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Methods of Preparing the 2,2′-Dipyridyl and 1,10-Phenanthroline Cobalt(III) Complexes of the $[CoX_2dip_2]$- and $[CoX_2phen_2]$-Type[1]

Nobufumi MAKI

Department of Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu

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The bis(2,2′-dipyridyl) and bis(1,10-phenanthroline)cobalt(III) complexes of the $[CoX_2N_4]$-type, including the following new compounds, have been prepared: $[Co(CN)_2dip_2]NO_3\cdot 7H_2O$, $[Co(CN)_2dip_2]_2SO_4\cdot 12H_2O$, $Na[Co(SO_3)_2dip_2]\cdot 5H_2O$, $Na[Co(S_2O_3)_2dip_2]\cdot 7H_2O$ $[Co(N_3)_2dip_2]N_3\cdot 2H_2O$, $[Co(N_3)_2dip_2]ClO_4$, $[Co(N_3)_2dip_2]_2SO_4\cdot 5H_2O$, $[Co(N_3)_2dip_2]NO_3\cdot 2H_2O$, $[Co(N_3)_2dip_2]Cl\cdot 3H_2O$, $[Co(SCN)_2dip_2]NCS\cdot \frac{5}{2}H_2O$, $[Co(SCN)_2dip_2]ClO_4\cdot 2H_2O$, $[Co(SCN)_2dip_2]Cl\cdot 3H_2O$, $K[Co(SO_3)_2phen_2]\cdot 5H_2O$, $[Co(NO_2)_2phen_2]Cl\cdot 4H_2O$, $Na[Co(S_2O_3)_2phen_2]$, $[Co(N_3)_2phen_2]N_3$, $[Co(CN)_2phen_2]NO_3\cdot 6H_2O$, $[Co(CN)_2phen_2]Cl\cdot 4H_2O$. The known compounds, including the cobalt(II) and cobalt(III) complexes of the luteo type, have also been prepared by methods other than those described hitherto in the literature. The absorption spectra in the visible and ultraviolet regions have been measured and compared with those of the bis(ethylenediamine)cobalt(III) complexes. The rhodanato-cobalt(III) complexes, $[Co(SCN)_2dip_2]ClO_4\cdot 2H_2O$ and $[Co(SCN)_2phen_2]NCS$, have been ascertained to be the sulfur-bonded thiocyanato complexes on the evidence of the absorption spectra in the visible and infrared regions.

A number of papers have been published concerning the preparation and the absorption spectra of the bis(ethylenediamine)cobalt(III) complexes, but very few concerning the corresponding cobalt(III) complexes with 2,2′-dipyridyl and 1,10-phenanthroline have appeared.[2]

The purpose of this work was to prepare the cobalt(III) complexes of the $[CoX_2dip_2]$- and $[Co X_2phen_2]$-type and to elucidate the difference between their absorption spectra and those of the ammine and amine cobalt(III) complexes. Above all, an effort was made to solve the problem of whether or not the rhodanate ligand, SCN^-, is bound to the cobalt(III) ion by the sulfur atom within the coordination sphere of the 2,2′-dipyridyl and 1,10-phenanthroline cobalt(III) complexes, in which the contribution of the π-bonding character to their coordinate bonds is considered to be fairly large.

In addition, the cobalt(III) and cobalt(II) complexes of the $[CoN_6]$-type were prepared by a more convenient and simple method than those described hitherto in the literature.

Experimental

The dichloro complexes, *trans*-$[CoCl_2dip_2]Cl$[3] and *trans*-$[CoCl_2phen_2]Cl\cdot 4H_2O$,[4] were used as the starting complexes for the preparation.

Preparation of $[Co(SCN)_2dip_2]NCS\cdot \frac{5}{2}H_2O$. A water solution (100 m*l*) containing 0.46 g of KNCS was stirred, a drop by drop, into 300 m*l* of a water solution of $[CoCl_2dip_2]Cl$ (1.0 g). First, a green precipitate

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[1] Presented in part at the 9th Symposium on the Coordination Chemistry, held at Kyushu University, October 21, 1959.

[2] A. A. Vlček, *Inorg. Chem.*, **6**, 1425 (1967).

[3] F. M. Jaeger and J. A. van Dijk, *Z. anorg. u. allgem. Chem.*, **227**, 273 (1936).

[4] P. Pfeiffer and Br. Werdelmann, *ibid.*, **236**, 31 (1950).

immediately separated from the solution; then, its gradually turned a reddish brown. The product was filtered and washed with water several times. The crude complex was recrystallized from hot 60% ethanol twice. Ruby-like red crystals were thus obtained. Found: Co, 9.71; C, 46.93; N, 16.60; H, 3.81%. Calcd for $[Co(SCN)_2dip_2]NCS\cdot\frac{5}{2}H_2O$: Co, 9.98; C, 46.78; N, 16.60; H, 3.58%.

The perchlorate and chloride salts were obtained by treating the complex with 10% $HClO_4$ and 6 N HCl respectively. Found: Co, 9.31; C, 42.37; N, 13.53; H, 3.48%. Calcd for $[Co(SCN)_2dip_2]ClO_4\cdot 2H_2O$: Co, 9.46; C, 42.42; N, 13.49; H, 3.24%.

Found: Co, 10.19; C, 45.88; N, 14.71; H, 4.02%. Calcd for $[Co(SCN)_2dip_2]Cl\cdot 3H_2O$: Co, 10.21; C, 45.79; N, 14.57; H, 3.84%. The complex is insoluble in water, but soluble in alcohol.

Preparation of $[Co(NO_2)_2dip_2]Cl\cdot 5H_2O$. One gram of *trans*-$[CoCl_2dip_2]Cl$, dissolved in 40 m*l* of water, was mixed with 0.4 g of KNO_2 dissolved in 10 m*l* of water, and the mixture was heated on a water bath for half an hour. The yellow product was recrystallized from hot water containing acetic acid.[5] Found: Co, 9.87; C, 40.77; N, 14.32; H, 4.23%. Calcd for $[Co(NO_2)_2dip_2]Cl\cdot 5H_2O$: Co, 10.01; C, 40.80; N, 14.27; H, 4.45%.

Preparation of $Na[Co(SO_3)_2dip_2]\cdot 5H_2O$. A water solution (100 m*l*) of $[CoCl_2dip_2]Cl$ (1.0 g) was mixed with 0.53 g of Na_2SO_3 dissolved in 20 m*l* of water, and the mixture was warmed on a water bath below 60°C. The yellow precipitate which deposited from the solution was filtered and washed with water, ethanol, and ether. The complex is scarcely soluble in water or ethanol. Found: Co, 9.02; C, 37.05; N, 8.80; H, 3.89%. Calcd for $Na[Co(SO_3)_2dip_2]\cdot 5H_2O$: Co, 9.14; C, 37.27; N, 8.69; H, 4.07%.

Preparation of $[Co(N_3)_2dip_2]N_3\cdot 2H_2O$. A water solution (100 m*l*) of *trans*-$[CoCl_2dip_2]Cl$ (1.0 g) was heated on a water bath (60—70°C) with 0.26 g of NaN_3. On cooling, lustrous brown crystals deposited on the wall of the beaker. The crude complex was recrystallized twice from hot water below 70°C. The azido complex is very soluble in both water and ethanol. Found: Co, 11.00; C, 44.94; N, 34.21; H, 3.89%. Calcd for $[Co(N_3)_2dip_2]N_3\cdot 2H_2O$: Co, 11.05; C, 45.04; N, 34.14; H, 3.75%.

By treating the complex with 5% $HClO_4$, 3 N H_2SO_4, 3 N HNO_3, and 3 N HCl, the salts of each the respective acid were obtained. Found: Co, 10.71; C, 43.28; N, 25.18; H, 3.05%. Calcd for $[Co(N_3)_2dip_2]ClO_4$ (anhydrous): Co, 10.62; C, 43.30; N, 25.25; H, 2.91%.

Found: Co, 11.02; C, 43.76; N, 25.40; H, 3.97%. Calcd for $[Co(N_3)_2dip_2]_2SO_4\cdot 5H_2O$: Co, 10.93; C, 43.80; N, 25.54; H, 3.86%.

Found: Co, 10.71; C, 43.34; N, 27.95; H, 3.80%. Calcd for $[Co(N_3)_2dip_2]NO_3\cdot 2H_2O$: Co, 10.65; C, 43.41; N, 27.84; H, 3.62%.

Found: Co, 11.20; C, 45.49; N, 26.63; H, 3.99%. Calcd for $[Co(N_3)_2dip_2]Cl\cdot 2H_2O$: Co, 11.19; C, 45.60; N, 26.59; H, 3.80%.

Preparation of $Na[Co(S_2O_3)_2dip_2]\cdot 7H_2O$. Two grams of *trans*-$[CoCl_2dip_2]Cl$, suspended in 30 m*l* of water, were mixed with 20 m*l* of a water solution containing 2.1 g of $Na_2S_2O_3\cdot 5H_2O$. The mixture was then heated on a water bath at 55°C for ten minutes. The solution assumed a brown color. When the solution was then allowed to stand under ice cooling, bright brown crystals separated from the solution, they were filtered and washed with cold 80% ethanol and ether. More crystals were obtained by the drop-by-drop addition of cold absolute ethanol to the mother liquor. The complex solution tends to decompose slowly, even at room temperature, evolving hydrogen sulfide. The complex is very soluble in water, but less soluble in ethanol. Found: Co, 7.99; C, 32.13; N, 7.60; H, 4.21%. Calcd for $Na[Co(S_2O_3)_2dip_2]\cdot 7H_2O$: Co, 7.91; C, 32.23; N, 7.52; H, 4.03%.

Preparation of $[Co(CN)_2dip_2]NO_3\cdot 7H_2O$. Fifteen grams of *trans*-$[CoCl_2dip_2]NO_3$(anhydrous), suspended in 500 m*l* of distilled water, were mixed with 10 g of AgCN, and the mixture was heated on a water bath (80°C) for three hours. The color of the solution changed from green to yellow. The solution was filtered, and the residue containing AgCl was repeatedly extracted with hot water. Then, the filtrate and the extracted solution were joined and concentrated into one-third in the former volume by evaporation. When the solution was then allowed to stand, lustrous, needle-shaped yellow crystals deposited from the solution; they were filtered and washed with cold water, ethanol, and ether. The crude product was recrystallized from hot water. Found: Co, 9.58; C, 43.15; N, 15.97; H, 5.03%. Calcd for $[Co(CN)_2dip_2]NO_3\cdot 7H_2O$: Co, 9.64; C, 43.22; N, 16.04; H, 4.95%. Before elementary analysis, the complex was dried overnight at room temperature in a vacuum desiccator on silica gel. In a preliminary report,[6] however, the elementary analysis was carried out on a sample of the complex which had been dried out *in vacuo* for three hours at 110°C, because the complex lost part of its crystallization water in the vacuum desiccator on concentrated sulfuric acid. The anhydrous complex is hygroscopic.

The corresponding sulfate of the complex was obtained by treating *trans*-$[CoCl_2dip_2]_2SO_4$ (anhydrous) with an excess of AgCN at 80°C. Found: Co, 10.12; C, 45.54; N, 14.45; H, 5.01%. Calcd for $[Co(CN)_2dip_2]_2SO_4\cdot 12H_2O$: Co, 10.17; C, 45.60; N, 14.50; H, 4.88%.

The attempt to react the dithiosulfato complex, $Na[Co(S_2O_3)_2dip_2]\cdot 7H_2O$, with KCN has failed due to the disruption of the complex. Hence, the analogous method of synthesis for *cis*-$[Co(CN)_2en_2]Cl$[7] is not suitable for obtaining the dicyanobis(2,2′-dipyridyl)-cobalt(III) complex.

Preparation of $[Co(gly)dip_2]Cl_2$.[*1] To a water solution (100 m*l*) containing 9.56 g of *trans*-$[CoCl_2dip_2]Cl$ (anhydrous) 1.6 g of glycine were added, and the mixture was heated on a water bath (80°C) for three hours. When the reaction was over, the solution was further concentrated *in vacuo* with a rotatory evaporator

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[5] Independent of this work, another method of preparation has already appeared in R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nucl. Chem.*, **1**, 341 (1955).

[6] N. Maki, T. Hamazaki and S. Sakuraba, This Bulletin, **41**, 1735 (1968).

[7] P. R. Rây and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).

[*1] gly=a glycinato ligand, $NH_2CH_2COO^-$

below 50°C. Into the deep-violet viscous liquid thus obtained there were then stirred, in small portions, 50 m*l* of ethanol containing 30% ether. Violet or almost black powders were thus obtained; they were stocked in the vacuum desiccator over concentrated sulfuric acid. The purifications were carried out in the usual manner, *i.e.*, by the addition of ethanol and ether to a water solution of the complex, since the solubility of the complex in water is quite large. The complex is hygroscopic. The absorption spectrum in the visible and ultraviolet regions agrees with that obtained by Murakami *et al.*[8] Found: Co, 11.31; C, 51.09; N, 13.37; H, 3.80%. Calcd for $[Co(gly)dip_2]Cl_2$: Co, 11.42; C, 51.18; N, 13.57; H, 3.90%.

The carbonato complexes, $[Co(CO_3)dip_2]Cl \cdot 3H_2O$ and $[Co(CO_3)dip_2]NO_3 \cdot 5H_2O$, were prepared according to the directions of Jaeger and van Dijk.[9] Found: Co, 11.03; C, 48.51; N, 10.70; H, 4.09%. Calcd for $[Co(CO_3)dip_2]Cl \cdot 3H_2O$: Co, 11.32; C, 48.43; N, 10.76; H, 4.26%.

Found: Co, 10.04; C, 43.11; N, 11.93; H, 4.58%. Calcd for $[Co(CO_3)dip_2]NO_3 \cdot 5H_2O$: Co, 10.10; C, 43.24; N, 12.01; H, 4.49%.

The 2,2′-dipyridyl reagent used was synthesized according to the method of Badger and Sasse.[10] Namely, the pyridines undergo condensation in the presence of Raney nickel to yield 2,2′-dipyridyl. As a by-product, 2,2′,2′′-terpyridyl (black powder) was obtained. The crude dipyridyl was purified by sublimations.

Preparation of $[Co(NO_2)_2phen_2]Cl \cdot 4H_2O$. Analogously to the case of the dipyridyl complex, a solution (100 m*l*) of *trans*-$[CoCl_2phen_2]Cl \cdot 4H_2O$ (5.98 g) was treated with 1.8 g of KNO_2 at 80°C for half an hour. The product was recrystallized from hot water containing acetic acid. Found: Co, 9.42; C, 46.83; N, 13.55; H, 4.02%. Calcd for $[Co(NO_2)_2phen_2]Cl \cdot 4H_2O$: Co, 9.52; C, 46.58; N, 13.58; H, 3.91%.

Preparation of $[Co(CO_3)phen_2]Cl \cdot 5H_2O$. A solution (150 m*l*) of *trans*-$[CoCl_2phen_2]Cl \cdot 4H_2O$ (5.98 g) was treated with 1.4 g of K_2CO_3 at 80°C for fifteen minutes. Orange-red crystals were thus obtained.[11] Found: Co, 9.80; C, 50.00; N, 9.29; H, 4.42%. Calcd for $[Co(CO_3)phen_2]Cl \cdot 5H_2O$: Co, 9.74; C, 49.64; N, 9.26; H, 4.33%.

Preparation of $K[Co(SO_3)_2phen_2] \cdot 5H_2O$. By treating *trans*-$[CoCl_2phen_2]Cl \cdot 4H_2O$ (5.98 g) with 3.2 g of K_2SO_3 in 100 m*l* of water at 60°C, lustrous brown crystals were obtained. The product was purified by recrystallization from hot water below 60°C. Found: Co, 8.40; C, 40.81; N, 8.01; H, 3.87%. Calcd for $K[Co(SO_3)_2phen_2] \cdot 5H_2O$: Co, 8.32; C, 40.68; N, 7.91; H, 3.70%.

Preparation of $[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$. Analogously to the case of the dicyano-bis(2,2′-dipyridyl) cobalt(III) complex, 20 g of *trans*-$[CoCl_2phen_2]NO_3$ were treated with 15 g of AgCN in 500 m*l* of distilled water at 70—80°C for three hours. The suspension was filtered, and the filtrate was concentrated by evaporation. When the solution was then allowed to stand, silky yellow crystals deposited on the wall of the beaker. The complex was stored in the vacuum desiccator over silica gel.[12] Found: Co, 9.11; C, 48.39; N, 15.17; H, 4.67%. Calcd for $[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$: Co, 9.19; C, 48.68; N, 15.29; H, 4.40%.

The chloride of the complex was obtained by treating the nitrate with a solution of KCl, because the chloride of the complex is less soluble in water than the nitrate. Found: Co, 10.08; C, 54.07; N, 14.66; H, 4.52%. Calcd for $[Co(CN)_2phen_2]Cl \cdot 4H_2O$: Co, 10.18; C, 53.95; N, 14.52; H, 4.18%.

Preparation of $[Co(bathophen)_3]Cl_3$ (anhydrous). To a suspension (50 m*l*) of $[CoCl(NH_3)_5]Cl_2$[13] (0.25 g) there were added 1.1 g of bathophenanthroline,*2 and the mixture was heated on a water bath (80—85°C) for an hour. The starting complex dissolved slowly in solution and reacted, evolving ammonia, to yield the tris(bathophenanthroline)cobalt(III) complex. The product was purified by recrystallizations in ethanol, since the complex is more soluble in ethanol than in water. The complex was dried out *in vacuo* on concentrated sulfuric acid before the elementary analyses. Found: Co, 4.95; C, 74.48; N, 7.03; H, 4.33%. Calcd for $[Co(bathophen)_3]Cl_3$: Co, 5.07; C, 74.39; N, 7.23; H, 4.16%.

Preparation of $[Co\ trip_2]Cl_3 \cdot 7H_2O$. Quite analogously to the previous case, the bis(2,2′,2′′-terpyridyl)cobalt(III) chloride was prepared directly from the pentamminecobalt(III) complex. Namely, the suspension (80 m*l*) of $[CoCl(NH_3)_5]Cl_2$ (0.54 g) in a 50% ethanol-water solution was refluxed for ten hours with 1.05 g of terpyridyl in a flask equipped with a reflux condenser. Lustrous brown crystals separated from the solution when the reaction was over. Found: Co, 7.83; C, 47.44; N, 10.96; H, 4.91%. Calcd for $[Co\ trip_2]Cl_3 \cdot 7H_2O$: Co, 7.78; C, 47.54; N, 11.09; H, 4.79%. The absorption spectrum agreed with that of the complex obtained by the method of Morgan and Burstall.[14]

Preparation of $[Co(N_3)_2phen_2]N_3$. A water solution (100 m*l*) containing 5.98 g of *trans*-$[CoCl_2phen_2]Cl \cdot 4H_2O$ was treated with 1.9 g of NaN_3 dissolved in 50 m*l* of water at 70°C for half an hour. The product was recrystallized from ethanol and dried out *in vacuo* on $CaCl_2$. Found: Co, 10.92; C, 52.84; N, 33.42; H, 3.05%. Calcd for $[Co(N_3)_2phen_2]N_3$: Co, 10.81; C, 52.85; N, 33.39; H, 2.96%. The complex is more soluble in ethanol than in water.

Preparation of $Na[Co(S_2O_3)_2phen_2]$ (anhydrous). A water solution (100 m*l*) of 5.98 g of *trans*-$[CoCl_2$-

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[8] M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J.-W. Kang, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 823 (1962).

[9] F. M. Jaeger and J. A. van Dijik, *Proc. Acad. Amsterdam*, **39**, 164 (1936).

[10] G. M. Badger and W. H. Sasse, *J. Chem. Soc.*, **1956**, 616 (1956).

[11] The description of this compound is found in the following report: A. V. Ablov and S. M. Palade, *Z. neorg. Chem.*, **6**, 601 (1961).

[12] The elementary analyses reported promptly in the preliminary communication (see Ref. 6) were carried out on a sample of the anhydrous compound which had been dried out in a vacuum drying chamber at 110°C for three hours, because the crystallization water was partly lost *in vacuo* on concentrated sulfuric acid.

[13] W. A. Hynes and L. K. Yanaoski, *J. Am. Chem. Soc.*, **30**, 3053 (1938).

*2 bathophen=4,7-diphenyl-1,10-phenanthroline

[14] G. Morgan and F. H. Burstall, *J. Chem. Soc.*, **1937**, 1649.

phen$_2$]Cl·4H$_2$O was treated with 5.0 g of $Na_2S_2O_3 \cdot 5H_2O$ at room temperature. The mixture turned dark brown. To this solution there were added drop by drop under ice cooling 100 m*l* of a mixture of ethanol and ether. The brown powder which separated from the solution was filtered and washed with ethanol and ether. The product was purified in the same manner. Found: Co, 8.92; C, 43.38; N, 8.57; H, 2.61%. Calcd for $Na[Co(S_2O_3)_2phen_2]$: Co, 8.84; C, 43.24; N, 8.41; H, 2.42%. The complex is unstable in solution and tends to decompose in itself, evolving hydrogen sulfide, thus producing the metallic cobalt.

Preparation of $[Co(bathophen)_3]Cl_2 \cdot 8H_2O$. The water solution (30 m*l*) of 0.13 g of hexaquocobalt(II) chloride was treated with 1.0 g of bathophenanthroline at 80°C for five minutes. On cooling, brown crystals were obtained. Found: Co, 4.58; C, 67.95; N, 6.58; H, 5.24%. Calcd for $[Co(bathophen)_3]Cl_2 \cdot 8H_2O$: Co, 4.64; C, 68.03; N, 6.61; H, 5.08%. The complex is more soluble in ethanol than in water.

Preparation of $[Co\,dip_3]Cl_2 \cdot 3H_2O$. To a 30% methanol-water solution (100 m*l*) in which 5 g of $[CoCl(NH_3)_5]Cl_2$ had been suspended, 9.4 g of 2,2′-dipyridyl were added; the mixture was then refluxed on a water bath for eight hours. The crude product was recrystallized from hot water containing acetic acid. Found: Co, 8.52; C, 52.43; N, 12.41; H, 4.51%. Calcd for $[Co\,dip_3]Cl_3 \cdot 3H_2O$: Co, 8.59; C, 52.38; N, 12.22; H, 4.40%.

Preparation of $[Co\,phen_3]Cl_3 \cdot 7H_2O$. A suspension (130 m*l*) of a 30% methanol-water solution containing 5 g of $[CoCl(NH_3)_5]Cl_2$ and 12.1 g of 1,10-phenanthroline was refluxed on a water bath for ten hours. Dark brown crystals were thus obtained. Found: Co, 6.97; C, 51.98; N, 9.98; H, 4.80%. Calcd for $[Co\,phen_3]Cl_3 \cdot 7H_2O$: Co, 7.08; C, 51.97; N, 10.10; H, 4.60%.

Preparation of $[Co(SCN)_2phen_2]NCS$ (anhydrous). To a hot water solution (50 m*l*) containing 1.2 g of *trans*-$[CoCl_2phen_2]Cl \cdot 4H_2O$ there were added 1.1 g of KNCS dissolved in 50 m*l* of water, and the mixture was heated on a water bath for an hour. Dark brown precipitates separated from the solution, they were filtered and washed with water several times, and then with ethanol and ether. Found: Co, 9.79; C, 54.80; N, 16.72; H, 2.86%. Calcd for $[Co(SCN)_2phen_2]NCS$: Co, 9.93; C, 54.63; N, 16.52; H, 2.72%. The complex is insoluble in both water and alcohol, but soluble in dimethyl sulfoxide.

Measurement. The absorption spectra in the visible and ultraviolet regions were determined manually with a Beckmann DU spectrophotometer. The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, Model 337, equipped with a KBr-pellet.

Results and Discussion

Figure 1 shows the absorption spectra of the cobalt(III) complexes of the $[Co^{III}X_2dip_2]$-type measured in the aqueous phase except that of the thiocyanato complex. The first spin-allowed band, which is assigned to a d–d transition, shifts towards a shorter wavelength according to this order of the ligands: $S_2O_3^{2-}$, SCN^-, N_3^-, CO_3^{2-}, gly$^-$, dip, NO_2^-, CN^-. This order of the ligands agrees with that of the spectrochemical series[15] except for the SCN^- ligand. The absorption intensity of the first band for the $[Co(SCN)_2dip_2]^+$ ion is seen to be abnormally larger than those of the corresponding 2,2′-dipyridyl cobalt(III) complexes of the nitrogen-hexacoordinated $[Co\,N_6]$-type. This fact may be explained as being due to the hyperchromic effect of the sulfur-bonded ligand, SCN^-. As far as the cobalt(III) complexes are concerned, the rhodanato-ligand has been well known to be bound to the central cobalt(III) ion by the nitrogen atom; indeed, the isothiocyanatocobalt(III) complexes are more familiar than the thiocyanato complexes, in which the SCN^- ligand is bound by the sulfur atom.

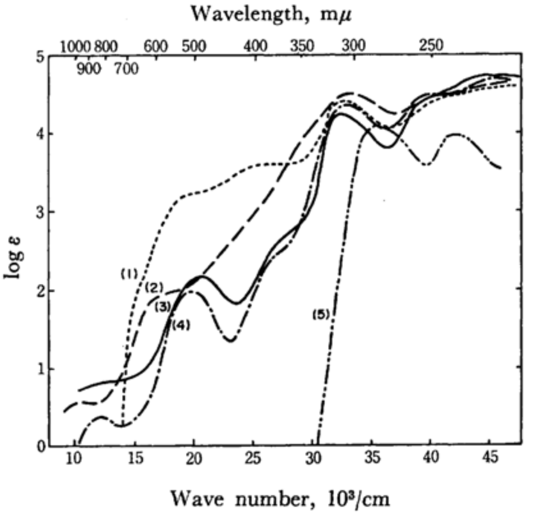

Fig. 1. The absorption spectra of the bis(2,2′-dipyridyl)cobalt(III) complexes of the $[CoX_2\,dip_2]$-type: (1) ---- $[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$ in methanol; (2) —— $Na[Co(S_2O_3)_2dip_2] \cdot 7H_2O$ in methanol; (3) —— $[Co(gly)dip_2]Cl_2$; (4) —— $[Co(CO_3)dip_2]Cl \cdot 3H_2O$; (5) —·— 2,2′-dipyridyl in ethanol.

Several years ago, however, the pentacyanocobaltate(III) complex, $K_3[Co(CN)_5SCN]$, was described as belonging to the group of thiocyanato complexes.[16] Recently, Stotz *et al.*[17] have reported the synthesis of an isothiocyanato complex, $K_3\,[Co(CN)_5NCS]$ (a linkage-isomer).

The dithiocyanato-bis(2,2′-dipyridyl) and bis(1,10-phenanthroline)cobalt(III) complexes, $[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$ and $[Co(SCN)_2phen_2]NCS$, prepared here have also been ascertained to

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[15] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

[16] N. Maki, J. Fujita and R. Tsuchida, *Nature*, **183**, 458 (1959).

[17] I. Stotz, W. K. Wilmarth and A. Haim, *Inorg. Chem.*, **7**, 1250 (1968).

TABLE 1. THE ABSORPTION MAXIMA OF THE COBALT(III) COMPLEXES WITH 2,2'-DIPYRIDYL AND 1,10-PHENANTHROLINE

Compound	I-band	II-band	III-band	IV-band	V-band
$\mathrm{Na[Co(S_2O_3)_2dip_2]\cdot 7H_2O}$	*ca.* 18(1.98)*	*ca.* 23(2.50)*	33.0(4.49)	40.0(4.48)	
$\mathrm{[Co(SCN)_2dip_2]ClO_4\cdot 2H_2O}$	*ca.* 19(3.18)*	26.3(3.60)	32.8(4.40)	——*	
$\mathrm{[Co(N_3)_2dip_2]N_3\cdot 2H_2O}$	19.4(2.60)	*ca.* 30(3.99)*	33.1(4.43)	*ca.* 41(4.37)	47.2(4.74)
$\mathrm{[Co(CO_3)dip_2]Cl\cdot 3H_2O}$	20.0(2.01)	*ca.* 27(2.5)*	32.8(4.35)	40.5(4.80)	
$\mathrm{[Co(gly)dip_2]Cl_2}$	20.8(2.18)	*ca.* 28(2.6)*	32.2(4.24)	45.0(4.75)	
$\mathrm{[Co\ dip_3]Cl_3\cdot 3H_2O}$	22.1(1.82)	*ca.* 29(3.14)*	32.6(4.48)	*ca.* 41(4.80)	
$\mathrm{[Co(NO_2)_2dip_2]Cl\cdot 5H_2O}$	22.3(2.30)	*ca.* 29(3.9)*	33.0(4.68)	40.7(4.84)	
$\mathrm{[Co(CN)_2dip_2]NO_3\cdot 7H_2O}$	*ca.* 24(2.02)*	*ca.* 27(2.34)*	31.8(4.32)	32.9(4.34)	41.0(4.34)
$\mathrm{Na[Co(S_2O_3)_2phen_2]}$	*ca.* 18(2.16)*	*ca.* 28(4.0)*	——*	36.3(4.77)	43.3(4.82)
$\mathrm{[Co(SCN)_2phen_2]NCS}$	*ca.* 19(2.98)*	*ca.* 26(3.42)*	*ca.* 29(3.55)*	*ca.* 32(4.08)	*ca.* 34(4.24)
$\mathrm{[Co(N_3)_2phen_2]N_3}$	18.9(2.43)	*ca.* 28(3.80)*	——*	36.3(4.48)	——**
$\mathrm{K[Co(SO_3)_2phen_2]\cdot 5H_2O}$	*ca.* 19(2.26)*	*ca.* 28(3.67)*	——*	36.3(4.49)	45.7(4.71)
$\mathrm{[Co(CO_3)phen_2]Cl\cdot 5H_2O}$	19.6(2.04)	*ca.* 26.7(2.40)*	*ca.* 29(3.2)*	36.3(4.67)	——**
$\mathrm{[Co\ phen_3]Cl_3\cdot 7H_2O}$	*ca.* 21.5(2.0)*	27.9(3.54)		36.3(4.90)	44.7(5.16)
$\mathrm{[Co(NO_2)_2phen_2]Cl\cdot 4H_2O}$	*ca.* 23(2.60)*	*ca.* 29(3.35)*	*ca.* 32(3.90)*	36.3(4.58)	*ca.* 40(4.8)
$\mathrm{[Co(CN)_2phen_2]NO_3\cdot 6H_2O}$	*ca.* 24(2.14)*	*ca.* 27(2.56)*	28.7(3.30)	*ca.* 31(3.49)*	*ca.* 34(4.22)* 36.8(4.77)
$\mathrm{[Co\ trip_2]Cl_3\cdot 7H_2O}$	22.5(2.53)	28.1(4.04)	29.3(4.18)	35.7(4.48)	47.0(4.76)
$\mathrm{[Co(bathophen)_3]Cl_3}$	*ca.* 23(2.3)*	*ca.* 25.8(3.3)*	*ca.* 29(4.25)*	35.2(5.21)	46.7(5.06)
2,2'-dipyridyl				35.5(4.08)	42.3(3.96)
1,10-phenanthroline		31.0(2.81)	38.0(4.51)	43.3(4.82)	44.3(4.68)
2,2',2''-terpyridyl			35.5(4.30)	43.0(4.32)	
bathophenanthroline			*ca.* 32(4.14)	36.1(4.61)	45.4(4.60)

* Shoulder band; ** Broad band; Unit=Wave number 10^3/cm (log ε)

be bound by the sulfur atom on the evidence of the absorption spectra in the far-infrared regions.

Table 1 shows the numerical data of the absorption maxima and intensities (log ε) of the cobalt(III) complexes with 2,2'-dipyridyl and 1,10-phenanthroline.

Table 2 summarizes the frequencies of the C–N and C–S stretching-vibrations for the rhodanato-cobalt(III) complexes. The values of the stretching-vibration, C–S, for the 2,2'-dipyridyl and 1,10-phenanthroline complexes fall within the range, 690—720 cm^{-1}, characteristic of sulfur-bonded thiocyanato-complexes, while the values for the usual isothiocyanato-ammine and amine complexes come within the range, 780—860 cm^{-1}, characteristic of nitrogen-bonded isothiocyanato-complexes.[18]

TABLE 2. THE FREQUENCIES OF THE C–N AND C–S STRETCHING VIBRATIONS FOR THE THIOCYANATO- AND ISOTHIOCYANATO-COBALT(III) COMPLEXES IN A SOLID STATE

Compound	C–N	C–S
$\mathrm{[Co(SCN)_2dip_2]ClO_4\cdot 2H_2O}$	2080_{s}	705_{w}
$\mathrm{[Co(SCN)_2dip_2]Cl\cdot 3H_2O}$	2075_{s}	704_{w}
$\mathrm{[Co(SCN)_2dip_2]NCS\cdot 5/2H_2O}$	2070_{s}	705_{w}
$\mathrm{K_3[Co(SCN)(CN)_5]}$	2110_{s}	719_{w}
$\mathrm{[Co(SCN)_2phen_2]NCS}$	2060_{s}	695_{w}
cis-$\mathrm{[Co(NCS)_2en_2]Cl\cdot H_2O}$	2110_{m} 2060_{s}	803_{w} 788_{m}
trans-$\mathrm{[Co(NCS)_2en_2]Cl\cdot H_2O}$	2120_{s} 2080_{w}	788_{m}
$\mathrm{[Co(NCS)(NH_3)_5]Cl_2}$	2140_{s}	850_{m} 808_{m}
$\mathrm{[Co(NCS)(NH_3)_5]SO_4\cdot 2H_2O}$	2140_{s}	848_{m} 803_{m}

s=strong; m=medium; w=weak

The linkage-isomers of the rhodanato-complexes can be distinctly distinguished from each other on the evidence of their polarographic behavior in solution. The isothiocyanato-complexes, such as *trans*-$\mathrm{[Co(NCS)_2en_2]Cl\cdot H_2O}$ and $\mathrm{[Co(NCS)(NH_3)_5]Cl_2}$, exhibit the strong adsorption on the surface of the dropping mercury electrode (DME) which was pointed out by Tanaka *et al.*[19] as being due to interaction between the naked sulfur and the mercury of the electrode, while the thiocyanato complexes, which have no naked sulfur on the outside of the coordination sphere, show no adsorption at the DME. The adsorptions of *trans*-$\mathrm{[Co(NCS)_2en_2]^+}$ and $\mathrm{[Co(NCS)(NH_3)_5]^{2+}}$ ions were observed to exist at the range +0.2—−0.5 V *vs.* SCE on the electrocapillary curves and on the current-time curves. No adsorptions were observed for the $\mathrm{[Co(SCN)_2dip_2]^+}$ ion on the

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[18] A. Turco and C. Pecile, *Nature,* **191**, 66 (1961).

[19] N. Tanaka, E. Kyuno, G. Sato and R. Tamamushi, *J. Phys. Chem.*, **66**, 2706 (1962); N. Tanaka, T. Ito and R. Tamamushi, This Bulletin, **37**, 1430 (1964).

DME in the 80% methanol-water solution containing 1 M lithium chloride.

The 2,2′-dipyridyl and 1,10-phenanthroline are considered to have a strong π-bonding character as ligands in the sphere of coordination; *i. e.,* these are considered to have the nature of the "back coordination." In such mixed ligand cobalt(III) complexes, the rhodanate ion is interpreted as having a tendency to coordinate to the cobalt(III) ion by means of the sulfur atom rather than by means of the nitrogen atom, since the six coordinate bonds also tend, in general, to resemble each other in the nature of bonding as far as possible within the same coordination sphere.

Figure 2 shows the absorption spectrum of the bis(2,2′,2′′-terpyridyl)cobalt(III) complex, [Co-trip$_2$]Cl$_3$·7H$_2$O, in comparison with that of [Co-dip$_3$]Cl$_3$·3H$_2$O.20) The first absorption band is located at a shorter wavelength than that of the corresponding tris(2,2′-dipyridyl)cobalt(III) ion.

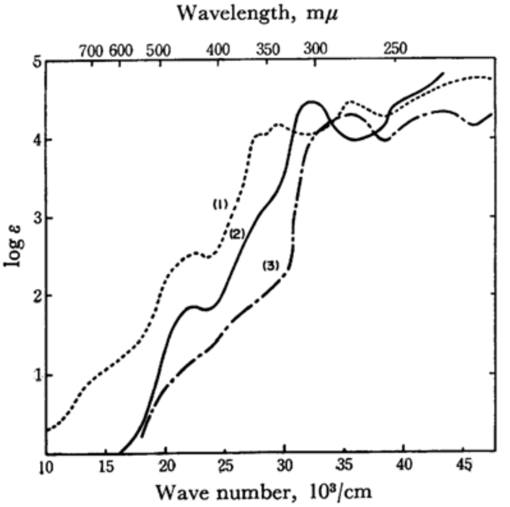

Fig. 2. The absorption spectra of the bis(2,2′,2′′-terpyridyl)cobalt(III) complex and of its ligand only: (1) ---- [Co trip$_2$]Cl$_3$·7H$_2$O; (2) —— [Co dip$_3$]Cl$_3$·3H$_2$O; (3) —·— 2,2′,2′′-terpyridyl in ethanol.

Figure 3 shows the absorption spectra of the tris(bathophenanthroline)cobalt(III) complex and of its ligand only.

The first d–d band for the d^6-complexes of the [Co N$_6$]-type shifts to a shorter wavelength according to this order of the ligands: phen, dip, trip, bathophen.

Figure 4 shows the absorption spectra of the bis(1,10-phenanthroline)cobalt(III) complexes of the [CoX$_2$ phen$_2$]-type. The first band shifts towards a shorter wavelength in this order of the ligands: S$_2$O$_3$$^{2-}$, N$_3$$^-$, SO$_3$$^{2-}$, CO$_3$$^{2-}$, phen, NO$_2$$^-$, CN$^-$.

Figure 5 shows the absorption spectra of the dinitro-bis(2,2′-dipyridyl) and bis(1,10-phenanthroline)cobalt(III) complexes in relation to the *cis*- and *trans*-bis(ethylenediamine)cobalt(III) complexes. The d–d bands shift to a shorter wavelength according to this order of the ligands: phen, dip, en.

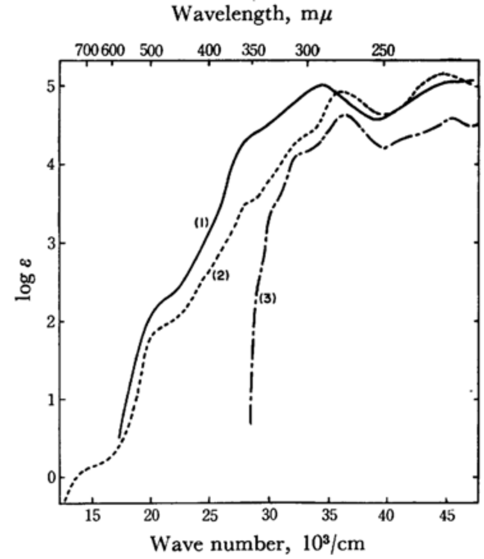

Fig. 3. The absorption spectra of tris(bathophenanthroline) and tris(1,10-phenanthroline)cobalt(III) complexes: (1) —— [Co(bathophen)$_3$]Cl$_3$ in ethanol; (2) ---- [Co dip$_3$]Cl$_3$·3H$_2$O; (3) —·— bathophenanthroline in ethanol.

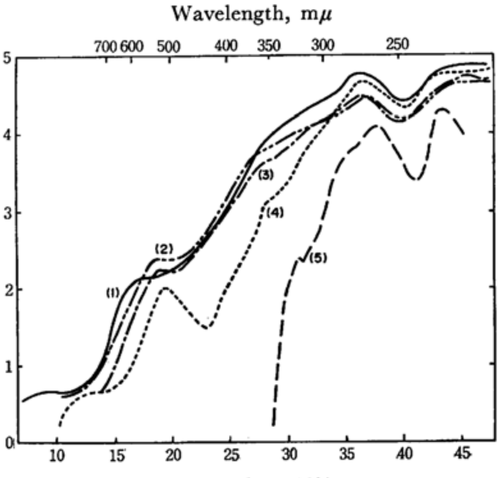

Fig. 4. The absorption spectra of the bis(1,10-phenanthroline)cobalt(III) complexes of the [CoX$_2$ phen$_2$]-type: (1) —— K[Co(S$_2$O$_3$)$_2$phen$_2$] in methanol; (2) —·– [Co(N$_3$)$_2$phen$_2$]N$_3$ in methanol; (3) —·— K[Co(SO$_3$)$_2$phen$_2$]·5H$_2$O in water; (4) ---- [Co(CO$_3$)phen$_2$]Cl·5H$_2$O in water; (5) - - - 1,10-phenanthroline in ethanol.

Figure 6 shows the absorption spectra of the dicyano-bis(2,2′-dipyridyl) and bis(1,10-phenanthroline)cobalt(III) complexes and their respective

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20) K. Yamasaki, This Bulletin, **12**, 390 (1937).

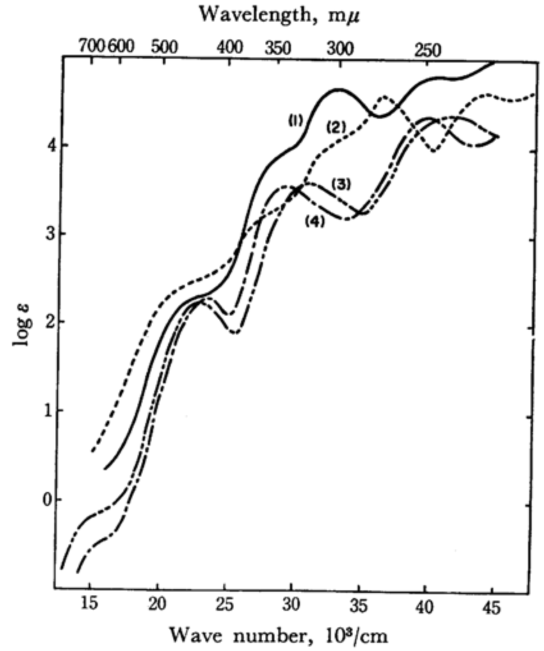

Fig. 5. The absorption spectra of the dinitrocobalt(III) complexes obtained in water: (1) —— $[Co(NO_2)_2dip_2]Cl \cdot 5H_2O$; (2) - - - $[Co(NO_2)_2phen_2]Cl \cdot 4H_2O$; (3) —–— *trans*-$[Co(NO_2)_2 \cdot en_2]ClO_4$; (4) —–— *cis*-$[Co(NO_2)_2en_2]ClO_4$.

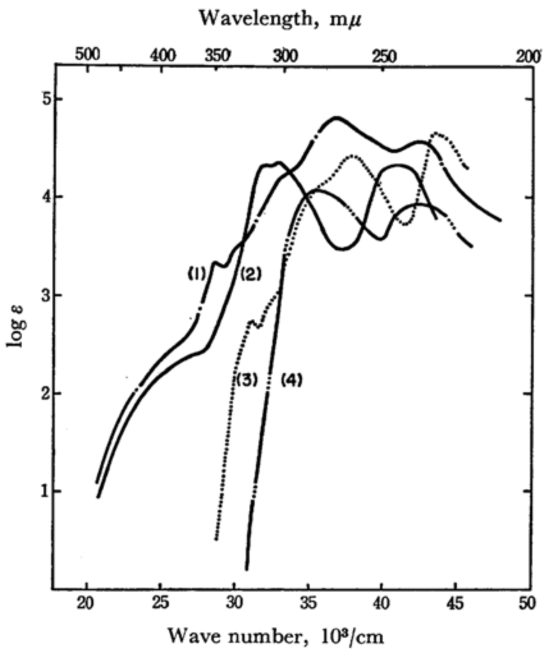

Fig. 6. The absorption spectra of the dicyanocobalt(III) complexes with 2,2′-dipyridyl and 1,10-phenanthroline: (1) —·— *cis*-$[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$; (2) —— *cis*-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$; (3) ······ 1,10-phenanthroline in ethanol; (4) —···— 2,2′-dipyridyl in ethanol.

ligands only. The spectrum of the latter agrees with that reported by Favini *et al.*[21] as a whole, but it does not necessarily coincide in detail, especially in the matter of a small peak present at around 27—29 kK.[*3]

The author is indebted to Mr. Taihei Hamazaki for his experimental assistance of preparing the dicyano cobalt(III) complexes. The author also wishes to express his appreciation to the late Professor Ryutaro Tsuchida and Professor Shukichi Sakuraba for their encouragements and discussions throughout this work.

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[21] G. Favini and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 155 (1958); G. Favini and E. Paglia, Proceedings of the 4th I. C. C. C., Rome (1957), ed. by L. Cambi, Pergamon Press, New York, N. Y. p. 155.

[*3] No description of the preparation of $[Co(CN)_2phen_2]OH \cdot 7H_2O$ has been found, but the complex might have been prepared by treating the praseo-salt with KCN in solution.