# *Studies on the Cobalt(III) Complexes of Monothiophosphate Ion*

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Recently, Yasuda and Lambert[1] reported that the monothiophosphate ion shows an interesting color reaction with the cobalt(II) ion in aqueous solution. Except for this report there has been no description heretofore about the coordinative nature of the monothiophosphate ion. In the present paper, the syntheses of di-monothiophosphato - bis - ethylenediamine and monothiophosphato - bis - ethylenediamine cobalt(III) complexes will be reported. Furthermore, their visible and ultraviolet and also the infrared absorption spectra will be discussed mainly in comparison with those of the known thiosulfato complexes of cobalt(III).

## Experimental

**Preparation.**—*1*) *Dark green complex*: $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$. — This complex was prepared as follows: 3.2 g. anhydrous sodium monothiophosphate[1,2], was completely dissolved in 80 ml. of water, and the solution was added to the aqueous solution (20 ml.) of 2.5 g. *trans*-$[Co\,en_2Cl_2]Cl$. The color of the mixture changed from dark red to dark greenish red. To complete the reaction the mixture was preserved for one hour. The resulting solution was filtered quickly, and ethanol was added carefully to the clear filtrate on cooling. Dark greenish crystalline powder was obtained. The crude product was recrystallized from a small quantity of cold water by the addition of ethanol. The fine crystals obtained were dried in a desiccator over sulfuric acid.

*Anal.* Found: Co, 9.58; P, 9.72; N, 8.97; C, 7.67; H, 5.05; $H_2O$, 23.66. Calcd. for $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O = C_4H_{16}O_6S_2N_4P_2Na_3Co\cdot 8H_2O$: Co, 9.59; P, 10.10; N, 9.12; C, 7.82; H, 5.25; $H_2O$, 23.46%.

*2*) *Dark red complex*: $[Co\,en_2(SPO_3)]\cdot 2H_2O$.— To the aqueous solution (30 ml.) of 5 g. *trans*-$[Co\,en_2Cl_2]Cl$, was added on cooling an aqueous solution (70 ml.) of 3.2 g. of anhydrous sodium monothiophosphate. The resulting solution was dark red. A large amount of ethanol was added carefully to the solution. The desired complex was obtained as dark reddish crystalline powder.

*Anal.* Found: Co, 17.8; P, 9.35; N, 16.93; C, 14.37; H, 6.51; $H_2O$, 11.82. Calcd. for $[Co\,en_2(SPO_3)]\cdot 2H_2O = C_4H_{16}O_3SN_4PCo\cdot 2H_2O$: Co, 18.07; P, 9.5; N, 17.18; C, 14.73; H, 6.19; $H_2O$, 11.05%.

**Measurements.** — The visible and ultraviolet absorption measurements were made by a Beckman DU spectrophotometer in cold aqueous solutions to prevent the aquation of the complexes. The concentration of the solutions varied from $1/2\times10^{-2}$ to $1/8\times10^{-3}$ F. The infrared spectra were obtained by a Parkin-Elmer Model 21 (double beam) and a Hilger H-800 infrared spectrophotometer using sodium chloride prisms. The potassium bromide disk method and nujol mull technique were employed.

**Materials.**—Thiosulfato-pentammine cobalt(III) chloride, $[Co(NH_3)_5(SSO_3)]Cl$[3], and sodium dithiosulfato-bis-ethylenediamine cobaltate(III), $Na[Co\,en_2(SSO_3)_2]$[4], were obtained as dark red and green crystals, respectively, in the usual way as done by Rây and his coworker. The visible and ultraviolet absorption curves of these compounds are shown in Figs. 1 and 2. These absorption curves were in good agreement with those obtained by Kiss et al.[5,6].

## Results and Discussion

*Dark green complex*: $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$.—The visible and ultraviolet absorption curve of this compound is shown in Fig. 1, in which the spectrum of the corresponding thiosulfato-complex, $Na[Co\,en_2(SSO_3)_2]$, is also plotted for comparison. These two absorption curves are similar to each other on the whole. The frequencies of the absorption maxima for each complex are listed in Table I.

The first absorption bands of these complexes are shifted towards longer wavelengths than those of complexes of $[Co^{III}N_4O_2]$ type[7,8] and distinctly split into two components. Moreover, the type of these splittings differ from those of $[Co^{III}N_4O_2]$ and $[Co^{III}N_5O]$ type complexes.

1) S. K. Yasuda and J. L. Lambert, *J. Chem. Educ.*, **31**, 572 (1954).
2) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, Longmans, Green & Co., New York (1931), p. 1068—1069.
3) P. R. Rây, *J. Indian Chem. Soc.*, **4**, 71 (1927).
4) P. R. Rây and S. N. Maulik, ibid., **10**, 655 (1933).
5) A. Kiss and D. Czeglédy, *Z. anorg. u. allgem. Chem.*, **235**, 407 (1938).
6) A. Kiss, G. Auer and E. Major, ibid., **264**, 28 (1941).
7) M. Linhard and M. Weigel, ibid., **264**, 321 (1951).
8) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

TABLE I. THE FIRST, SECOND AND THE CHARGE-TRANSFER BANDS OF MONOTHIOPHOSPHATO AND THIOSULFATO Co(III) COMPLEXES
(in frequency unit $10^{13}$/sec.)

| Complex salt | First band $\nu_{max}$ ($\log \varepsilon$) | Second band $\nu_{max}$ ($\log \varepsilon$) | Charge-transfer band $\nu_{max}$ ($\log \varepsilon$) |
|---|---|---|---|
| $[Co(NH_3)_5(SSO_3)]Cl$ | 58.8 (1.82) | ca. 82 (2.3) | 103.4 (4.9) 126 (3.6) |
| $Na[Co\,en_2(SSO_3)_2]$ | 54.9 (1.93) | | 89.6 (4.28) |
| $Na_3[Co\,en_2(SPO_3)_2]$ | 53.9 (2.10) | | 87.0 (4.36) 108 (3.83) |
| $[Co\,en_2(SPO_3)]$ | 56.0 (2.31) | ca. 82 (2.6) | 107.3 (4.16) |

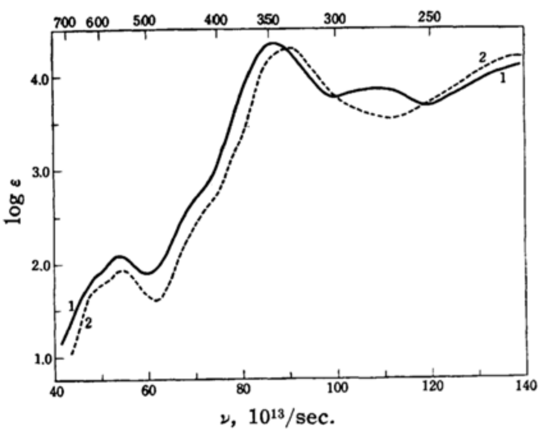


Fig. 1. Absorption spectra of:
1, $Na_3[Co\,en_2(SPO_3)_2]\cdot 8H_2O$;
2, $Na[Co\,en_2(SSO_3)_2]$.

These facts indicate that the cobalt(III) ion in these complex ions coordinates monothiophosphate or thiosulfate ions by their sulfur atoms. This conclusion is also supported by the fact that these complexes show intense absorption bands in the near ultraviolet, which are probably originated from charge transfer between the central cobalt(III) ion and the coordinated monothiophosphate or thiosulfate ion. As to the charge transfer band of di-thiosulfato-bis-ethylenediamine cobalt(III) ion, it is located at a longer wavelength than that of thiosulfato-pentammine cobalt(III) ion. Judging from the position of the thiosulfate ion in the spectrochemical series, it is evident that $[Co\,en_2(SSO_3)_2]^-$ has *trans* structure with regard to two thiosulfate ions in coordination[8]. It may be concluded, therefore, that the structure of $[Co\,en_2(SPO_3)_2]^{3-}$ is also *trans*, since its absorption curve is quite similar to the corresponding thiosulfato-complex.

**Structure of the Dark Red Complex.**—From the result of the chemical analysis, there was two possibilities of the structure of the "dark red complex". The one is $[Co\,en_2(OH_2)(SPO_3)]\cdot H_2O$ in which the monothiophosphate ion is coordinated as a monodentate ligand, and the other, $[Co\,en_2(SPO_3)]\cdot 2H_2O$ in which the monothiophosphate ion is coordinated as a chelate ligand.

Being heated for dehydration, sodium di-monothiophosphato-bis-ethylenediamine cobaltate(III) is rather unstable and changes into black sulfide of cobalt at about 110°C with evolution of hydrogen sulfide. On the contrary, the dark red complex is more stable against heating. Even after the two molecules of water were expelled at 110°C, the dark red color of the complex was well preserved and no indication of the decomposition of the complex was observed. These facts suggest that the structure of the dark red complex is $[Co\,en_2(SPO_3)]\cdot 2H_2O$ and not $[Co\,en_2(OH_2)(SPO_3)]\cdot H_2O$.

The visible and ultraviolet absorption curve of the dark red complex is shown in Fig. 2, in which the spectrum of thiosulfato-pentammine cobalt(III) ion is also plotted for comparison.

The trend that the two absorption curves resemble each other on the whole, is similar to the case of Fig. 1. There are, however, a few important differences between the two curves in Fig. 2. In the

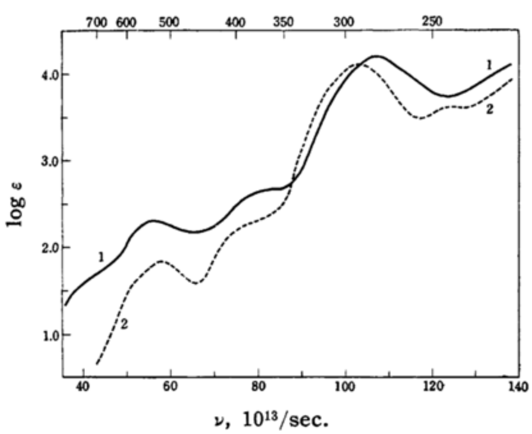


Fig. 2. Absorption spectra of:
1, $[Co\,en_2(SPO_3)]\cdot 2H_2O$;
2, $[Co(NH_3)_5(SSO_3)]Cl$.

first place, the charge transfer band of the dark red complex ($\nu=107.3\times10^{13}$/sec.) is in a shorter wavelength than that of the thiosulfato-pentammine complex. The second difference is seen in the first and the second absorption bands. In this region, the absorption of the dark red complex is stronger in intensity than that of the thiosulfato-pentammine complex. These phenomena may be considered as a proof for the structural difference between the two complexes, especially the difference in the type of coordination of the sulfur-containing ligands.

**Infrared Absorption Spectra.** — Fig. 3 indicates the infrared spectra of the thiosulfato cobalt(III) complexes and of sodium thiosulfate pentahydrate in 1250~850 $cm^{-1}$ region. Except for the absorption bands which are due to the vibration of ethylenediamine, two absorption bands appear in this region, which are assigned as the S-O vibration[9].

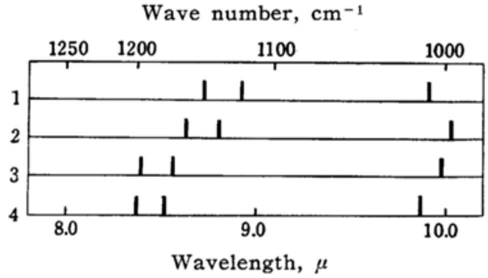


Fig. 3. Infrared absorption bands of:
1, $Na_2S_2O_3\cdot5H_2O$ (KBr disk);
2, $[Co(NH_3)_5(SSO_3)]Cl$ (nujol mull);
3, $Na[Co\,en_2(SSO_3)_2]$ (nujol mull);
4, $K_4[Co(CN)_5(SSO_3)]$ (KBr disk).

The free thiosulfate ion has the symmetry of $C_{3v}$, and the symmetry is not altered by coordination, because the central cobalt(III) ion is attached to the sulfur atom of the monodentate thiosulfate ion in these complexes. As is seen in Fig. 3, although the band at 1000 $cm^{-1}$ is hardly shifted by coordination, the bands at 1120 $cm^{-1}$ are shifted to higher frequencies by coordination. A similar trend is seen in the cobalt(III) complex which contains monothiophosphate ions as monodentate ligand (Fig. 4).

These facts will be explained from the assumption that the free ligand ($SPO_3^{3-}$) and the coordinated ligand have the same symmetry $C_{3v}$. The two sharp bands of the free ligand are due to the $PO_3$ group

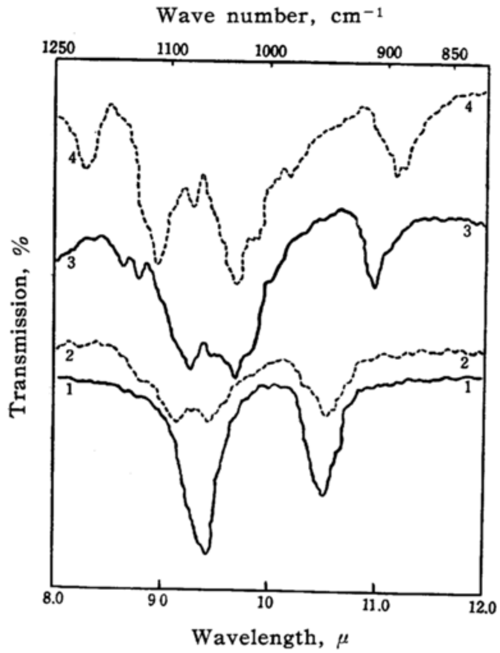


Fig. 4. Infrared absorption spectra of:
1, $Na_3SPO_3$ (KBr disk);
2, $Na_3[Co\,en_2(SPO_3)_2]\cdot8H_2O$ (KBr disk);
3, $[Co\,en_2(SPO_3)]\cdot2H_2O$ (nujol mull);
4, $[Co\,en_2(SPO_3)]$ (nujol mull).

and the vibrations are assumed to be symmetric $PO_3$ stretching vibration (950 $cm^{-1}$) and degenerate $PO_3$ asymmetric vibration (1064 $cm^{-1}$), respectively[10]. In the di-monothiophosphato-bis-ethylenediammine cobalt(III) ion, the band at 950 $cm^{-1}$ is hardly shifted, but the band at 1064 $cm^{-1}$ is shifted to a higher frequency and splits into two peaks. This trend is in good accordance with that of the thiosulfato complexes mentioned above. These relationships led us to the conclusion that the cobalt(III) ion in this complex coordinates the monothiophosphate ion by the sulfur atom, in good agreement with the conclusion from the visible and ultraviolet spectra. On the contrary, in the spectra of the dark red complex, the symmetric $PO_3$ stretching vibration of the monothiophosphate ion is shifted to a lower frequency by coordination. If it is assumed that the dark red complex has the structure containing the monodentate monothiophosphate ligand, namely, $[Co\,en_2(OH_2)(SPO_3)]\cdot H_2O$, the symmetry of the coordinated $SPO_3^{3-}$ ions is $C_{3v}$, but if the chelate structure in $[Co\,en_2(SPO_3)]\cdot2H_2O$, is assumed, the symmetry of the ligand is lowered to $C_s$. It is presumed, therefore,

9) K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4909 (1957).

10) M. Tsuboi, ibid., **79**, 1351 (1957).

that the shift of the band at 950 $cm^{-1}$ is caused by the chelate coordination. Furthermore, in the spectra of the dehydrated complex (Fig. 4), no new band by degradation symmetry appears, though the bands are more or less shifted. These shifts probably result from the vanishing of the hydrogen-bond between the water molecules and the $SPO_3^{3-}$ group. Similar shifts were reported for some inorganic phosphorus compounds[11].

**Summary**

Two new complexes, sodium di-monothiophosphato-bis-ethylenediamine cobaltate(III) octa-hydrate and monothiophosphato-bis-ethylenediamine-cobalt(III) dihydrate, have been synthesized by the reaction of *trans*-dichloro-bis-ethylenediamine cobalt(III) chloride with anhydrous sodium monothiophosphate in cold aqueous solution. The infrared and the visible and ultraviolet absorption spectra of these compounds and of the corresponding thiosulfato-Co(III) complexes have been measured and discussed in relation to the structures of the complexes.

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11) D. E. C. Corbridge and E. J. Lowe., *J. Chem. Soc.*, **1957**, 493.