July, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 2375—2378 (1989) 2375

A Resonance Raman Study of Polymeric Thiolato Cobalt(III) Complexes: Possible Bridging Modes

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(Received January 13, 1989)

The resonance Raman spectra of polymeric $Co^{III}\{SCH_2CH(NH_2)COOH\text{-}S\}_3$ and $Na_3Co^{III}(SCH_2COO\text{-}S)_3$ complexes were investigated. The complexes gave two totally symmetric Co–S stretchings, indicating the presence of two different Co–S–Co bridging modes in the complexes. Possible bridging modes are discussed in relation to their structures.

Schubert[1)] first obtained the red H_3Co(cysteinato)$_3$ complex, which is insoluble in acids and water, but soluble in alkali to give cherry-red solutions. Neville and Gorin[2)] and Gorin and Spessard[3)] proposed that, in this complex, both thiolato and carboxylato groups are coordinated to cobalt(III). However, when the complex was reinvestigated by McCormick and Gorin,[4)] they concluded, on the basis of the infrared spectra, that the complex is polymeric and consists only of thiolate bridges. Similar polymeric complexes have been prepared with hexanethiol,[4)] 3-mercaptopropionate,[4)] 2-mercaptoethanol,[5)] mercaptoacetate,[6)] and ethyl mercaptoacetate.[6)] However, no difinitive data have been reported so far concerning the bridging mode in the polymeric thiolato complexes. We here wish to present the first report on the bridging mode of the polymeric thiolato cobalt(III) complexes, as studied by means of the resonance Raman spectra.

Experimental

Preparation. The polymeric complexes, $Co\{SCH_2CH(NH_2)COOH\text{-}S\}_3$[1)] and $Na_3Co(SCH_2COO\text{-}S)_3$,[6)] and the trinuclear complex, $K_3[Co\{Co(SCH_2CH(NH_2)COO\text{-}N,S)_3\}_2]$,[7)] were prepared according to the methods in the literature and were identified by means of their electronic-absorption spectra.

Measurements. The samples used for Raman measurements were in the form of aqueous solutions or disks. The disks were spun to avoid thermal decomposition induced by laser illumination. The Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer. Excitation profiles were obtained by using the laser lines of a Spectra Physics 164 Ar^+ laser (514.5, 501.7, 496.5, 488.0, 476.5, 465.8, and 457.9 nm) and of a Coherent Radiation model CR599 dye laser employing Rhodamine 6G dye (610.0, 588.0, and 567.8 nm). The laser power was below 100 mW for solid samples. The spectral band width was set at 5 cm^{-1}. The Raman intensities were measured relative to the totally symmetric S–O stretching mode of the potassium sulfate incorporated in the sample. Corrections of the observed intensity were applied to the fourth power of the wavenumber of scattered radiation and the instrumental response. The intensities were averaged over more than three measurements.

Results and Discussion

Raman Spectra. A polymeric complex, $Co(SCH_2CH(NH_2)COOH\text{-}S)_3$, gives very intense Raman bands in the 200—500 cm^{-1} region and some very weak bands in the 600—1000 cm^{-1} region in the solid state with 488.0-nm excitation. An alkaline solution of the complex gives essentially the same spectrum as that obtained in the solid state, indicating that the polymeric structure is retained also in the solution. Figure 1 shows the polarized resonance Raman spectra in the 200—500 cm^{-1} region of the complex in a 0.1 mol dm^{-3} NaOH solution. The depolarization ratios of the 406-, 341-, 280-, and 220-cm^{-1} bands are all near to 1/3; ρ=0.34, 0.33, 0.31, and 0.32 respectively. Thus, all these bands can reasonably be assigned to totally symmetric

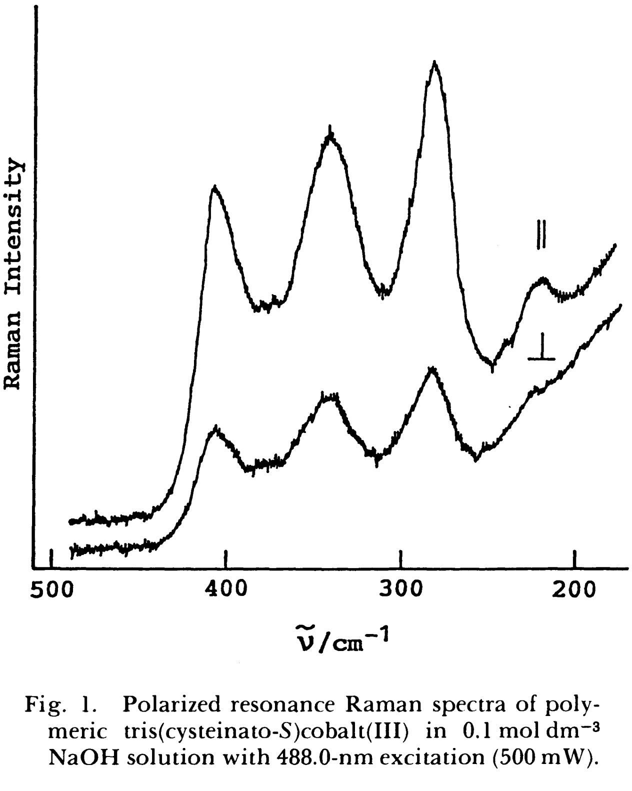


Fig. 1. Polarized resonance Raman spectra of polymeric tris(cysteinato-S)cobalt(III) in 0.1 mol dm^{-3} NaOH solution with 488.0-nm excitation (500 mW).

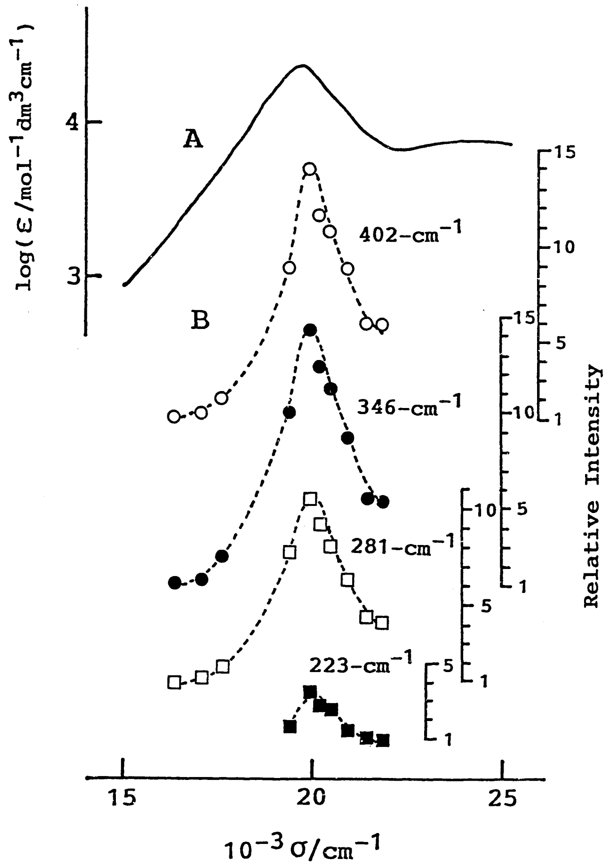


Fig. 2. Electronic absorption spectrum of polymeric tris(cysteinato-*S*)cobalt(III) in 0.1 mol dm^{-3} NaOH solution and the excitation profiles of the 402-, 346-, 281-, and 223-cm^{-1} bands in the solid state.

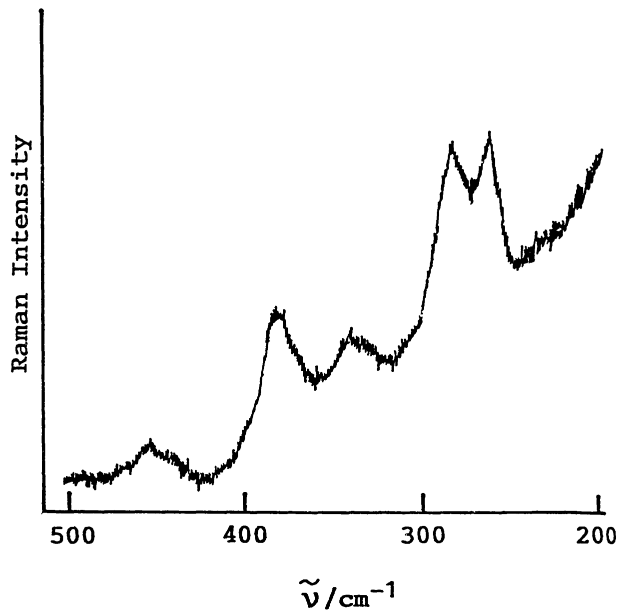


Fig. 3. Resonance Raman spectra of polymeric $Na_3Co(SCH_2COO\text{-}S)_3$ in aqueous solution with 514.5-nm excitation (150 mW).

modes. The depolarization ratios, 1/3, under these resonance condition correspond well with those expected for an electronic transition between the nondegenerate states of symmetries lower than cubic, but still not very low.[8]

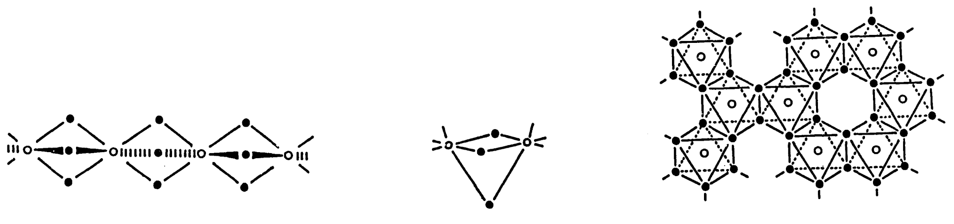
Figure 2-A shows the electronic absorption spectrum of the $Co(SCH_2CH(NH_2)COOH\text{-}S)_3$ complex in an alkaline solution. The electronic absorption band at 19600 cm^{-1} has been assigned to the charge-transfer transition between the cobalt(III) and bridging sulfur because of its high intensity.[6] This charge-transfer-band position corresponds well with those of the charge-transfer bands of the trinuclear complexes containing sulfur bridges, such as $[Co\{Co(SCH_2CH_2NH_2)_3\}_2]^{3+}$[9] and $[Co\{Co(SCH_2CH(NH_2)COO\text{-}N,S)_3\}_2]^{3-}$.[10,11]

The excitation profiles of the four bands (402, 346, 281, and 223 cm^{-1}) of the polymeric $Co(SCH_2CH(NH_2)COOH\text{-}S)_3$ complex were obtained for the solid sample, because the solid sample gives more intense Raman bands than does the solution; the results are shown in Fig. 2-B. The excitation profiles of the four bands reach their maxima at 20500 cm^{-1}, close to the electronic absorption maximum at 19600 cm^{-1}, indicating that the resonant transition is a charge-transfer one between the cobalt(III) and bridging sulfur.

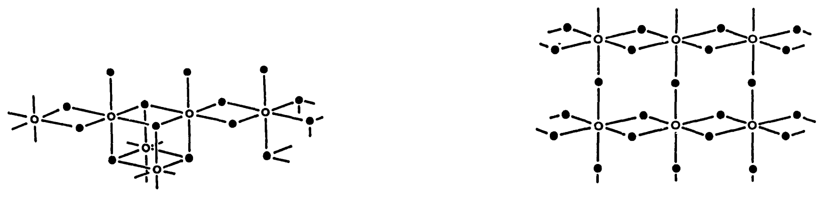
When the electron giving rise to a resonant transition is localized on the coordinating atom, an intense resonance enhancement can not be expected for intraligand vibrational modes. The resonant transition of the present polymeric thiolato complexes is just such a case. Therefore, all the four resonance-enhanced Raman bands observed for each polymeric thiolato complex should be assigned to the vibrational modes of the Co–S moiety and not to the intraligand modes—that is, they should be assigned to the Co–S stretchings and Co–S–Co or S–Co–S bendings.

Figure 3 illustrates the resonance Raman spectrum in an aqueous solution of the polymeric $Co(SCH_2COO\text{-}S)_3^{3-}$. $Na_3Co(SCH_2COO\text{-}S)_3$ and $Co(SCH_2COOH\text{-}S)_3$ in the solid state give practically the same spectra. The four bands in the 200—400 cm^{-1} region can be assigned to modes similar to those observed for the polymeric $Co(SCH_2CH(NH_2)COOH\text{-}S)_3$ in the corresponding region, since all the bands are polarized and since the excitation profiles of the bands reach their maxima at ca. 20000 cm^{-1}.

Bands characteristic of metal–sulfur stretchings have been observed in the region of 300—400 cm^{-1}.[12] For the trinuclear μ-S complex, $[Co\{Co(SCH_2CH_2NH_2)_3\}_2]^{3+}$, the Co–S stretchings have been assigned to the 358- and 345-cm^{-1} bands, and the bendings, to the 278- and 262-cm^{-1} bands.[9] We observed the Co–S stretching at 370 cm^{-1} and the bendings at 301 and 258 cm^{-1} for $K_3[Co\{Co(SCH_2CH(NH_2)COO\text{-}N,S)_3\}_2]$. On the basis of the assignment for the trinuclear complexes and the measurement of the depolarization ratios, the bands at



A: linear chain **B: asymmetric triple μ_2** **C: honeycomb**



D: cubane **E: sheet**

Fig. 4. Possible bridging modes of polymeric Co-(S–R)$_3$ complex (● and O denote sulfur and cobalt atom, respectively).

402 and 346 cm^{-1} of the polymeric Co(SCH$_2$CH(NH$_2$)-COOH-*S*)$_3$ complex can be assigned to the totally symmetric Co–S stretchings, and the bands at 281 and 223 cm^{-1}, to the totally symmetric bending modes. Similarly, the bands at 379 and 339 cm^{-1} of the polymeric Na$_3$Co(SCH$_2$COO-*S*)$_3$ complex can be assigned to the totally symmetric Co–S stretchings, and those at 281 and 262 cm^{-1}, to the totally symmetric bendings.

It is noted that, on going from the polymeric Co(SCH$_2$CH(NH$_2$)COOH-*S*)$_3$ to the polymeric Na$_3$Co-(SCH$_2$COO-*S*)$_3$, the band at 402 cm^{-1} shifts to lower wavenumbers, and the band at 223 cm^{-1}, to higher wavenumbers, while the other two bands remain at almost the same position. This spectral behavior may suggest that, in these complexes, there are two types of bridging modes and that the bridging geometry (Co–S bond length and/or Co–S–Co angle) of one of them is affected by the nature (probably the bulkiness) of pendant group, while the other is not. A change in the bridging geometry would result in the frequency shift of the Co–S stretching and the Co–S–Co bending.

The weak band at 453 cm^{-1} of the polymeric Na$_3$Co(SCH$_2$COO-*S*)$_3$ complex can not be assigned at present. The position is, however, somewhat higher for a Co–S stretching band.

Possible Bridging Modes. Figure 4 shows possible bridging modes for the present polymeric thiolato complexes, Co(S–R)$_3$. It is well-known that thiolates can take a variety of bridging modes because of the flexibility of the sulfur bridging. For example, the M–S–M angles are ca. 60° in [(Me$_2$S)Cl$_2$W(SEt)$_3$WCl$_2$-(SMe$_2$)][13] while they are ca. 140° in [Fe$_3$(SPh)$_3$Cl$_6$]$^{3-}$.[14] Though these facts allow us to apply a variety of bridging modes to the present polymeric thiolato complex, the present results of the totally symmetric Co–S stretchings restrict the possibility of the bridging mode as follows!

(A) The linear chain structure with two triple μ_2-bridges proposed by McCormick and Gorin[4] has been found in the trinuclear complexes, [Co{Co(SCH$_2$CH$_2$-NH$_2$-*N*,*S*)$_3$}$_2$]$^{3+}$ [15] and [Co{Co(SCH$_2$CH(NH$_2$)COO-*N*,*S*)$_3$}$_2$]$^{3-}$.[10] This structure is, however, inconsistent with the present Raman results, because the structure gives only one totally symmetric Co–S stretching band if the triple μ_2-bridge is symmetric.

(B) An asymmetric triple μ_2-bridge caused by the elongation of an M–S–M moiety has been found in low-symmetry mixed-ligand complexes such as [Re$_2$-(SC$_6$H$_4$Me)$_7$(NO)$_2$]$^-$.[16] A lowering of the symmetry of the triple μ_2-bridge caused by this kind of distortion gives two totally symmetric Co–S stretchings. This distortion, however, seems to be unlikely in the present polymeric complexes, with only one kind of ligand, as in [Co{Co(SCH$_2$CH$_2$NH$_2$-*N*,*S*)$_3$}$_2$]$^{3+}$ [15] and [Co{Co-(SCH$_2$CH(NH$_2$)COO-*N*,*S*)$_3$}$_2$]$^{3-}$.[10]

(C) A honeycomb structure with three double μ_2-bridges such as [Co{(OH)$_2$Co(en)$_2$}$_3$]$^{6+}$ [17] is also inconsistent with the Raman results for the same reason as has been mentioned in (A).

(D) Structure **D** containing a cubane structure has three μ_3-bridging thiolates, one double μ_2-bridging thiolate, and one nonbridging thiolate. A cubane structure with thiolato-bridges has also been found in [Re$_4$(CO)$_{12}$(SMe)$_4$].[18] For Structure **D**, the three Co–S(μ_3) bonds are not equivalent; that is, two of them are trans to the Co–S(μ_2) bond, while one is trans to the Co–S (nonbridging) bond. Thus, this structure should give three totally symmetric Co–S(bridging) stretchings (two Co–S(μ_3) stretchings and one Co–S(μ_2) stretching).

(E) The sheet structure proposed by McCormick and Gorin[4] consists of two different μ_2-bridging modes—namely, two double μ_2-bridges and two single μ_2-bridges. Structure **E** gives two totally symmetric Co–S stretchings. Such greatly different Co–S–Co bridging modes are probable causes of the appreciable difference in the wavenumbers of the two Co–S stretchings of the present polymeric thiolato complexes. In conclusion, the present polymeric thiolato cobalt(III) complexes are highly likely to have the sheet structure **E**.

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