

Ethylene Sulphite as a Solvent. II.\* Pseudohalide  
Complex Compounds of Cobalt(II)

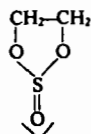
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The formation of azido-, cyano-, and isothiocyanato complex compounds of cobalt(II) has been investigated in solution of ethylene sulphite (ES) by spectrophotometric, potentiometric and conductometric methods. The following species appear to be formed: octahedral  $\text{Co}(\text{N}_3)_2$ , tetrahedral  $[\text{Co}(\text{N}_3)_3]^-$ ,  $[\text{Co}(\text{N}_3)_4]^{2-}$ ,  $\text{Co}(\text{CN})_2$ , octahedrally distorted  $[\text{Co}(\text{CN})_5\text{ES}]^{3-}$ ,  $[\text{Co}(\text{NCS})(\text{ES})_5]^+$ , and tetrahedral  $[\text{Co}(\text{NCS})_3\text{ES}]^-$  and  $[\text{Co}(\text{NCS})_4]^{2-}$ .

## Introduction

The formation of pseudohalide complexes of cobalt(II) has been studied in a variety of non aqueous solvents of different donor properties, such as trimethylphosphate,<sup>1</sup> nitromethane,<sup>2</sup> acetonitrile,<sup>1</sup> propanediol-1,2-carbonate,<sup>3</sup> N,N-dimethylacetamide<sup>3,4</sup> or dimethylsulphoxide.<sup>1,5</sup> Ethylene sulphite



has been found to behave as a suitable solvent<sup>6</sup> for complex formation.\* Cobalt(II) is coordinated to six solvent molecules apparently through the oxygen. The formation of halide complexes of cobalt(II) indicated that ethylene sulphite appears to be slightly stronger bonded to cobalt(II) than solvent molecules of comparable donor number such as acetonitrile or propanediol-1,2-carbonate. The following investigation is concerned with the formation of pseudohalide complexes of cobalt(II) in ethylene sulphite.

## Experimental Section

Ethylene sulphite was obtained from ethylene glycole and thionyl chloride\* and purified by fractionated distillation in a vacuum b.p. 63°/13, water content

below  $10^{-3}$  M. Anhydrous cobalt(II) perchlorate was prepared by dehydration of the hexahydrate with 2,2'-dimethoxypropane<sup>7,8</sup> and treated with ethylene sulphite. Tetraethylammoniumazide,<sup>9</sup> tetraethylammoniumthiocyanate,<sup>10</sup> and tetraethylammoniumcyanide<sup>10</sup> were made as described previously.<sup>9,10</sup>

For the spectrophotometric measurements a Zeiss PMQ II-spectrophotometer was used, for the conductometric titrations a Philips-type bridge PR 9501. Potentiometric titrations were carried out with Tl/TlN<sub>3</sub> electrodes<sup>1</sup> and with silver electrodes<sup>11</sup> respectively.

All operations were carried out in the absence of moisture, the concentrations of the cobalt(II) solutions were  $2 \times 10^{-3}$  M.

## Results

Addition of tetraethylammonium azide to a solution containing octahedral  $[\text{Co}(\text{ES})_6]^{2+}$ \* causes the formation of a pink precipitate, which is redissolved at  $x(\text{N}_3^-:\text{Co}^{2+})=2.7$ . This solution shows a spectrum with two maxima, namely between 660 and 680 nm and at 612 nm as well as a shoulder at 520 nm. At  $x=3$  the broad maximum is split into two maxima at 678 and 655 nm and the shoulder has disappeared (Figure 1). Further azide ion addition causes a shift of the maximum from 678 to 690 nm while the maximum at 612 nm is converted into a shoulder. No changes are observed in the spectrum at  $x>10$  (Figure 2). The potentiometric titration curve shows an inflexion at  $x=2.25$  (Figure 3), while a break in the conductivity curve is observed at  $x=1.95$  (Figure 4).

In the cyano-system a bluish-green precipitate is formed at  $x(\text{CN}^-:\text{Co}^{2+})<3$ . The colour of the solution changes to yellow at  $x\sim 3$ . In the spectrum at  $x=2.5$  a maximum is found at 581 nm and a shoulder at 555 nm, while at  $x=2.8$  the maximum is shifted to 593 nm and the shoulder to 560 nm (Figure 5). At  $ax=3.5$  two maxima appear at 595 and 1015 nm with the shoulder at 560 nm still being present. At  $x>3.5$  the spectrum shows no shoulder

(\*) Part I: V. Gutmann and A. Scherhauser, *Mh. Chem.*, in press.  
(1) V. Gutmann and O. Leitmann, *Mh. Chem.*, 97, 926 (1966).  
(2) V. Gutmann and K. H. Wegleitner, *Mh. Chem.*, 99, 368 (1968).  
(3) V. Gutmann and O. Bohunovsky, *Mh. Chem.*, 99, 751 (1966).  
(4) R. E. Dodd and R. P. Gasser, *Proc. Chem. Soc.*, 415 (1964).  
(5) E. Rupp and F. Pfennig, *Chem. Ztg.*, 34, 322 (1910).  
(6) V. Gutmann and A. Scherhauser, *Mh. Chem.*, 99, 335 (1968).

(7) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 1, 866 (1962).  
(8) K. Starke, *J. Inorg. Nucl. Chem.*, 11, 77 (1959).  
(9) V. Gutmann, G. Hampel, and O. Leitmann, *Mh. Chem.*, 95, 1034 (1964).  
(10) V. Gutmann and H. Bardy, *Z. anorg. allg. Chem.*, in press.  
(11) E. Müller and W. Schluttig, *Z. anorg. allg. Chem.*, 121, 178b (1922).

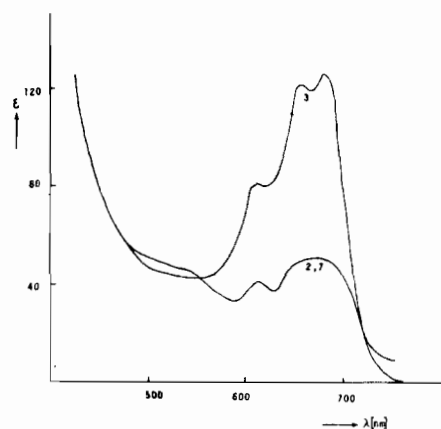


Figure 1. Absorption spectra in the  $\text{Co}^{\text{II}}$  azido system in ES at molar ratios  $x=2.7$  and  $3.0$  ( $x=\text{N}_3^-/\text{Co}^{2+}$ ).

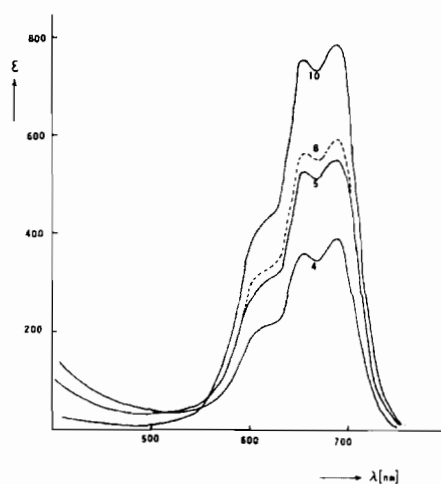


Figure 2. Absorption spectra in the  $\text{Co}^{\text{II}}$  azido system in ES at  $x > 4$ .

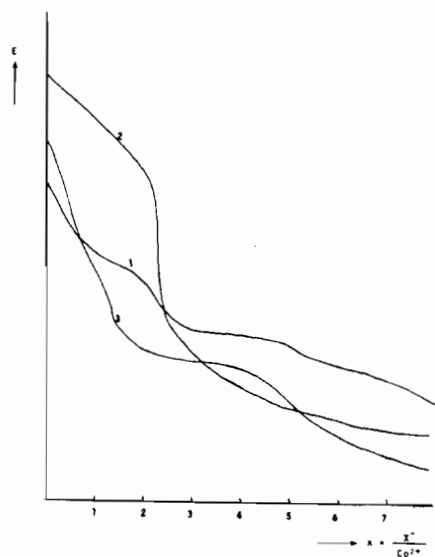


Figure 3. Potentiometric titration curves in the azido(1)-cyano(2)-, and isothiocyanato(3)-system of  $\text{Co}^{\text{II}}$  in ES.

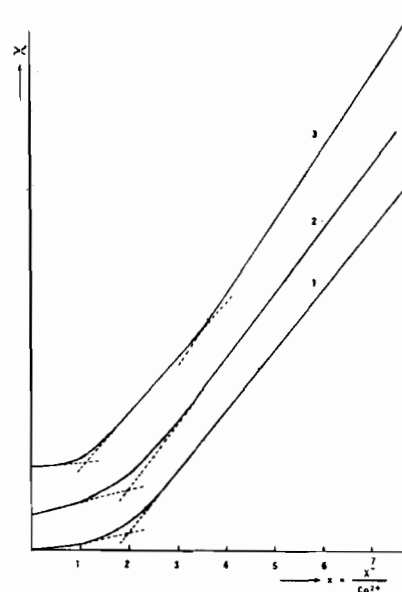


Figure 4. Conductometric titration curves in the azido(1)-, cyano(2)-, and isothiocyanato(3)-system of  $\text{Co}^{\text{II}}$  in ES.

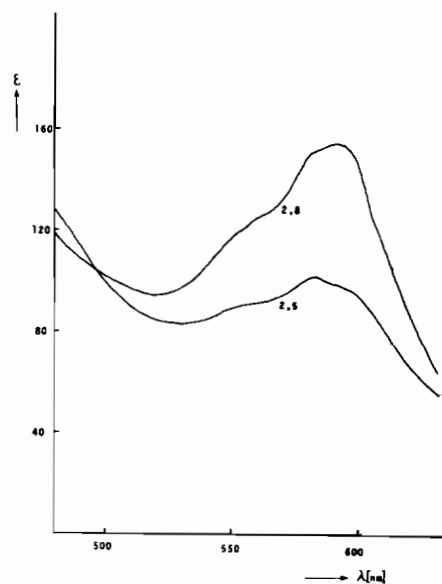


Figure 5. Absorption spectra in the  $\text{Co}^{\text{II}}$  cyano system in ES at molar ratios  $x=2.5$  and  $2.8$  ( $x=\text{CN}^-/\text{Co}^{2+}$ ).

and only one maximum, namely at 1015 nm, the extinction of which reaches its final value at  $x=12$  (Figure 6) with only a slight increase between  $x=7$  and  $x=12$ . The potentiometric titration curve shows an inflexion at  $x=2.25$  (Figure 3) and the conductometric curve a break at  $x=2$  (Figure 4).

The thiocyanate system gives at  $x(\text{NCS}^-:\text{Co}^{2+})=1$  a spectrum with a maximum at 530 nm and with shoulders at 622 and 486 nm. At  $x=1.5$  a second maximum appears at 540 nm, and a shoulder at 590 nm. At  $x=2$  only the maximum at 625 nm is retained and the shoulders are found at 590 and

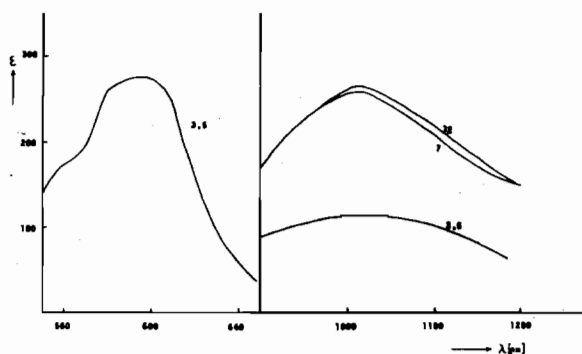


Figure 6. Absorption spectra for the  $\text{Co}^{\text{II}}$  cyano system in ES at  $x > 3.5$  and wavelengths between 560 and 640 nm, and 900 and 1200 nm.

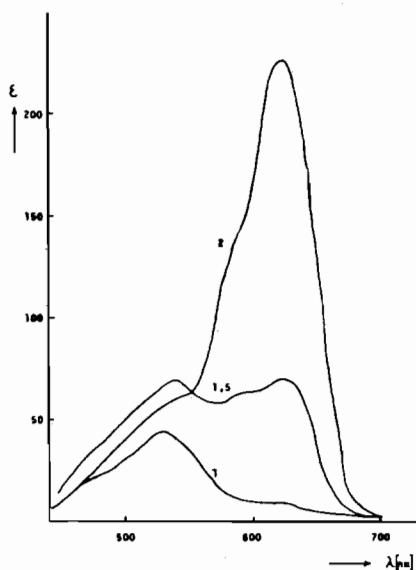


Figure 7. Absorption spectra in the  $\text{Co}^{\text{II}}$  isothiocyanato system in ES at molar ratios up to  $x=2$  ( $x = \text{NCS}^- / \text{Co}^{2+}$ ).

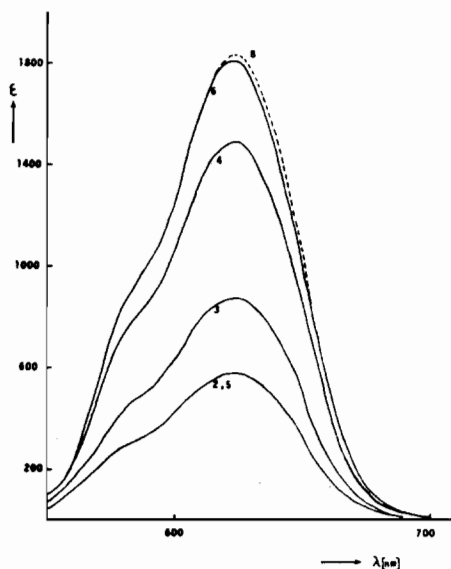


Figure 8. Absorption spectra in the  $\text{Co}^{\text{II}}$  isothiocyanato system in ES at  $x > 2.5$ .

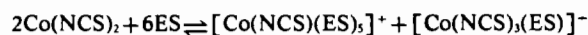
550 nm (Figure 7). A shoulder at 495 nm is formed at  $x=2.5$ , while the shoulder at 550 nm disappears. At  $x=6$  a maximum at 492 nm with  $\epsilon_{\text{max}}=23$  appears. Further addition of thiocyanate ions causes no further changes of the spectrum (Figure 8). Slight inflexions are found in the potentiometric curve at  $x=1.35$  and 4.65 (Figure 3), breaks in the conductometric titration curve at  $x=1.1$  and  $x=3.55$  (Figure 4).

## Discussion

The pink precipitation present in the azido-system at  $c_{\text{Co}^{2+}} = 2 \times 10^{-3} M$  between  $x=1$  and  $x=2.7$  appears to be partly soluble as diazide, the formation of which is supported by the spectrophotometric, conductometric and potentiometric results. According to spectral evidence the diazide is hexacoordinated. An octahedral cobalt(II) diazide has also been found in propanediol-1,2-carbonate,<sup>3</sup> but not in other solvents.<sup>2,3</sup> A change in the coordination number appears to occur at  $x \sim 3$ , when tetrahedral triazidocobaltate(II) apparently of composition  $[\text{Co}(\text{N}_3)_3(\text{ES})]^-$  is formed according to spectral results. At higher  $x$ -values the spectrum characteristic for tetrahedral tetraazidocobaltate(II)<sup>1,3</sup> is obtained. A  $2\frac{1}{2}$  fold excess of azide ions ( $x=10$ ) is required to achieve complete conversion into the tetraazido complex.

In the cyano-system the final spectrum in ES is similar to that in propanediol-1,2-carbonate<sup>3</sup> and in water<sup>12,13</sup> and thus due to pentacyanocobaltate(II). This is apparently pseudooctahedral in ES e.g.  $[\text{Co}(\text{CN})_5(\text{ES})]^{3-}$  as well as in other systems,<sup>3,14</sup> since the maxima show a clear dependence from the solvent, which therefore seems to be coordinated. The bluish-green precipitate appearing at  $x=0.5$  and disappearing at  $x=2.8$  consists of tetrahedral cobalt(II) dicyanide. The formation of the dicyanide is also supported potentiometric and conductometric results.

IR-evidence shows that the thiocyanate ion is coordinated to cobalt(II) through the nitrogen atom.<sup>15</sup> The spectrum at  $x=1$  suggests the presence of the hexacoordinated mono-thiocyanato complexes  $[\text{Co}(\text{NCS})(\text{ES})_5]^+$ , the formation of which is also roughly indicated by potentiometric and conductometric results. No indications are obtained for the formation of a neutral species, but anionic complexes are definitely formed. Any dithiocyanate is therefore subjected to considerable autocomplex formation apparently according to



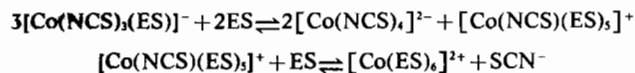
Autocomplex formation has been found in several other solvents<sup>3</sup> with the exception of nitromethane,<sup>2</sup> which has a much lower donor number.<sup>6</sup> The appearance of shoulder in the absorption range for octahedral cobalt thiocyanate complexes between  $x=2$  and

- (12) T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi*, **87**, 825 (1966).  
 (13) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **87**, 395 (1966).  
 (14) J. M. Pratt and R. J. P. Williams, *J. Chem. Soc.*, London, **A**, 1291 (1967).  
 (15) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

**Table 1.** Molar ratios  $x=X^-:Co^{2+}$  required for the quantitative formation of  $[CoX_4]^{2-}$  in different solvents

Solvent	Donor-Number <sup>6,16-18</sup> SbCl <sub>5</sub>	X <sup>-</sup> = NCS <sup>-</sup>	X <sup>-</sup> = N <sub>3</sub> <sup>-</sup>	Ref.
Nitromethane	2.7	4	4	2
Acetonitrile	14.1	7	8	3
Propanediol-1,2-carbonate	15.1	4	4	3, 11
Ethylene Sulphite	15.3	6	10	present results
Dimethyl Sulphoxide	29.7	200	20	3, 11

$x=4$  may be due to complex forms which may be present according to the equilibria



The final spectrum at  $x=6$  is due to the presence of  $[Co(NCS)_4]^{2-}$ , as can be seen by comparing the spectrum with that described in the literature.<sup>2</sup> Its formation is also indicated by the results of a potentiometric titration.

The results in ES are similar to those in acetonitrile<sup>1,3</sup> and propanediolcarbonate,<sup>3</sup> all of which have

almost identical donor properties.<sup>16-18</sup> The respective  $x$ -values, required to achieve practically the quantitative formation of tetrapseudohalocobaltate(II) are similar to those in acetonitrile and propanediol-1,2-carbonate.

Ethylene Sulphite, which has a pyramidal structure, is somewhat stronger bound to cobalt(II), than the planar propanediol-1,2-carbonate molecules, as has also been found by comparing the relative stabilities of tetrahalocobaltate(II) in these solvents.\* The results confirm the rule that solvents with similar donor number and with not vastly different steric properties and dielectric constants will act as equally suitable media for complex reactions.<sup>17,18</sup>

(16) V. Gutmann and E. Wychera, *Rev. Chim. Min.*, 3, 941 (1967).  
(17) V. Gutmann, *Coord. Chem. Revs.*, 2, 239 (1967).

(18) V. Gutmann, «Coordination Chemistry in Non Aqueous Solutions», Springer-Verlag, Wien-New York (1968).