutes; on cooling, yellow-brown needles of a *chloride* [Co en_2SO_3,NH_3]Cl were precipitated. These were filtered off and washed with methanol and acetone (Found: C, 15·3; H, 6·5; N, 21·2; S, 10·4. $C_4H_{19}ClCoN_5O_3S$ requires C, 15·4; H, 6·15; N, 22·4; S, 10·3%). An aqueous $3{\cdot}84 \times 10^{-3}$M-solution had a molar conductivity of 91 ohm^{-1} at 18·5°. Both the solid and the aqueous solution became bright orange at $>60°$. On cooling, they revert to their original colour.

Hydroxosulphitobisethylenediaminecobalt(III).—This was prepared from the complex [Co en_2SO_3,Cl]^0 by the action of 2N-sodium hydroxide. Methanol, followed by acetone, was added to the mixture and the *complex* [Co en_2SO_3,OH]^0 then appeared as golden-yellow plates. It was filtered off and washed with acetone. It is soluble in water and in methanol (Found: C, 15·7; H, 6·8; S, 9·9. $C_4H_{17}CoN_4O_4$ requires C, 15·4; H, 6·7; S, 10·2%). [Co en_2SO_3,OH] was also prepared by addition of sodium hydroxide to *cis*-[Co $en_2(SO_2)_2$]Na.

Sulphitobisethylenediaminecobalt(III) *Chloride*.—The chloro-complex *trans*-[Co en_2Cl_2]Cl was dissolved in a large excess of water, sodium sulphite was added, and the mixture was allowed to evaporate in the dark until red-brown crystals appeared (about 6 weeks). These were filtered off and washed with alcohol and ether. The compound was a *monohydrate* (Found: C, 15·3; H, 6·3; N, 18·1; S, 10·2. $C_4H_{18}ClCoN_4O_4S$ requires C, 15·35; H, 5·8; N, 17·9; S, 10·0%).

Sulphitobisethylenediaminecobalt(III) *perchlorate* was obtained immediately on addition of sodium perchlorate to a solution of the preceding chloride. It formed sparingly soluble orange-brown needles (Found: C, 13·4; H, 4·7; S, 9·2. $C_4H_{16}ClCoN_4O_7S$ requires C, 13·45; H, 4·5; S, 8·9%).

Sulphitobisethylenediaminecobalt(III) *nitrite* was obtained more slowly after addition of sodium nitrite to a solution of the chloride. The orange-brown *monohydrate* was formed

(Found: C, 14·8; H, 5·7. $C_4H_{18}CoN_5O_6S$ requires C, 14·9; H, 5·6%). The conductivity of its aqueous 5·1 × 10^{-4}M-solution was 102·9 ohm^{-1} at 20°.

Sulphitobisethylenediaminecobalt(III) *iodide* was similarly prepared by use of sodium iodide. The brown-orange crystals of the monohydrate were filtered off and washed, with methanol and ether (Found: C, 11·8; H, 4·5; S, 7·9. $C_4H_{18}CoIN_4O_4S$ requires C, 11·9; H, 4·2; S, 7·9%).

Sulphitobisethylenediaminecobalt(III) *thiocyanate* was similarly prepared by addition of sodium thiocyanate, and formed brown-orange needles of the monohydrate which were filtered off and washed with acetone and ether (Found: C, 18·2; S, 19·7. $C_5H_{18}CoN_5O_4S$ requires C, 18·3; S, 19·7%).

Sodium trans-*Disulphitobisethylenediaminecobalt*(III).—The dichloro-chloride *trans*-[Co en_2Cl_2]Cl was dissolved in a little water and an excess of solid sodium sulphite was added. The mixture was boiled, becoming brown and then bright yellow, and, on cooling, yellow crystals of the *sodium salt* appeared. They were filtered and recrystallised as trihydrate from dilute sodium sulphite solution (Found: C, 11·4; H, 5·4; N, 13·4; S, 15·8. $C_4H_{22}CoN_4NaO_9S_2$ requires C, 11·6; H, 5·3; N, 13·6; S, 15·6%). On drying over calcium chloride the crystals crumbled to a yellow powder which was the anhydrous *salt* (Found: C, 13·5; H, 4·2; S, 17·7. $C_4H_{16}CoN_4NaO_6S_2$ requires C, 13·2; H, 4·4; S, 17·8%).

Sodium cis-*Disulphitobisethylenediaminecobalt*(III).—(i) A saturated solution of sodium sulphite was added to the dithionate, *cis*-[Co en_2NCS,OH_2]S_2O_6 prepared by using an ion-exchange column.[3b] The solution became brown and then yellow on warming, and finally a yellow powder appeared. The solid anhydrous *salt* was filtered off, washed with ethanol and ether, and dried over calcium chloride (Found: C, 13·3; H, 3·9; N, 16·15; S, 18·5. $C_4H_{16}CoN_4NaO_6S_2$ requires C, 13·2; H, 4·4; N, 15·6; S, 17·8%).

(ii) A solution of the bromide, *trans*-[Co en_2NCS,OH_2]Br_2, prepared by Werner's method,[5] was boiled with a large excess of sodium sulphite until a yellow powder was formed. This was filtered off and washed with methanol and ether. Its infrared and visible absorption spectra were identical with those of the compound prepared as in (i).

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