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ISOLATION OF ALL THE FIVE GEOMETRICAL AND CONFORMATIONAL ISOMERS OF BIS(ISOTHIOCYANATO)(TRIETHYLENETETRAMINE)COBALT(III) COMPLEX

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All the five geometrical and conformational isomers of bis(isothiocyanato)(triethylenetetramine)cobalt(III) ion were isolated. Each isomer was identified on the basis of its chemical properties, ^{13}C NMR spectrum and absorption spectrum.

Triethylenetetramine ("trien") is one of the well-known ligands, and the stereochemistry of its complexes has been studied in detail. As Fig. 1 shows, five geometrical and conformational isomers are possible for $[CoX_2(trien)]^{n+}$ (X=unidentate ligand). However, no report has been found on the isolation of all such isomers. Except for some trien complexes containing amino acidate ions,$^{1)}$ only diaqua complex was known to exist as the cis-β-RS,SR isomer which was assumed to be present in solution upon the aquation and isomerization of trans-SS-$[CoCl_2(trien)]^+$.$^{2)}$ Moreover, $[Co(CN)_2(trien)]^+$ was the only complex which possessed the trans-RS conformation.$^{3)}$

Recently, we have reported the isolation of all the three possible stereoisomers of trans-$[Co(NH_3)_2(trien)]^{3+}$ $^{4)}$ which was derived from trans-$[Co(NCS)_2(trien)]^+$ by

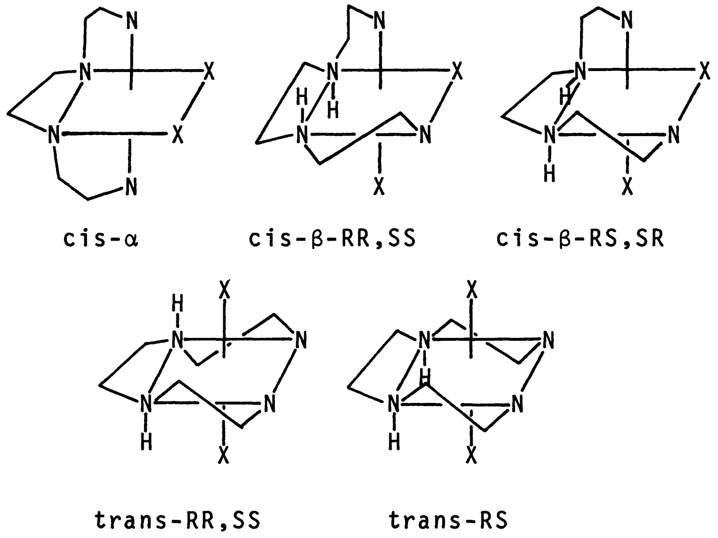
cis-α
cis-β-RR,SS
cis-β-RS,SR
trans-RR,SS
trans-RS

Fig. 1 Five possible geometrical and conformational isomers of $[CoX_2(trien)]^{n+}$.

the ligand oxidation with KIO_3.[5)] Because these isomers were prepared and separated in acidic conditions, it is expected for the isothiocyanato complex to be also constituted of the trans-RR,SS and trans-RS isomers. Thus the separation of each isomer has been conducted for trans-$[Co(NCS)_2(trien)]^+$, together with that of the three cis isomers.

Cis-α-$[Co(NCS)_2(trien)]Cl$ was prepared by heating an aqueous mixture of NaNCS and cis-α-$[CoCl_2(trien)]Cl$, and purified by the recrystallization from hot water.

Cis-β-RR,SS-$[Co(NCS)_2(trien)]ClO_4$ was obtained by stirring, for a week, a mixture of cis-β-$[CoCO_3(trien)]ClO_4 \cdot H_2O$ and excess HNCS in ethanol which was prepared from KNCS and 70% $HClO_4$. The resulting yellowish orange crystals were washed repeatedly with a large quantity of 10^{-3} M (=mol/dm^3) $HClO_4$. The complex was dissolved in 10^{-3} M HCl and adsorbed on a column of SP-Sephadex C-25 (5 ml of swelled Sephadex per 1 mmol of the complex) and then eluted with 0.1 M NaCl (pH~3). Pure solid was obtained by the addition of $NaClO_4$ to the eluate.

The crude cis-β-RR,SS isomer was also obtained by heating an aqueous mixture of NaNCS and cis-β-$[CoCl_2(trien)]ClO_4$.

The other isomers, the trans and cis-β-RS,SR isomers, were derived by the isomerization of the cis-β-RR,SS isomer. A solution of 5 g of crude cis-β-RR,SS-$[Co(NCS)_2(trien)]NCS$ and 18 g of its perchlorate in 1 dm^3 of water was heated at 70°C for 3 hours. The resulting solution was acidified with $HClO_4$, followed by stirring overnight at a room temperature. After filtering the precipitated cis-β isomers, one third of the filtrate was passed through a column of SP-Sephadex C-25 (ϕ3x30 cm). With a hot solution of 0.15 M NaNCS, unipositive complex was eluted. The eluate was successively poured on a column of SP-Sephadex C-25 (ϕ5x50 cm). With 0.15 M $NaClO_4$ as eluent, the trans, cis-β-RS,SR, cis-β-RR,SS, and cis-α isomers were eluted in the order of elution. Upon the concentration of each eluate by a rotatory evaporator, each isomer crystallized out as perchlorate.

Fractional crystallization of the trans isomer gave the trans-RR,SS and trans-RS

Table 1 The Analytical Data

Complex perchlorate		Co(%)	C(%)	H(%)	N(%)
cis-α*	Found	16.53	26.84	5.26	23.55
	Calcd	16.52	26.93	5.09	23.55
cis-β-RR,SS	Found	14.01	22.79	4.44	20.15
	Calcd	14.01	22.83	4.31	19.97
cis-β-RS,SR	Found	13.94	22.86	4.32	20.38
	Calcd	14.01	22.83	4.31	19.97
trans-RR,SS	Found	12.92	21.09	3.96	18.73
$\cdot 1/4 NaClO_4$	Calcd	13.07	21.29	4.02	18.67
trans-RS	Found	13.95	22.82	4.27	20.31
	Calcd	14.01	22.83	4.31	19.97

* Chloride

isomers. The latter was a less soluble isomer. Their conformations were ascertained by the fact that the more soluble isomer could be partially resolved by a column chromatography of QAE-Sephadex A-25 ($[Sb_2(tart)_2]^{2-}$ form) using 3x10^{-3} M $Na_2[Sb_2(tart)_2]$ as eluent.[6)]

The two cis-β isomers were characterized by deriving the corresponding cis-β-$[Co(NH_3)_2(trien)]^{3+}$ isomers.[4)]

Analytical data are tabulated in Table 1.

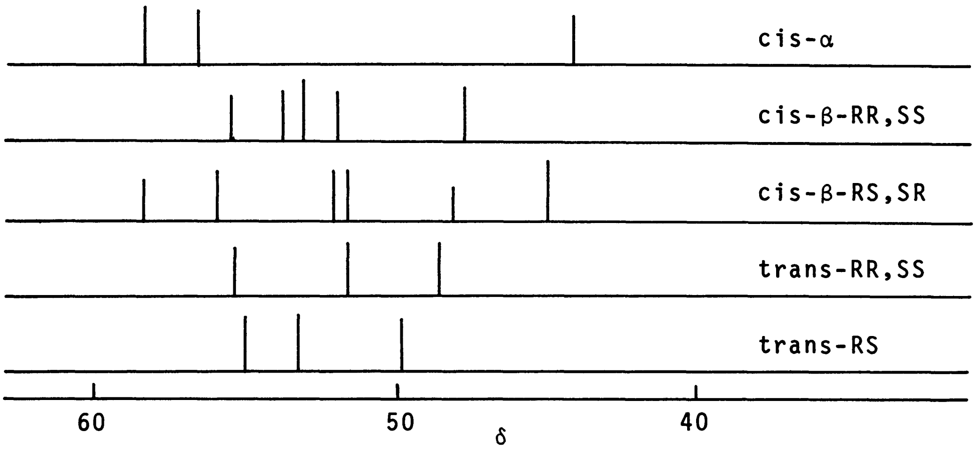

Fig. 2 Diagramatic representation of the ^{13}C NMR spectra of $[Co(NCS)_2(trien)]^+$ in $(CH_3)_2SO$ with TMS as an external standard.

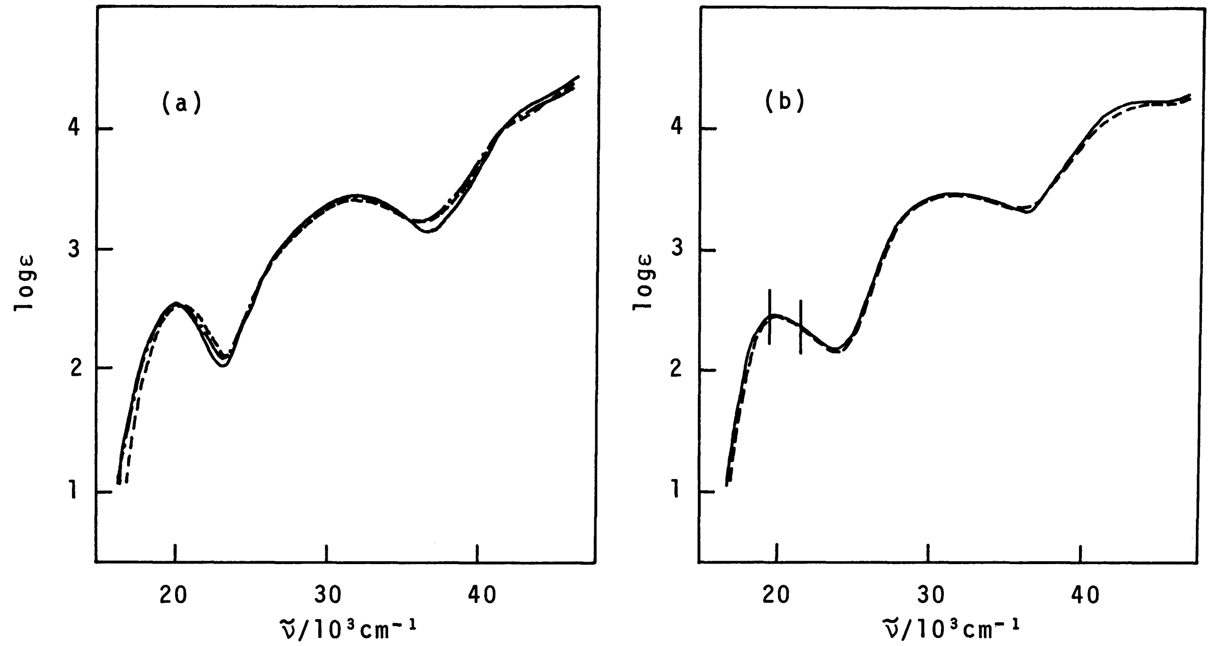

Fig. 3 Absorption spectra of $[Co(NCS)_2(trien)]^+$. (a) cis-α (——), cis-β-RR,SS (----), and cis-β-RS,SR (—·—). (b) trans-RR,SS (——) and trans-RS (----).

Figure 2 shows the ^{13}C NMR spectra of the five isomers, which were recorded on a JNM FX-60 spectrometer using TMS as an external standard. An ambient temperature of each sample solution was 30°C. The cis-α and two trans isomers exhibit three resonance lines, which reflect the presence of a C_2 axis or symmetry plane in these isomers. Five resonance lines are found for the cis-β-RR,SS isomer, although six resonances are found for its conformer. Because a dimethylformamide solution of the cis-β-RR,SS isomer resonates at δ=43.01, the highest field resonance must be overlapped by a strong resonance of the solvent, $(CH_3)_2SO$. The spectrum of each cis-β isomer quite resembles that of the corresponding cis-β diammine isomer.$^{4)}$ This fact is consistent with the structural assignment of cis-β-RR,SS- and cis-β-RS,SR-$[Co(NCS)_2(trien)]^+$.

Figure 3 shows the absorption spectra of the present isomers. The three cis isomers exhibit quite similar spectra with each other, and the same is true for the two trans isomers. The spectra of the trans isomers show some splitting of the first absorption bands. This splitting is in good agreement with the predicted transitions,$^{7)}$ which is shown in Fig. 3 with the short lines.

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