BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (2), 533—534 (1977)

Absorption Spectra of Bis(sulfito) and Bis(thiosulfato) Complexes of Cobalt(III)

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(Received September 27, 1976)

Synopsis. It has been shown that the near ultraviolet "specific band" of a *trans* isomer of bis(sulfito) or bis(thiosulfato) cobalt(III) complexes is more bathochromic than the corresponding *cis* isomer. The *cis*-$[Co(SO_3)_2(en)_2]^-$ complex was optically resolved and its circular dichroism spectrum reported.

This note deals with "specific bands" of the *cis-trans* isomers of bis(aniono-*S*) cobalt(III) complexes, *i.e.*, bis(sulfito) and bis(thiosulfato) ones. It has been shown that the "specific bands" due to the aniono-*S* or aniono-*N* ligands such as SO_3^{2-} or NO_2^- are mostly of charge-transfer character,[1,2] but we retain the old name for convenience.

There had been a confusion as to the configuration assignment of tetraamminebis(sulfito)cobaltate(III) complex, but recent crystal structure[3] and other[4] studies of the *cis* isomer have solved the problem; thus the *cis-trans* assignment of Hofmann and Jenny,[5] and of Bailar and Peppard[6] are correct, while that of one of the present authors in 1952[7] incorrect. The isomers of the corresponding bis(ethylenediamine) complexes were assigned by infrared spectral[8] and lability[9] studies, and the result has been confirmed by the optical resolution of the *cis* isomer in the present study.

Results and Discussion

Figure 1 shows the visible and ultraviolet absorption spectra of bis(sulfito) and bis(thiosulfato) complexes, of which those of the *trans* bis(sulfito) complexes were measured in 0.1 M aqueous Na_2SO_3 solution to prevent the aquation due to the strong *trans* effect of sulfito ligand.[4] Table 1 presents the data of specific bands of the bis(aniono-*S*) complexes together with those of bis(aniono-*N*) ones for the purpose of comparison, and shows that the specific band of a *trans* isomer is in a longer wavelength region than that of the *cis* isomer is. It is remarkable that the specific bands of the *cis* isomers of tetraamminebis(sulfito)- and bis(ethylenediamine)-bis(sulfito) complexes split into distinct components. The *cis* isomer of bis(ethylenediamine)bis(thiosulfato) complex also shows a tendency to split in the specific band region (Fig. 1). A probable splitting of the specific band has been suggested for the *cis* isomers of dinitro-, diazido-, or diisothiocyanatobis(ethylenediamine) cobalt(III) complexes from their circular dichroism (CD) measurements.[1] Now, the *cis* isomer of $[Co(SO_3)_2(en)_2]^-$ was optically resolved and the CD spectrum is shown in Fig. 1. Since the major CD component of the first d-d transition in the longer wavelength region is negative for the obtained isomer, the absolute configura-

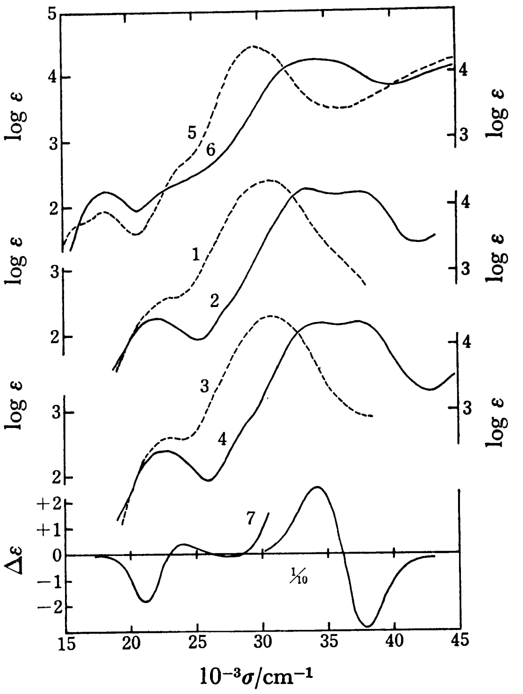

Fig. 1. Absorption spectra of (1) *trans* and (2) *cis* isomers of $[Co(SO_3)_2(NH_3)_4]^-$; (3) *trans* and (4) *cis* isomers of $[Co(SO_3)_2(en)_2]^-$; (5) *trans* and (6) *cis* isomers of $[Co(S_2O_3)_2(en)_2]^-$; and CD spectrum of (7) $(-)^{CD}_{475}$-*cis*-$[Co(SO_3)_2(en)_2]^-$.

Table 1. The specific absorption bands of geometrical isomers of bis(aniono-*S*) and bis(aniono-*N*) cobalt(III) complexes

(Wave numbers are given in 10^3 cm^{-1}, and log ε values in parentheses).

Complex	*cis* isomer	*trans* isomer	Ref.
$[Co(SO_3)_2(NH_3)_4]^-$	34.13(4.21) 37.59(4.19)	30.68(4.38)	
$[Co(SO_3)_2(en)_2]^-$	34.48(4.35) 37.25(4.36)	308.6(4.46)	
$[Co(SO_3)_2(CN)_4]^{5-}$	38.65(4.27)	38.00(4.10)	10
$[Co(S_2O_3)_2(en)_2]^-$	35.34(4.20)	29.94(4.43)	
$[Co(NO_2)_2(NH_3)_4]^+$	30.86(3.62)	28.82(3.68)	11
$[Co(NO_2)_2(en)_2]^+$	31.1 (3.56)	29.5 (3.56)	12
$[Co(NO_2)_2(R,R\text{-chxn})_2]^+$	30.9 (3.65)	29.2 (3.51)	13
$[Co(NO_2)_2(tn)_2]^+$	30.3 (3.67)	28.6 (3.49)	14
$[Co(N_3)_2(NH_3)_4]^+$	32.98(4.01)	29.68(4.14)	15
$[Co(N_3)_2(en)_2]^+$	33.1 (4.06)	30.0 (4.13)	12
$[Co(NCS)_2(en)_2]^+$	32.5 (3.46)	31.6 (3.49)	12
$[Co(NCS)_2(tn)_2]^+$	29.4 (3.44)	28.8 (3.52)	16, 17

tn=trimethylenediamine; *R*, *R*-chxn=(1*R*, 2*R*)-diaminocyclohexane.

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tion is Δ from a criterion of McCaffery *et al.*[18] The CD of Δ isomer shows a pattern of positive and then negative in the order of increasing energy in the specific band region. This sign pattern coincides well with those found for dinitro-, diazido-, and diisothiocyanatobis-(ethylenediamine) complexes in this region.[1]

Experimental

Preparations. *(1)* cis- *and* trans-*$M[Co(SO_3)_2(NH_3)_4]$* *(M=Na, or NH_4)*: The *cis* isomer was prepared by the method of Bailar and Peppard.[6] Absorp. max. 10^{-3} σ/cm^{-1} (log ε): 22.12 (2.27), 34.13 (4.21), 37.59 (4.19). Found: H, 6.01; N, 20.12%. Calcd for *cis*-$NH_4[Co(SO_3)_2(NH_3)_4]\cdot 2.5H_2O$: H, 6.05; N, 19.99%.

To the filtrate from the *cis* isomer was added twice the volume of methanol and the resulting yellowish brown *trans* isomer was recrystallized from 0.1 M aqueous Na_2SO_3 and dried in air. Absorp. max. 10^{-3} σ/cm^{-1} (log ε): 23 sh (2.60), 30.68 (4.38). Found: H, 5.00; N, 14.99; S, 17.42%. Calcd for *trans*-$Na[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$: H, 4.99; N, 15.38; S, 17.60%.

(2) cis- *and* trans-*$Na[Co(SO_3)_2(en)_2]$*: The isomers were prepared as in literature.[19] Absorp. max 10^{-3} σ/cm^{-1} (log ε): *cis* 22.73 (2.40), 34.48 (4.35), 37.25 (4.36); *trans* 23.10 (2.62), 30.86 (4.46). Found: C, 9.00; H, 4.23; N, 10.38%. Calcd for *cis*-$Na[Co(SO_3)_2(en)_2]\cdot NaClO_4\cdot 3H_2O$: C, 8.91; H, 4.12; N, 10.40%. Found: C, 13.21; H, 4.63; N, 15.59%. Calcd for *trans*-$Na[Co(SO_3)_2(en)_2]$: C, 13.26; H, 4.46; N, 15.46%.

(3) Optical Resolution of cis-*$Na[Co(SO_3)_2(en)_2]\cdot NaClO_4$*: The resolving agent $(+)_{589}$-$[Co(ox)(en)_2]I$ (2.7 g, 6.0×10^{-3} mol) was suspended in 10 cm^3 of water, and converted into the acetate by treating with silver acetate (1.0 g, 6.0×10^{-3} mol). This solution was added to a solution of *cis*-$[Co(SO_3)_2(en)_2]\cdot NaClO_4\cdot 3H_2O$ (1.6 g, 3.0×10^{-3} mol) in 10 cm^3 of water. Red crystals, $(+)_{589}$-$[Co(ox)(en)_2]ClO_4$, appeared immediately. After filtration, the filtrate was evaporated at about 20 °C in a rotary evaporator to about half the initial volume. During the process, another crop of the red crystals (perchlorate of the resolving agent) precipitated, and this was filtered off. The filtrate was kept for a week in a refrigerator, when the less soluble reddish brown diastereomer gradually crystallized out. The diastereomer was converted into the sodium salt by using a cation exchanger SP-Sephadex C-25 (Na^+ form), and the eluate was evaporated. Sodium perchlorate was added to the concentrated solution to precipitate the active complex. CD extrema 10^{-3} σ/cm^{-1} ($\Delta\varepsilon$): 21.05 (-1.83), 23.81 ($+0.42$), 27.66 (-0.07), 34.25 ($+25.7$), 38.02 (-28.7). Found: C, 10.13; H, 4.46; N, 11.81%. Calcd for $Na[Co(SO_3)_2(en)_2]\cdot 2.5H_2O\cdot 0.5NaClO_4$: C, 10.25; H, 4.53; N, 11.96%.

(4) cis- *and* trans-*$M[Co(S_2O_3)_2(en)_2]$* *(M=Na or Li)*: Ammonium thiosulfate (0.5 g) dissolved in 1 cm^3 of water was added to 10 cm^3 of dimethyl sulfoxide. To this solution 1 g of *cis*-$[CoCl_2(en)_2]Cl$ was added and the mixture was stirred for half an hour at about 70 °C; then this was cooled to room temperature. The precipitated dark green crystals were filtered off, and the filtrate was poured into an anion exchanger column (QAE-Sephadex A-25, Cl^- form; ϕ 2.6 cm, l 30 cm). The column was washed with water and eluted with 0.07 M aqueous LiCl or NaCl solution. A dark green (*trans*)[20] and a brownish violet (*cis*) band were eluted in this order. The *cis* eluate was condensed below 20 °C, and isolated as the lithium salt, while the *trans* one as the sodium salt. Absorp. max. 10^{-3} σ/cm^{-1} (log ε): *trans* 16.5 sh (1.76), 18.32 (1.92), 29.94 (4.43); *cis* 18.35 (2.22), 35.34 (4.20). Found: C, 11.17; H, 3.88; N, 13.39%. Calcd for *trans*-$Na[Co(S_2O_3)_2(en)_2]$: C, 11.26; H, 3.78; N, 13.13%. Found: C, 8.50; H, 4.72; N, 9.47%. Calcd for *cis*-$Li[Co(S_2O_3)_2(en)_2]\cdot 6H_2O\cdot 1.6LiCl$: C, 8.21; H, 4.83; N, 9.57%.

Measurements. The absorption spectra were measured by a Shimadzu UV-200 Spectrophotometer in 0.1 M aqueous Na_2SO_3 solution for the *trans*(SO_3) isomers, in 3% aqueous NH_3 solution for the *cis*-$NH_4[Co(SO_3)_2(NH_3)_4]$, and in H_2O for all the other complexes. The CD spectrum was recorded on a JASCO MOE-1 Spectropolarimeter.

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