CHEMISTRY LETTERS, pp. 1043-1046, 1990.

A New Class of S-Bridged Polynuclear Complex. The Formation and Crystal Structure of Spontaneously Resolved $[\{Rh(aet)_3\}_4Zn_3O]^{4+}$ (aet = 2-aminoethanethiolate)

Takumi KONNO,* Ken-ichi OKAMOTO, and Jinsai HIDAKA
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Reaction of fac(S)-$[Rh(aet)_3]$ with Zn^{2+} in water gave spontaneously resolved $[\{Rh(aet)_3\}_4Zn_3O]^{4+}$ (aet = 2-aminoethanethiolate), of which structure and absolute configuration have been determined by X-ray crystallographic method. In the $(+)^{CD}_{350}$ isomer each Zn(II) is tetrahedrally coordinated by three thiolato atoms from three different Λ-fac(S)-$[Rh(aet)_3]$ and a central oxygen atom.

The fac(S)-$[M(aet)_3]$ (aet = 2-aminoethanethiolate) and fac(S)-$[M(L\text{-}cys\text{-}N,S)_3]^{3-}$ (L-cys = L-cysteinate) complexes (M = Co(III) and Rh(III)) have been recognized to react with M' = Fe(III), Co(II), Co(III), Ni(II), and Ru(III) to give linear-type S-bridged trinuclear complexes, $[M'\{M(\text{aet or L-cys-}N,S)_3\}_2]^{n+\text{ or }n-}$; the central M' is coordinated by two S_3 faces to take $M'S_6$ octahedral geometry.1-10) The fac(S)-$[M(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$ complexes also react with Zn(II) and Cd(II) which commonly take a tetrahedral geometry. However, none of these reaction products have been structurally characterized, although it has been assumed that fac(S)-$[Co(aet)_3]$ functions as a terdentate ligand to these metal ions as does to Fe(III), Co(III), and Ni(II).2,4) Here we report the X-ray crystal structure of spontaneously resolved $[\{Rh(aet)_3\}_4Zn_3O]^{4+}$, which was formed by the reaction of fac(S)-$[Rh(aet)_3]$ with Zn^{2+}, together with its stereochemical and spectrochemical behavior.

To a suspension of fac(S)-[Rh(aet)$_3$]$^{10,11)}$ (1.0 g, 3.0 mmol) in 50 cm^3 of water was added ZnBr$_2$ (0.8 g, 3.6 mmol) in 10 cm^3 of water. The mixture was stirred at room temperature for 30 min, whereupon the suspension became a clear orange-yellow solution. To this was added 10 g of NaBr in 40 cm^3 of water, followed by cooling in a refrigerator overnight. The resulting orange-yellow complex was collected by filtration. The spontaneously resolved orange-yellow and yellow crystals were obtained by the recrystallization from water. One of the yellow crystals was used for X-ray structural analysis.

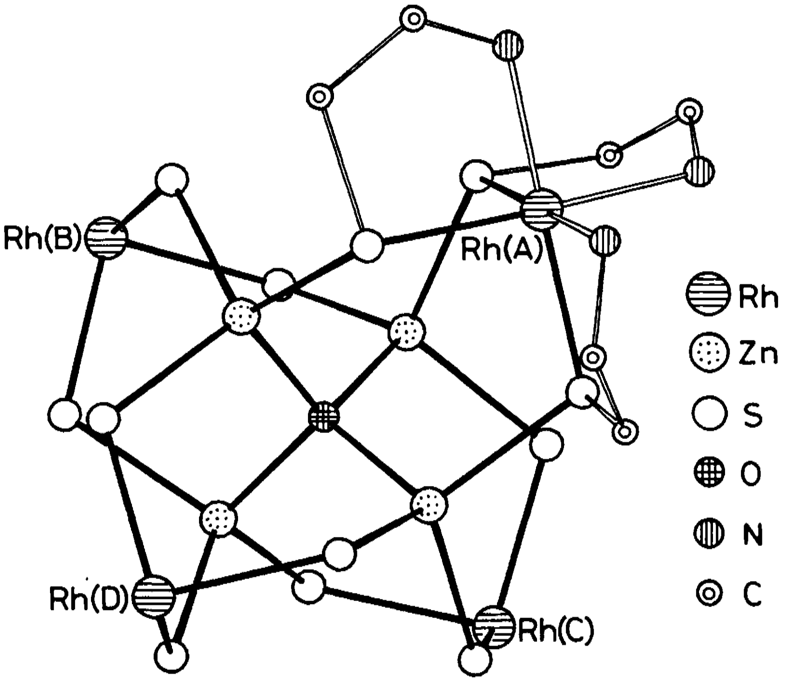

Fig. 1. Perspective view of $[\{Rh(aet)_3\}_4Zn_3O]^{4+}$ (the -N-C-C- moieties bound to Rh(B), Rh(C), and Rh(D) are omitted). Selected bond distances (Å) and angles (°) (averaged); Rh-S 2.322(6), Rh-N 2.11(2), Zn-S 2.338(6), Zn-O 1.99(1), S-Rh-S 94.2(2), N-Rh-N 92.2(7), Zn-S-Rh 114.6(2), S-Zn-S 111.8(2), O-Zn-S 107.1(4), Zn-O-Zn 109.5(5).

The X-ray crystal structure of the complex cation is shown in Fig. 1.$^{12)}$ The zinc atoms appear to be distributed in four different locations and refining the occupancy factor yielded a value of 0.76, 0.76, 0.77, and 0.78. The Br anions are not well-behaved and are distributed in ten different locations, and refining the occupancy factor yielded a total value of 4.26. These facts seems to indicate that the number of zinc atoms is three and the charge of complex is 4+. Thus, the complex cation consists of four fac(S)-[Rh(aet)$_3$] moieties, three zinc atoms, and one oxygen atom, taking the cage-type polynuclear structure. Each zinc atom is coordinated by three sulfur atoms from three different fac(S)-[Rh(aet)$_3$] and oxygen atoms at the center of the polynuclear structure, completing tetrahedral geometry (av. S-Zn-S = 111.8(2)° and O-Zn-S = 107.1(4)°). This structure is in contrast to the linear-type trinuclear structure where three thiolato atoms in fac(S)-[M(aet or L-cys-N,S)$_3$]$^{0 \text{ or } 3-}$ (M = Co(III) or Rh(III)) coordinate to one central metal ion (Fe(III), Co(II), Co(III), Ni(II), or Ru(III)).[1-10] The absolute configuration was estimated by using the anomalous scattering technique.[13] For the present $(+)^{CD}_{350}$ isomer, all the fac(S)-[Rh(aet)$_3$] moieties and asymmetric sulfur atoms are regulated to the Λ and R configurations respectively (Fig. 1). Molecular model constructions reveal that a significant nonbonding interaction exists among the adjacent aet chelate rings when the absolute configurations of the four fac(S)-[Rh(aet)$_3$] moieties are not unity. Accordingly, the optical isomer of fac(S)-[Rh(aet)$_3$] can be selectively incorporated in the present polynuclear structure.

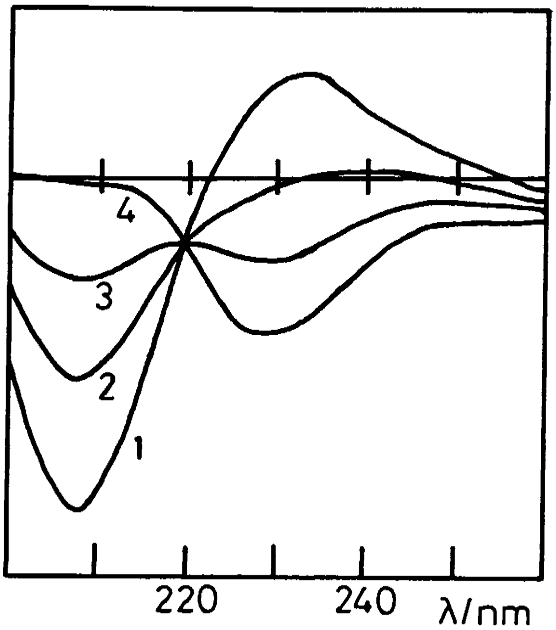

Fig. 2. CD spectral change for Λ-$(+)^{CD}_{350}$-[{Rh(aet)$_3$}$_4$Zn$_3$O]$^{4+}$ in water at 22 °C; the curves 1-4 were measured at 0, 20, 60, and 180 min respectively. CD scale is arbitrary.

The absorption spectral pattern of the present polynuclear complex is quite similar to that of the starting fac(S)-[Rh(aet)$_3$],[10,11] giving two d-d absorption shoulders at ca. 29 and 32 x 10^3 cm^{-1} and sulfur-to-rhodium charge transfer band at 45.5 x 10^3 cm^{-1}. In the charge transfer band region the $(+)^{CD}_{350}$ isomer shows a drastic CD spectral change with time from Curve 1 to Curve 4 in water (Fig. 2), while the change in the d-d band region is very slight. The well-defined isodichroic point is recognized at 219 nm. The absorption spectral change is also observed in the corresponding region, however, the change is very small as compared with the CD spectral change. These facts suggest that the cleavage of Zn-S bonds of the polynuclear complex occurs in water, retaining the absolute configuration of fac(S)-$[Rh(aet)_3]$ moieties.

References

1) D. H. Bush and D. C. Jicha, Inorg. Chem., 1, 884 (1962).
2) G. R. Brubaker and B. E. Douglas, Inorg. Chem., 6, 1562 (1967).
3) R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, Inorg. Chem., 14, 1313 (1975).
4) E. L. Blinn, P. Butler, K. M. Chapman, and S. Harris, Inorg. Chim. Acta, 24, 139 (1977).
5) M. J. Heeg, E. L. Blinn, and E. Deutsch, Inorg. Chem., 24, 1118 (1985).
6) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, Chem. Lett., 1985, 1017.
7) K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, Bull. Chem. Soc. Jpn., 59, 3859 (1986).
8) S. Aizawa, K. Okamoto, H. Einaga, and J. Hidaka, Bull. Chem. Soc. Jpn., 61, 1601 (1988).
9) T. Konno, S. Aizawa, and J. Hidaka, Bull. Chem. Soc. Jpn., 62, 585 (1989).
10) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, Bull. Chem. Soc. Jpn., 63, 792 (1990).
11) M. Kita, K. Yamanari, and Y. Shimura, Bull. Chem. Soc. Jpn., 56, 3272 (1983).
12) Crystal data for $[\{Rh(C_2H_6NS)_3\}_4Zn_3O]Br_4\cdot 9.5H_2O$: M = 2028.2, orthorhombic, $P2_12_12_1$, a = 19.149(10), b = 19.184(9), c = 19.194(9) Å, V = 7051(6) Å^3, Z = 4, D_c (D_m) = 1.91 (1.92) g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 44.05 cm^{-1}, room temperature, R (wR) = 0.0714 (0.0635) for 4501 independent reflections with $|Fo| > 3\sigma(|Fo|)$ ($2 \leqq 2\theta \leqq 50°$). The plasma emission spectral analysis gave the value of Rh : Zn = 4 : 2.99 in the complex. The structure was solved by direct methods (P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. -P. Declercq, and M. M. Woolfson, MULTAN80, University of York, England, and Louvain, Belgium (1980)) and difference Fourier technique, and refined by full-matrix least-squares using anisotropic thermal parameters for non-hydrogen atoms. Attempts to solve the crystal structure as the cubic space group were unsuccessful. All calculations were performed with use of the programs of SHELX76 (G. M. Sheldric, University of Cambridge, England (1976)).
13) For atomic parameters containing the Λ configuration of fac(S)-$[Rh(aet)_3]$ moieties R = 0.0714 and wR = 0.0635 ($w = 1.5885/(\sigma^2(Fo) + 0.001059|Fo|^2)$), and for that containing the Δ configuration R = 0.0762 and wR = 0.0693 ($w = 1.6417/(\sigma^2(Fo) + 0.001141|Fo|^2)$). The enantiomeric structure could be rejected at the 0.005 significance level by the Hamilton test (W. C. Hamilton, Acta Crystallogr., 18, 502 (1965)).

(Received February 26, 1990)