CHEMISTRY LETTERS, pp. 1123-1126, 1993.

Double Sulfur Trans Influence in the Dithiolato Complex: *trans*(S)-$[Co(aet)_2(en)]ClO_4$ (aet = 2-Aminoethanethiolate)

Toshiaki YONEMURA,* Ken-ichi OKAMOTO,*† Tomoharu AMA,
Hiroshi KAWAGUCHI, and Takaji YASUI
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

The title aliphatic thiolato complex, whose trans positions were occupied by two sulfur atoms, was newly prepared and its crystal structure was determined by the X-ray diffraction study. The Co-S bond distances in that complex are longer than the ordinary one. Reaction of the complex at 50 °C in water gave *cis*(S)-$[Co(aet)_2(en)]^+$ and trinuclear complex, $[Co\{Co(aet)_3\}_2]^{3+}$.

The peculiar effects of the thiolate-type sulfur-containing ligands on the geometric and electronic structures in the dithiolato complexes are now well-known,1) and no more than one isomer has ever been isolated in all cases. In addition, the reactivities of the dithiolato cobalt(III) complexes are extremely high, whereas those of the chromium(III) analogues are not.2) One of these causes is attributable to the so-called "structural trans effects" (sulfur trans influence) of the thiolato donor atoms. Therefore, it is difficult to prepare the trans(S) or mer(S) isomer of the cobalt(III) complexes with two or three aliphatic thiolate ligands. In the present letter, we deal with the preparation of the trans(S)-type cobalt(III) complex, *trans*(S)-$[Co(aet)_2(en)]ClO_4$, using the aliphatic 2-aminoethanethiolate(aet) bidentate ligands. Further, we report the magnitude of the sulfur trans influence and also do the rapid isomerization, followed by the formation of the polynuclear complex from that dithiolato complex.

The complex was prepared by allowing to react 2-aminoethanethiol hydrochloride (Haet·HCl) 5.68 g in 20 cm^3 of water with *trans*-$[CoCl_2(en)_2]Cl$ 7.27 g in 50 cm^3 of water under the conditions of pH 8.5, 25 °C, and reaction time 1 h. In this preparation, it is very important to choose the Co(III) complex, not Co(II) ion as the starting material and to do the careful pH control throughout the reaction. The reaction mixture was chromatographed on an SP-Sephadex C-25 column (ϕ4.7 x 90 cm) with an eluent of 0.2 mol dm^{-3} KCl to give three bands. The eluate of the first band was transferred into another column (ϕ 4.7 x 90 cm) and circulated two or three times with the same eluent. The band separated into two bands of violet and dark brown colors. The eluate from the violet band, which contained a desired trans(S) isomer, was concentrated to a small volume and a large amount of methanol was added to the concentrated solution to deposit KCl. Then, by the use of a short QAE-Sephadex A-25 column (ϕ2.8 x 45 cm), the Cl salt was converted to the ClO_4 one.3)

X-Ray structural analysis of the violet complex revealed the presence of two discrete complex ions (Δ and Λ) in the unit cell.4) A perspective drawing of the only Λ isomer of the violet complex cation is shown in Fig. 1. One en and two aet ligands coordinate to central cobalt atom through the N and N, and N and S atoms, respectively. Two sulfur atoms of the aet ligands occupy trans position to each other. Therefore, the violet complex is assigned to *trans*(S)-[Co(aet)$_2$(en)]$^+$. The Co-S1 and Co-S2 bond distances (2.271(1) and 2.299(1) Å) are longer than the ordinary Co-S bond distance, such as 2.226 Å of [Co(aet)(en)$_2$]$^{2+}$ 1a). This indicates that the Co-S bonds are lengthened to each other by the sulfur trans influence due to two thiolato-type sulfur atoms. Further, the Co-N(**en**) bond distances (2.004(6) and 2.008(6) Å) are *ca.* 0.05 Å longer than the ordinary Co-N bond distance and the Co-N(**aet**) bond distances (1.962(5) and 1.955(5) Å) are slightly longer than the ordinary one. So far, it has been thought that the influence of the thiolato donor atoms acts on only trans position of the sulfur atoms.1a-c) In the present complex, however, the influence of the thiolato donor atoms is also observed at the cis positions. It is thought that this remarkable thing arises from the excess of sulfur trans influence due to two thiolato-type sulfur atoms which occupy the trans positions across cobalt center. Moreover, the five-membered chelate ring of the en, N3-C5-C6-N4, takes a δ conformation, whereas two aet rings, S1-C1-C2-N1 and S2-C3-C4-N2, take λ conformation. The en chelate ring is almost symmetrical gauche form; the methylene carbon atoms are

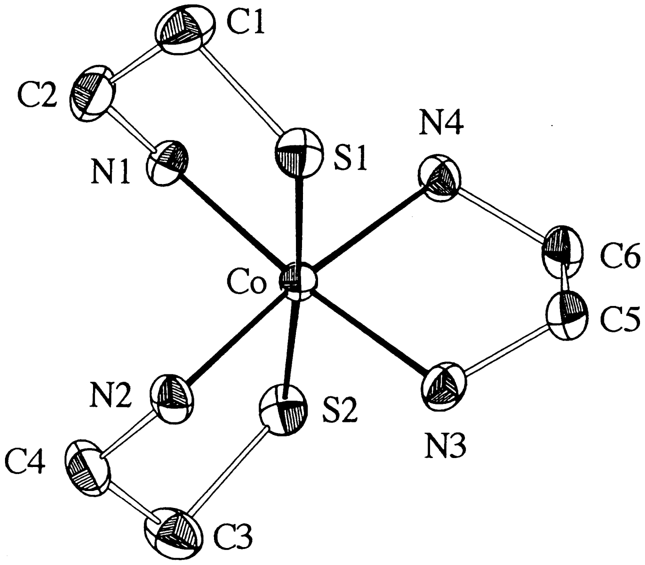

Fig. 1. Perspective view of the *trans*(S)-[Co(aet)$_2$(en)]$^+$ (Λ) ion.

shifted by 0.3532 Å (C5) and -0.3533 Å (C6) from the plane formed by the cobalt and two ligating nitrogen atoms. On the contrary, two aet chelate rings are unsymmetrical gauche form; the C1 (C3) and C2 (C4) atoms are shifted by -0.0936 Å (-0.1093 Å) and 0.5846 Å (0.5947 Å), respectively, from the plane formed by the cobalt and the ligating nitrogen and sulfur atoms.

The absorption spectral pattern of the present trans(S) complex is quite similar to that of the other *trans*(S)-$[Co(N)_2(S)_2(en)]^{2+}$-type complexes with a pyt or endet ligand,[1c,5] giving a sharp d-d absorption band at 17-18 ×10^3 cm^{-1} and characteristic sulfur-to-cobalt charge transfer (SMCT) band at 30-31 ×10^3 cm^{-1}. Over the whole region, the present complex shows a drastic absorption spectral change with time in water at 50 °C (Fig. 2). In the d-d absorption band and the charge transfer band at *ca.* 280 nm which are characteristic of the cis(S)-type complexes, the increase of the absorption intensities indicates that the S-bridged polynuclear complexes are formed from the trans(S) aet complex in an aqueous solution.[1d] This was supported by the column chromatogram of the reaction solution after 48 h; five bands of violet (trans(S) isomer), dark brown (cis(S) isomer), light brown (unknown), reddish brown (trinuclear complex; *meso*-$[Co\{Co(aet)_3\}_2]^{3+}$ [6]), and brownish green (trinuclear complex; *rac*-$[Co\{Co(aet)_3\}_2]^{3+}$ [6]) were eluted in this order. These facts suggest that the trans(S) isomer tends to isomerize to the cis(S) isomer, followed by the formation of the S-bridged polynuclear complex owing to both the double sulfur trans influence and high nucleophilicity of the thiolato donor atoms.

More detailed studies using analogous ligands are now in progress.

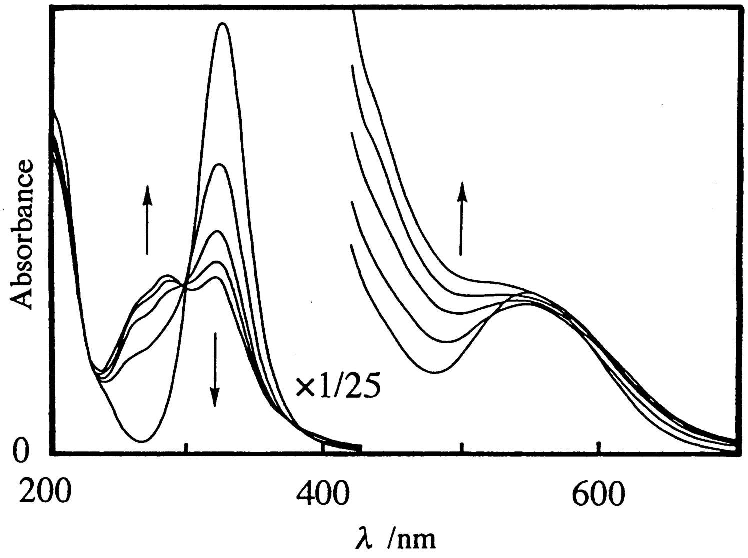

Fig. 2. Absorption spectral change of *trans*(S)-$[Co(aet)_2(en)]^+$ in water at 50 °C; the curves show the spectra measured at 12 h intervals. Absorbance scale is arbitrary.

References

1) a) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973); b) H. C. Freeman, C. J. Moore, and A. M. Sargeson, *ibid.*, **17**, 3513 (1978); c) M. Kita, K. Yamanari, and Y.

Shimura, *Bull. Chem. Soc. Jpn.*, **62**, 3081 (1989); d) K. Okamoto, T. Yonemura, T. Konno, and J. Hidaka, *ibid.*, **65**, 794 (1992).

2) C. J. Weschler and E. A. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973); C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, E. Deutsch, and K. O. Hodgson, *ibid.*, **15**, 1183 (1976).

3) Anal. Found: C, 19.57; H, 5.20; N, 15.14%. Calcd for $C_6H_{20}N_4O_4S_2ClCo$: C, 19.44; H, 5.44; N, 15.11%. Vis-UV spectrum, H_2O solvent [σ_{max} , 10^3 cm^{-1}(log(ε/$mol^{-1}dm^3cm^{-1}$))]: 18.25(2.36), 22.4(2.2 sh), 30.86(4.36), 41.3(3.5 sh), 46.3(4.1 sh). sh denotes a shoulder. ^{13}C NMR in D_2O (500MHz, ppm from DSS): $\delta = 30.15$(-CH_2S), 42.63(en), and 54.50(-CH_2NH_2).

4) Crystal data for $[Co(C_2H_6NS)_2(C_2H_8N_2)]ClO_4$: $M = 370.76$, $0.38 \times 0.40 \times 0.45$ mm^3, monoclinic, space group *P1*, $a = 9.447(2)$ Å, $b = 9.446(2)$ Å, $c = 10.038(2)$ Å, $\alpha = 106.92(1)°$, $\beta = 106.93(1)°$, $\gamma = 112.42(1)°$, $V = 705.6$ $Å^3$, $Z = 2$, $D_x = 1.74$ g cm^{-3}, λ (Mo Kα) = 0.71073 Å, μ (Mo Kα) = 17.0 cm^{-1}, $R = 0.039$, $R_w = 0.050$. 3939 independent reflections with $|Fo| > 3\sigma(|Fo|)$ ($2\theta < 60°$) were collected on an Enraf Nonius CAD4 diffractometer. The structure was solved and refined by the program package MOLEN (C. K. Fair, Enraf Nonius, Delft, The Netherlands).

5) a) K. Yamanari, N. Takeshita, T. Komorita, and Y. Shimura, *Chem. Lett.*, **1981**, 861; b) K. Yamanari, N. Takeshita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **57**, 1227 (1984). (pyt = 2-pyridinethiolate; endet = 3,6-dimethyl-3,6-diazaoctane-1,8-dithiolate)

6) D. H. Bush and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962); G. R. Brubaker and B. E. Douglas, *ibid.*, **6**, 1562 (1967).

(Received March 31, 1993)