A Thiocyanato Cobalt(III) Complex: $[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$*

Nobufumi MAKI and Shukichi SAKURABA

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

(Received November 11, 1968)

As far as the cobalt(III) complexes are concerned, the rhodanato-ligand has been well known to be bound to the central cobalt(III) atom by the nitrogen atom; ideed, the isothiocyanato-cobalt(III) complexes have been more familiar than the thiocyanato-ones, in which the ligand(SCN^-) is bound by the sulfur atom.

Several years ago, the pentacyanocobaltate(III) complex, $K_3[Co(CN)_5SCN]$, was described as belonging to the group of the thiocyanato-complexes.[2] Recently, Stotz *et al.*[2] have reported the synthesis of the isothiocyanato complex, $K_3[Co(CN)_5NCS]$.

In the present communication, the dithiocyanatobis(2,2′-dipyridyl)cobalt(III) complex (a new complex) has been prepared and has been ascertained to be bound by the sulfur atom on the evidence of the absorption spectrum in the visible and infrared regions.

Preparation of $[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$. A water solution (100 m*l*) containing 0.46 g of KNCS was stirred, drop by drop, into 300 m*l* of a water solution of *trans*-$[CoCl_2dip_2]Cl$[3] (1.0 g). First, a green precipitate separated from the solution, and then, it turned dark brown. The product was filtered and washed with water several times. The crude complex was twice recrystallized from a hot 60% ethanol-water mixture. Ruby-like red crystals were thus obtained. Found: Co, 9.81; C, 46.90; N, 16.62; H, 3.70%. Calcd for $[Co(SCN)_2dip_2]NCS \cdot 5/2H_2O$: Co, 9.98, C, 46.78; N, 16.60; H, 3.58%.

The perchlorate of the complex was obtained by treating the thiocyanate with 10% $HClO_4$ at 40°C. Found: Co, 9.28; C, 42.30; 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%.

The complex is insoluble in water but soluble in ethanol.

Figure 1 shows the absorption spectra of the dithiocyanato-cobalt(III) and its related complexes with 2,2′-dipyridyl. The absorptivity of the first spin-allowed band for the $[Co(SCN)_2dip_2]^+$ ion is seen to be considerably larger than those of the other complexes of the $[Co\,N_6]$ type. This fact may well be interpreted as being due to the hyperchromic effect of the sulfur-bonded ligand, SCN^-.

The infrared evidence is summarized in Table 1. The values of the C–S stretching-vibration fall within the 690—720 cm^{-1} range characteristic of sulfur-bonded thiocyanato-complexes, while the values for the usual isothiocyanato-ammine and -amine complexes come within the 780—860 cm^{-1} range characteristic of nitrogen-bonded isothiocyanato-complexes.[4]

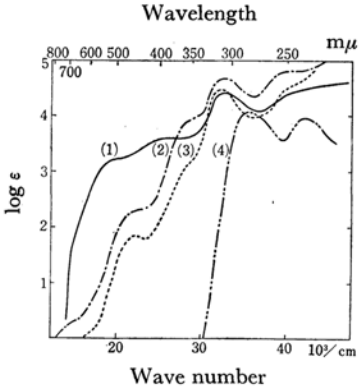

Fig. 1. The absorption spectra of the cobalt(III) complexes with 2,2′-dipyridyl:
(1) —— $[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$; (2) —·— $[Co(NO_2)_2dip_2]Cl \cdot 5H_2O$; (3) ------ $[Co\,dip_3](ClO_4)_3 \cdot 3H_2O$; (4) —·-·— 2,2-dipyridyl.

TABLE 1. 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
$[Co(SCN)_2dip_2]ClO_4 \cdot 2H_2O$	2080 s	718 m
$[Co(SCN)_2phen_2]NCS$	2060 s	714 m
cis-$[Co(NCS)_2en_2]Cl \cdot H_2O$	2110 m 2060 s	803 w 788 m
trans-$[Co(NCS)_2en_2]Cl \cdot H_2O$	2120 m 2080 w	788 m

phen=1,10-phenanthroline s=strong; m=medium; w=weak

---

* dip=2,2′-dipyridyl.

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

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

3) F. M. Jaeger and J. A. van Dijk, *Z. Anorg. Allgem. Chem.*, **227**, 273 (1936).

4) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).