October, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2739–2742 (1976) 2739

Preparation and Geometrical Isomers of Cobalt(III) Complexes with Tridentate O–S–O Ligand Thiodiacetate or 3,3′-Thiodipropionate

Kan Kanamori, Tokiko Sudani, and Kiyoyasu Kawai
Faculty of Literature and Science, Toyama University, Gofuku, Toyama 930

(Received March 31, 1976)

cis(S)-fac- and *trans(S)-fac-*Isomers of bis(thiodiacetato)cobaltate(III), *trans(O)-mer-*, *s-cis(O)-fac-*, and *u-cis(O)-fac-*isomers of (thiodiacetato)(diethylenetriamine)cobalt(III) and *trans(O)-mer-*isomer of (3,3′-thiodipropionato)(diethylenetriamine)cobalt(III) were prepared. Their geometrical configurations were assigned on the basis of their absorption and PMR spectra. The stereochemistry of the Co(III) complex with a tridentate ligand thiodiacetate is similar to that of the Co(III) complex with iminodiacetate.

Metal complexes with amino carboxylates containing the sulfide group have been recognized as regards their biochemical importance.[1] However, only a few studies have been carried out on stereochemistry of cobalt(III) complexes with sulfide ligands.[2] Thiodiacetic acid we chose is a simple ligand of typical linear type which contains one sulfide group. The framework of the coordinated ligand around Co(III) ion is similar to that of iminodiacetate ligand O–N–O.

In this paper,[3] the preparation and separation of isomers of bis(thiodiacetato)cobaltate(III), (thiodiacetato)(diethylenetriamine)cobalt(III) and (3,3′-thiodipropionato)(diethylenetriamine)cobalt(III) are reported. The stereochemistry of the complexes is discussed in relation to that of the ida Co(III) complexes.[4,5]

Experimental

Preparation of cis(S)- *and* trans(S)-*Hydrogen Bis(thiodiacetato)cobaltate(III) :* $H[Co(tda)_2]\cdot nH_2O$

(1) cis(S)-$H[Co(tda)_2]\cdot 3H_2O$ *(Green Isomer)*: To a suspension containing 3.0 g (0.02 mol) of thiodiacetic acid in 30 dm^3 of water was added 1.1 g (0.01 mol) of freshly prepared $Co(OH)_3$.[6] The mixture was stirred at room temperature for about an hour. The reaction mixture was filtered in order to remove a small amount of insoluble material. 20 dm^3 of ethanol was added to the filtrate. The green complex deposited was filtered and washed with ethanol and ether. The crude complex was recrystallized from as little water as possible by adding a small amount of ethanol. Found: C, 23.00; H, 3.22; S, 15.08%. Calcd for $H[CoC_8H_8O_8S_2]\cdot 3H_2O$: C, 23.42; H, 3.69; S, 15.63%.

(2) trans(S)-$H[Co(tda)_2]\cdot 6H_2O$ *(Violet Isomer)*: The reaction mixture obtained by the same method as in (1) was stirred at about 80 °C for half an hour. The resulting mixture was filtered in order to remove a fairly large amount of insoluble material. The violet filtrate was cooled to room temperature. A small amount of violet precipitate appeared. Recrystallization of the complex was unsuccessful because of its instability in water. Found: C, 20.48; H, 4.31; S, 14.11%. Calcd for $H[CoC_8H_8O_8S_2]\cdot 6H_2O$: C, 20.69; H, 4.57; S, 13.81%.

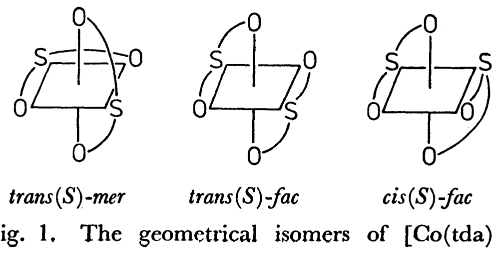
(3) Preparation and Separation of the Isomers of $[Co(tda)(dien)]^+$: A mixture containing 5.0 g (0.019 mol) of $[CoCl_3(dien)]$,[7] 4.2 g (0.028 mol) of thiodiacetic acid and 1.6 g (0.028 mol) of potassium hydroide in 50 dm^3 of water was heated at *ca.* 50 °C and stirred for about an hour. The resulting mixture was filtered in order to remove a small amount of insoluble material. The red filtrate was poured into a column (30 mm × 450 mm) containing strong-acid cation exchange resin (Dowex 50 W × 8 200—400 mesh, hydrogen form). After the column had been swept with water, the adsorbed band was eluted with 0.15 M sodium perchlorate at a rate of *ca.* 2.5 dm^3/min. Three colored bands, red (I), pinkish red (II), and pink (III) were eluted one after the other. Each eluate was concentrated to dryness in a vacuum evaporator. The resulting isomers contaminated with a large amount of sodium perchlorate were washed with ethanol. Each isomer obtained was dissolved in as little water as possible to recrystallize. The pure complex was obtained by adding ethanol to the solution. The yield of isomer (I) was less than those of other two. Found for isomer (I): C, 22.88; H, 4.31; N, 10.52%. Found for isomer (II): C, 22.93; H, 4.33; N, 10.21%. Found for isomer (III): C, 22.89; H, 4.55; N, 10.38%. Calcd for $[CoC_8H_{17}N_3O_4S]ClO_4\cdot 0.5H_2O$: C, 22.95; H, 4.34; N, 10.04%.

(4) Preparation of $[Co(tdp)(dien)]ClO_4\cdot H_2O$: The complex was prepared by the same method as in (3) except for the use of 3,3′-thiodipropionic acid instead of thiodiacetic acid. Only one violet band was eluted. Found: C, 26.13; H, 5.21; N, 9.38%. Calcd for $[CoC_{10}H_{21}N_3O_4S]ClO_4\cdot H_2O$: C, 26.35; H, 5.10; N, 9.22%.

Measurement. Electronic absorption spectra were measured with a Hitachi 124 spectrophotometer. PMR spectra were recorded on a JEOL MH-60 spectrometer. Deuterium oxide was used as a solvent with *t*-butyl alcohol (TBA) as an internal standard.

Results and Discussion

Three geometrical isomers, one meridional(*mer*) and two facial(*fac*) with respect to the coordination of O–S–O ligand thiodiacetate, are expected for bis(thiodiacetato)cobaltate(III) complex (Fig. 1). However, only two isomers were isolated. The electronic absorption spectra of the isomers obtained are shown in Fig. 2 and their data are given in Table 1. The charge transfer band due to the coordinated sulfide of bis(L-methioninato)Co(III) complex is situated at the lower energy side for *trans(S)*-isomer in comparison with *cis(S)*-isomer.[2] We see from Fig. 2 and Table 1 that the sulfide charge transfer band of the green isomer is situated at the energy side (*ca.* 32 × 10^3 cm^{-1}) higher



trans(S)-mer *trans(S)-fac* *cis(S)-fac*

Fig. 1. The geometrical isomers of $[Co(tda)_2]^-$.

TABLE 1. ABSORPTION DATA OF $[Co(tda)_2]^-$, $[Co(tda)(dien)]^+$, AND $[Co(tdp)(dien)]^+$ [a)]

	First band $\nu_{max}(\log \varepsilon_{max})$	Second band $\nu_{max}(\log \varepsilon_{max})$	Sulfide C.T. $\nu_{max}(\log \varepsilon_{max})$	Other bands $\nu_{max}(\log \varepsilon_{max})$
trans(*S*)-*fac*-$[Co(tda)_2]^-$ violet isomer	18.0 (2.06)	——	29.5 (3.75)	*ca.* 21 (1.6) 38.5 (3.98)
cis(*S*)-*fac*-$[Co(tda)_2]^-$ green isomer	16.9 (2.18)	*ca.* 24 (2.3)	*ca.* 32 (3.8)	39.5 (4.02)
trans(*O*)-*mer*-$[Co(tda)(dien)]^+$ isomer I	19.4 (1.95)	*ca.* 28 (2.3)	*ca.* 35 (3.7)	43.9 (4.26)
s-cis(*O*)-*fac*-$[Co(tda)(dien)]^+$ isomer II	19.9 (1.96)	*ca.* 29 (2.2)	*ca.* 35 (3.9)	44.6 (4.21)
u-cis(*O*)-*fac*-$[Co(tda)(dien)]^+$ isomer III	19.3 (2.05)	28.2 (2.39)	*ca.* 35 (3.8)	42.7 (4.25)
trans(*O*)-*mer*-$[Co(tdp)(dien)]^+$	18.2 (2.08) *ca.* 21 (1.7)	26.6 (2.39)	*ca.* 36 (3.7)	39.8 (3.72)

a) The frequencies are given in 10^3 cm^{-1}.

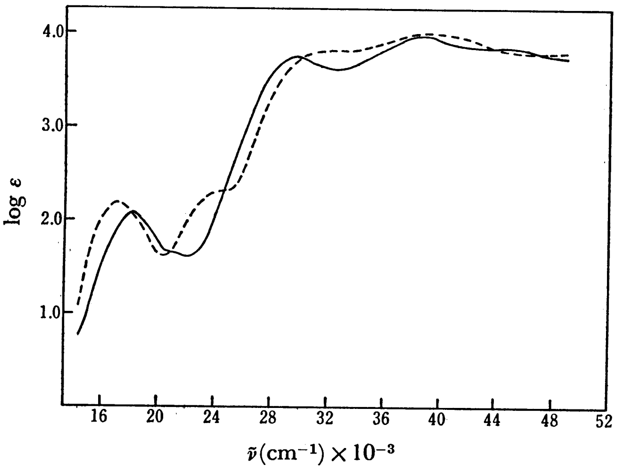


Fig. 2. Absorption (AB) curves of $[Co(tda)_2]^-$ ions in water: *trans*(*S*)-*fac*-$[Co(tda)_2]^-$; violet isomer (——), *cis*(*S*)-*fac*-$[Co(tda)_2]^-$; green isomer (----).

than that of the violet one (*ca.* 30×10^3 cm^{-1}). This indicates that the former has *cis(S)* configuration and the latter *trans(S)* one. This assignment is supported by the semiempirical consideration for the pattern of the first absorption band.[8)] Namely, *cis*(*S*)-isomer might be expected to show a sharp band in the lower energy side and *trans(S)*-isomer a broad one in the higher energy side. This is realized as shown in Fig. 2. Considering the framework of the coordinated ligands, iminodiacetate (ida) and tda, $[Co(tda)_2]^-$ is similar to $[Co(ida)_2]^-$ though the ligand field strength due to tda is slightly less than that of ida. In the case of ida Co(III) complex, the *mer*-isomer has not been obtained except for the mixed complex $[Co(ida)(dien)]^+$.[5)] This suggests that the *trans(S)*-isomer isolated in the present work is a *fac* coordinated one rather than a *mer* one.

The *trans(S)*-isomer shows an interesting shoulder at *ca.* 21×10^3 cm^{-1} (Fig. 2), which is independent of the degradation product or the isomerization of the complex, since its absorption intensity diminishes regularly with that of the main absorption peak at *ca.* 18×10^3 cm^{-1} (Fig. 3).

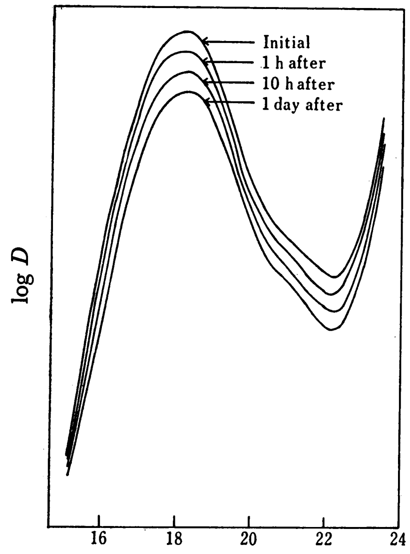


Fig. 3. Time dependence of absorption intensity of *trans*(*S*)-*fac*-$[Co(tda)_2]^-$ in water.

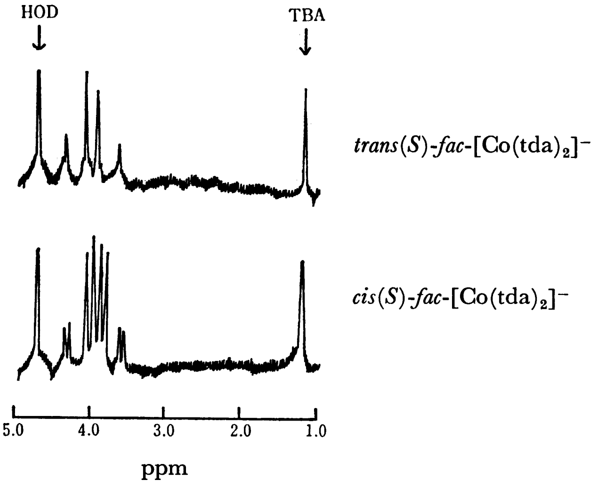


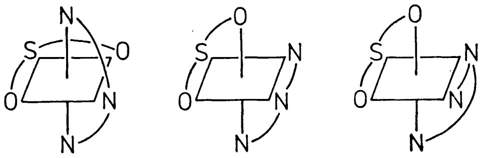
Fig. 4. Proton magnetic resonance spectra (60 MHz) of the two isomers of $[Co(tda)_2]^-$.

Table 2. Chemical shifts[a] and coupling constants[b] for the AB protons of $[Co(tda)_2]^-$ and $[Co(tda)(dien)]^+$

	$[Co(tda)_2]^-$		$[Co(tda)(dien)]^+$	
	trans(*S*)-*fac* violet isomer	*cis*(*S*)-*fac* green isomer	*s*-*cis*(*O*)-*fac* isomer II	*u*-*cis*(*O*)-*fac* isomer III
AB pattern	4.134	4.067	4.037	4.178
		3.988		4.083
	3.667	3.616	3.613	3.619
		3.530		
J_{AB} (Hz)	17	18	17	16

a) Values are ppm downfield from TBA at $\delta=1.234$ ppm (wrt DSS at 0).

b) Mean values in Hz; signs were not determined.



trans(*O*)-*mer* *s*-*cis*(*O*)-*fac* *u*-*cis*(*O*)-*fac*

Fig. 5. The geometrical isomers of $[Co(tda)(dien)]^+$.

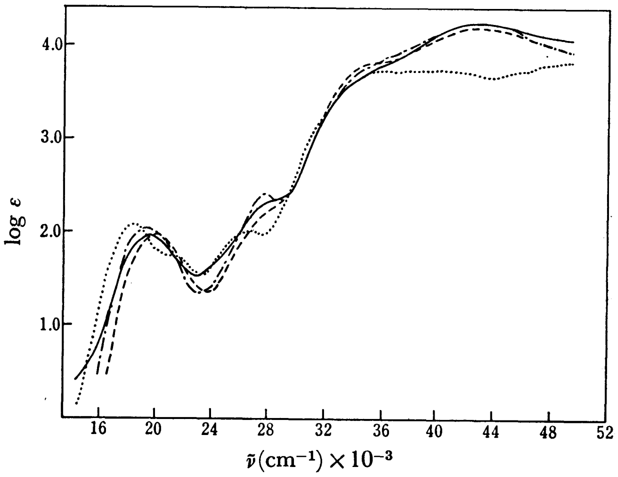


Fig. 6. Absorption (AB) curves of $[Co(tda)(dien)]^+$ isomers and $[Co(tda)(dien)]^+$ in water : *trans*(*O*)-*mer*-$[Co(tda)(dien)]^+$; isomer I(——), *s*-*cis*(*O*)-*fac*-$[Co(dta)(dien)]^+$; isomer II (----), *u*-*cis*(*O*)-*fac*-$[Co(tda)(dien)]^+$; isomer III (— — —), *trans*(*O*)-*mer*-$[Co(tdp)(dien)]^+$ (······).

The PMR spectra of *cis(S)*- and *trans(S)*-$[Co(tda)_2]^-$ are shown in Fig. 4 and their data in Table 2. Since the *trans(S)*-isomer has a plane of symmetry (Fig. 1), two pairs of methylene protons in the coordinated tda are fixed in the same chemical environment. The *trans(S)*-isomer is thus expected to exhibit one AB quartet due to two spin-coupled protons. On the other hand, the *cis(S)*-isomer is C_1 symmetry and two AB quartets are expected. As seen in Fig. 4, the *trans(S)*-isomer assigned from the absorption spectral consideration exhibits one AB quartet, whereas the *cis(S)*-isomer shows two AB quartets.

In order to confirm the assignment of geometrical isomers of $[Co(tda)_2]^-$, the mixed type complex $[Co(tda)(dien)]^+$ was synthesized. Three geometrcial isomers *trans(O)-mer*, *s-cis(O)-fac*, and *u-cis(O)-fac** are expected (Fig. 5). Three isomers were isolated by ion-exchange column chromatographic method (see Experimental). The electronic absorption spectra of the three isomers of $[Co(tda)(dien)]^+$ are shown in Fig. 6. From the splitting pattern of the first absorption band,[8] the isomer first eluted is assigned to *trans(O)*-type which only *mer* coordination is possible. Thus, it is considered that the remaining two isomers are *cis(O)-fac*-type. This designation coincides with that on the basis of the column chromatographic elution order,[9] *viz.*,

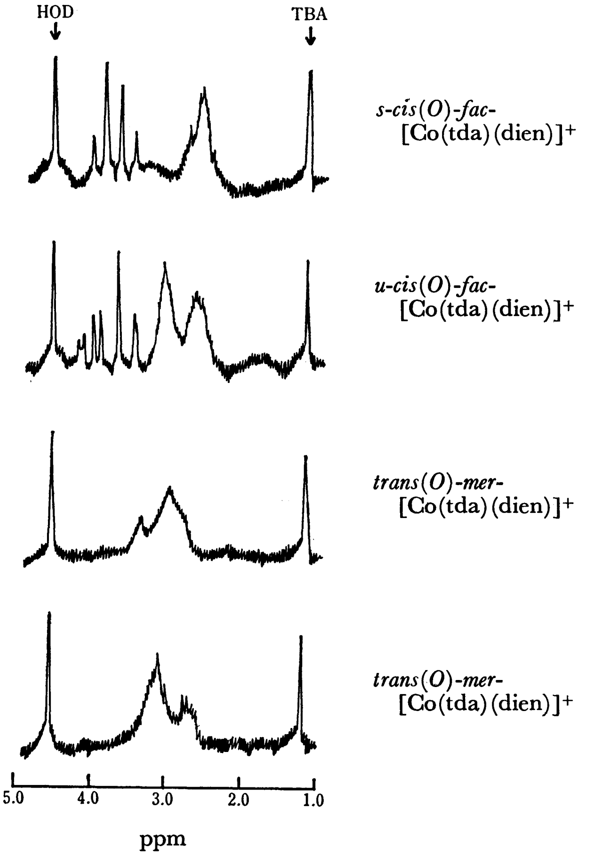


Fig. 7. Proton magnetic resonance spectra (60 MHz) of the three isomers of $[Co(tda)(dien)]^+$ and the one isomer of $[Co(tdp)(dien)]^+$.

---

* The prefix *s* denotes symmetrical arrangement and prefix *u* unsymmetrical arrangement.

the *trans(O)-mer*-isomer which has low dipole moment is eluted earlier than the two *cis(O)*-isomers.

In order to assign the remaining two *cis(O)*-isomers, their PMR spectra were recorded (Fig. 7 and Table 2). The plane of symmetry in *s-cis(O)-fac*-[Co(tda)(dien)]$^+$ gives rise to only one AB pattern as in the case of *trans-(S)-fac*-[Co(tda)$_2$]$^-$. On the other hand, *u-cis(O)-fac*-[Co(tda)(dien)]$^+$ has no plane of symmetry. The two pairs of methylene protons of the tda ligand should differ in the chemical environment (Fig. 5). In Fig. 7, the PMR spectrum of isomer II shows only one AB quartet and that of isomer III exhibits the split at the lower field component of the corresponding AB quartet. It is unknown in the present that the high field component does not split. This consideration leads isomer II to *s-cis(O)-fac*-[Co(tda)(dien)]$^+$ and isomer III to *u-cis(O)-fac*-[Co(tda)(dien)]$^+$. On the basis of this assignment, the column chromatographic elution order for the three isomers becomes *trans(O)-mer*, *s-cis(O)-fac* and *u-cis(O)-fac*. The order is similar to that for the isomers of analogous complex, [Co(ida)-(dien)]$^+$.⁵⁾ The PMR spectrum of *trans(O)-mer*-[Co-(tda)(dien)]$^+$ provided little information on the structure of the isomer because of its low solubility in D_2O.

The coordination mode of ida is regulated in [Co-(ida)(dien)]$^+$ by the dominant coordination of dien.⁵⁾ The present results are similar to the case of ida Co(III) complex. Of the three isomers of [Co(tda)$_2$]$^-$ complex, *viz.*, the two *fac*-isomers except for *mer*-type were obtained and the three isomers containing *mer*(tda)-type were obtained for [Co(tda)(dien)]$^+$ complex.

The above conclusion can be confirmed by the attempt to isolate the isomers of [Co(tdp)(dien)]$^+$. Molecular model examination suggests that in expansion from the five-membered chelate ring to the six-membered ring, the *fac* coordination of O–S–O ligand strains more than the *mer* one. Only one isomer was obtained for [Co(tdp)(dien)]$^+$ complex. The absorption spectral measurement indicates that the isomer obtained is *mer*(tdp)-form (Fig. 6). The broad splitting of the first absorption band is more remarkable for *trans(O)-mer*-[Co(tdp)(dien)]$^+$ than for *trans(O)-mer*-[Co(tda)(dien)]$^+$. This may arise from the weakness of the ligand field strength due to the change from the five-membered chelate ring to the six-membered ring.

The PMR spectrum of *trans(O)-mer*-[Co(tdp)(dien)]$^+$ where ABCD or AA′BB′ pattern can be expected is apparently similar in chemical shifts to that of *trans(O)-mer*-[Co(tda)(dien)]$^+$, but the assignment in detail is difficult. The results indicate that the only one isomer for [Co(tdp)(dien)]$^+$ is *trans(O)-mer*-form and that the molecular model consideration is reasonable.

In conclusion, the stereochemistry of Co(III) complex with tda is similar to that of ida Co(III) complex in both case of the bis type⁴⁾ and the mixed one.⁵⁾ The tda ligands in *trans(S)*-[Co(tda)$_2$]$^-$ is facially coordinated as in the case of *trans(N)*-[Co(ida)$_2$]$^-$.

References

1) C. A. McAuliffe, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **5**, 1996 (1966); S. E. Livingstone and J. D. Nolan, *ibid.*, **7**, 1447 (1968); C. A. McAuliffe, *ibid.*, **12**, 1699 (1973).

2) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969); J. Hidaka, S. Yamada, and Y. Shimura, *Chem. Lett.*, **1974**, 1478.

3) The following abbreviations are used for the ligands; “ida” for an iminodiacetate ion, “tda” thiodiacetate ion, “tdp” 3,3′-thiodipropionate ion and “dien” diethylenetriamine.

4) J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **35**, 567 (1962).

5) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

6) H. Ley and H. Winkler, *Ber.*, **42**, 3900 (1909); **45**, 375 (1912).

7) *Inorg. Synth.*, **7**, 207 (1963).

8) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

9) G. V. Kauffman, R. P. Pinnel, and L. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962).