

## Resonance Raman Spectra of Trinuclear Complexes Containing Tris-(2-mercaptoethylamine)cobalt(III) as Ligands

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*Raman spectra of  $\text{CoL}_3$  (HL: 2-mercaptoethylamine) and trinuclear complexes of the type  $[\text{M}(\text{CoL}_3)_2]^{n+}$ , where  $\text{M} = \text{Co(III)}, \text{Fe(III)}, \text{Ru(III)}, \text{Cd(II)}$  and  $\text{Ni(II)}$  and  $n = 2$  or  $3$ , have been obtained under resonance and off-resonance conditions. Two strong Raman bands near  $343$  and  $261 \text{ cm}^{-1}$  were observed for each of the trinuclear compounds. These have been respectively assigned to the totally symmetric  $\text{CoS}_3$  stretching and  $\text{CoS}_3$  bending vibrations of the  $\text{CoL}_3$  moiety which has been perturbed by interaction with the central metal. A companion band to each of these is revealed by the off-resonance spectra; we assign them to similar modes involving the central metal (M). Excitation profile studies of the bending vibrations indicate that the visible transitions which result in absorption at ca.  $450 \text{ nm}$  ( $500 \text{ nm}$  for the Fe complex) are due to CoS CT transitions localized on the  $\text{CoL}_3$  moiety.*

### Introduction

It is well-known that polymetallic complexes play a major role in physiological processes. Some examples of biologically active polymetallic complexes include nitrogenase, xanthine oxidase, ferredoxin and many others [1, 2]. In many of these cases the iron is coordinated to sulfur donors. Although a great deal is known about the types of reactions these complexes undergo, relatively little is known about the nature of metal–sulfur interactions in such complexes or the role of the bridging sulfur donors in mediating these interaction. This lack of information is due in part to the difficulty in interpreting vibrational spectra. In general, resonance Raman (RR) spectra are much simpler than IR or normal Raman spectra since only those vibrations localized on the chromophore are enhanced when the exciting laser frequency is tuned into the electronic absorption maximum which is associated with this particular chromophore. This feature greatly facilitates the vibrational assignments of large complex molecules containing multiple chromophoric

centers. Furthermore, excitation profile studies provide a means to identify the electronic band associated with a given vibration since its Raman intensity should be maximized at the laser energy corresponding to that of the electronic transition. In our previous investigations [3–9] we have utilized this ‘selectivity’ to assign either the vibrational modes or the electronic transition involved in RR enhancement. However, it will first be necessary to study model complexes by this technique in order to understand its limitations and to generate reference data to compare with that obtained from the associated biological species.

In this paper we wish to report the results and conclusions of our Raman studies on trinuclear complexes of the type  $[\text{M}(\text{CoL}_3)_2]^{n+}$  where L is the 2-mercaptoethylamine anion ( $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—S}^-$ ), M is Co(III), Fe(III), Ru(III), Cd(II) or Ni(II) and  $n = 2$  or  $3$ . Thus far, IR spectra of the  $[\text{M}(\text{CrL}_3)_2]^{2+}$  series (M = Mn(II), Co(II), Ni(II), Zn(II) and Cd(II)) [10] and RR spectra of  $\text{M}(\text{AlCl}_4)_2$  (M = Cu(II) and Pd(II)) [11, 12] have been reported. However, no vibrational studies are available for the  $[\text{M}(\text{CoL}_3)_2]^{3+}$  series.

### Experimental

$\text{CoL}_3$  and the trinuclear complexes were prepared by the methods described previously [13, 14]. The Raman spectra were recorded on a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034A photomultiplier tube in conjunction with a Spex digital photometer system. Excitations between 454.5 and 514.5 nm were made by a Spectra-Physics Model 164 Ar-ion laser. The spectra were measured as KBr pellets. Relative intensities of the bands plotted in the excitation profiles were measured against the  $454 \text{ cm}^{-1}$  band of the internal standard,  $\text{K}_2\text{SO}_4$ , which was mixed homogeneously with the sample in a KBr pellet. All intensities plotted were corrected for the  $\nu^4$  dependence and spectrophotometer response. Polarization



Fig. 1. Structure of the  $M(\text{CoS}_3\text{N}_3)_2$  core.

of Raman lines of the Fe(III) and Co(III) trinuclear complexes was measured in aqueous solution. Since  $\text{CoL}_3$  is not soluble in any common solvents, polarization of its Raman lines was measured in a KBr pellet which was mixed with  $\text{K}_2\text{SO}_4$ . The rotating sample technique was used throughout this work. All electronic spectra were measured in aqueous solution as well as in a KBr pellet using a Model EU-700 McPherson spectrophotometer.

## Results and Discussion

### Vibrational Assignments

While the results of an X-ray analysis are available for  $[\text{Ni}(\text{NiL}_2)_2]\text{Cl}_2$  [15], no structural information is in the literature for the trinuclear complexes except that the  $\text{Fe}(\text{CoN}_3\text{S}_3)_2$  skeleton of  $[\text{Fe}(\text{CoL}_3)_2]\text{Br}_3$  probably takes a  $D_{3d}$  structure (Fig. 1) although the possibility of a prismatic  $D_3$  geometry cannot be ruled out [16]. The  $\text{CoN}_3\text{S}_3$  skeleton of the precursor  $\text{CoL}_3$  may take  $C_{3v}$  (*fac*) or  $C_{2v}$  (*mer*) symmetry. Since our main interest in this work is the elucidation of structural and bonding information of these skeletons, the following discussion is limited to the vibrational spectra below  $600\text{ cm}^{-1}$  where the  $\nu(\text{CoN})$ ,  $\nu(\text{CoS})$ ,  $\nu(\text{MS})$  ( $\nu$ : stretching) and skeletal bending ( $\delta$ ) vibrations are expected to occur. Throughout this manuscript we will refer to vibrations as the stretching or bending of certain portions of the molecules. Of course, we do not mean to imply that these are pure modes, for in the low frequency region, extensive coupling is to be expected. A complete description of the modes can only be obtained from rigorous normal coordinate calculations. Nevertheless, the assignments we shall make are useful since they describe the major contributions to the molecular motion.

Figure 2 shows the Raman spectra of the trinuclear complexes in the solid state. Although not shown here, a doublet of weak or medium intensity appears in the  $495\text{--}545\text{ cm}^{-1}$  region in each case. These bands are assigned to the  $\nu(\text{CoN})$  made since many Co(III) ammine and amine complexes exhibit  $\nu(\text{CoN})$  in this region [17]. Doublets or triplets at  $418\text{--}430\text{ cm}^{-1}$  are assigned to the skeletal deformation of the chelating ligand (L) by analogy to the assignments made previously for  $\text{NiL}_2$ ,  $\text{PdL}_2$  and  $\text{PtL}_2$  in the  $450\text{--}475\text{ cm}^{-1}$  region [18].

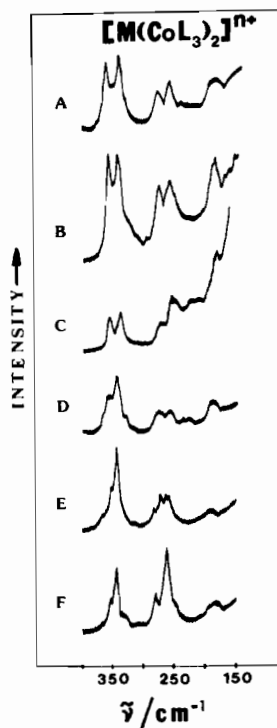


Fig. 2. Raman spectra of  $[\text{M}(\text{CoL}_3)_2]^{n+}$  ions in the solid state: A, M = Cd(II); B, M = Ni(II); C, M = Ru(III); D, M = Co(II); E, M = Fe(III); F, M = Fe(III). Exciting lines are  $514.5\text{ nm}$  except for E for which the  $457.9\text{ nm}$  line was used.

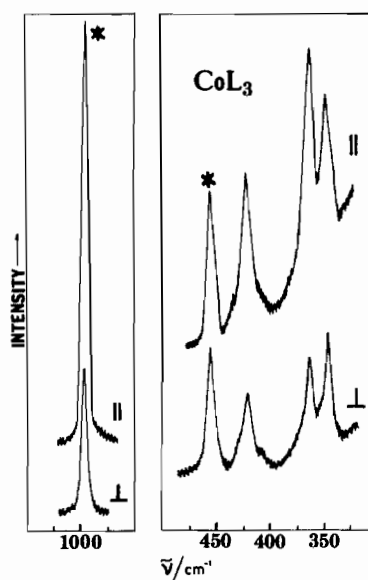


Fig. 3. Polarized Raman spectra of  $\text{CoL}_3$  in the solid state. The asterisks indicate the  $\text{K}_2\text{SO}_4$  bands impregnated with  $\text{CoL}_3$  in a KBr disk.

TABLE I. Electronic and Resonance Raman Spectra of  $\text{CoL}_3$  and  $[\text{M}(\text{CoL}_3)_2]^{n+}$  Complexes.<sup>a</sup>

Compound	Electronic Spectra ( $\lambda_{\text{max}}$ , nm)		Resonance Raman Spectra ( $\text{cm}^{-1}$ )			
	I	II				
$\text{CoL}_3$	(595)	465	—	366(p) 349(dp)	—	277
$[\text{Cd}(\text{CoL}_3)_2]\text{CdBr}_4$	(590) (563)*	445 438*	361	341	277	260
$[\text{Ni}(\text{CoL}_3)_2]\text{Br}_2$	(590) (563)*	448 438*	358	343	278	263
$[\text{Ru}(\text{CoL}_3)_2]\text{I}_3$	(590) (563)*	(450) 438*	359	341	(274)	258
$[\text{Co}(\text{CoL}_3)_2]\text{Br}_3$	(590) (563)*	450 438*	358	345	278	262
$[\text{Fe}(\text{CoL}_3)_2]\text{Cl}_3$	(590) (570)*	500 489*	354	345	(280)	261
Assignment	d-d	Co-S CT of $\text{CoL}_3$	$\nu(\text{MS}_6)$	$\nu(\text{CoS}_3)$	$\delta(\text{MS}_6)$	$\delta(\text{CoS}_3)$

<sup>a</sup>All the values listed are obtained in the solid state except for those asterisked which were obtained in aqueous solution. Estimated values for shoulder bands are given in parentheses.

$\text{CoL}_3$  itself exhibits two strong Raman bands at 366 and 349  $\text{cm}^{-1}$  (see Fig. 3). To determine the symmetry properties of the vibrations responsible for these bands, it is necessary to measure their depolarization ratios. However,  $\text{CoL}_3$  is quite insoluble in all common solvents. We have, therefore, taken polarization measurements of a rotating KBr disk that was impregnated with both  $\text{CoL}_3$  and an internal standard ( $\text{K}_2\text{SO}_4$ ). Although the molecules cannot be considered to be completely random in the KBr matrix and reflection off of microcrystalline surfaces may cause some error, inclusion of a standard can be used to obtain reasonable and useful estimates of the depolarization ratios. In this study we used the  $\nu_2(\text{E})$  mode of  $\text{SO}_4^{2-}$  which occurs at 454  $\text{cm}^{-1}$  and must be depolarized. We were able to establish that the bands at 418 and 366  $\text{cm}^{-1}$  of  $\text{CoL}_3$  were polarized but the band at 349  $\text{cm}^{-1}$  was depolarized (see Fig. 3). Figure 3 also shows the effect of reorienting the polarization analyzer on the totally symmetric stretching mode of  $\text{SO}_4^{2-}$  (983  $\text{cm}^{-1}$ ) in order to demonstrate the feasibility of this technique. Thus, the former two bands are assigned to totally symmetric modes ( $A_1$  under  $C_{3v}$  or  $C_{2v}$  symmetry) whereas the latter is assigned to a non-totally symmetric mode such as E or  $B_2$  under  $C_{3v}$  or  $C_{2v}$  symmetry, respectively.

The bands at 366 and 349  $\text{cm}^{-1}$  of  $\text{CoL}_3$  are assigned to  $\nu(\text{CoS}_3)$  for two reasons: (1) Tris(dithiocarbamate) complexes of Co(III) exhibit  $\nu(\text{CoS})$  in the region from 370 to 340  $\text{cm}^{-1}$  [19, 20], (2) Modes involving motion of sulfur atoms are typi-

cally strong in Raman spectra due to the associated large changes in polarizability.

Upon formation of the trinuclear complexes, the  $\text{CoL}_3$  band at 366  $\text{cm}^{-1}$  disappears and in off-resonance spectra doublet bands are observed at ca. 340–360  $\text{cm}^{-1}$  as well as ca. 260–280  $\text{cm}^{-1}$  (see Fig. 2). One member of each of these doublets shows Raman enhancement when the exciting line is varied. For example, traces E ( $\lambda_{\text{ex}} = 457.9$  nm) and F ( $\lambda_{\text{ex}} = 514.5$  nm) of Fig. 2 show the effect of this enhancement on  $[\text{Fe}(\text{CoL}_3)_2]\text{Br}_3$ . At maximum enhancement the two resulting bands occur at ca. 261  $\text{cm}^{-1}$  and 343  $\text{cm}^{-1}$  in each case. Since the trinuclear complexes are soluble in water and relatively stable, we were able to obtain polarization data in the usual fashion. When the 514.5 nm line was used for excitation, the depolarization ratio was near 0.5 for all the doublet bands near 350 and 270  $\text{cm}^{-1}$ , indicating that they arise from totally symmetric modes. Thus the  $A_1$  mode of  $\text{CoL}_3$  (366  $\text{cm}^{-1}$ ) has shifted to ca. 343  $\text{cm}^{-1}$  upon complexation; an event not altogether unexpected since the S atoms are now bonded to the central metal. The corresponding  $E(C_{3v})$  or  $B_2(C_{2v})$  mode (349  $\text{cm}^{-1}$  in  $\text{CoL}_3$ ) which belongs to  $E_u$  under  $D_{3d}$  symmetry is forbidden. Our first inclination was to assign the new polarized band at ca. 261  $\text{cm}^{-1}$  to the  $\nu(\text{MS})$  of the  $\text{MS}_6$  core since there is no strong band in this region of the spectrum of  $\text{CoL}_3$ . However, the frequency of this mode is almost completely insensitive to the central metal. It occurs at the same position ( $261 \pm 2$   $\text{cm}^{-1}$ ) for all the trinuclear com-

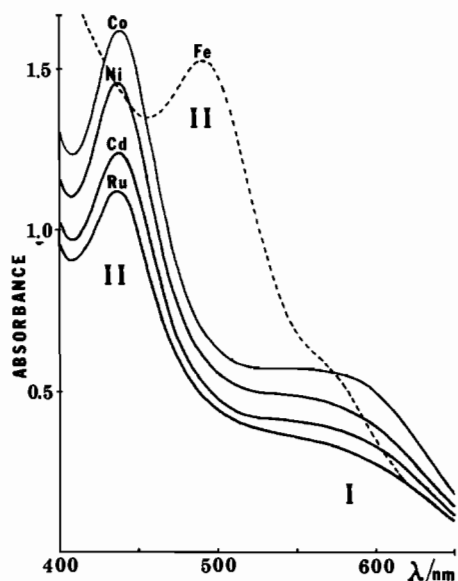


Fig. 4. Electronic absorption spectra of  $[M(\text{CoL}_3)_2]^{n+}$  ions in aqueous solution (*ca.*  $2 \times 10^{-4}$  M/L).

plexes we have studied (See Fig. 2 and Table I). We are therefore compelled to assign this band to a terminal  $\delta(\text{CoS}_3)$  mode that is perturbed by the central metal. The two higher frequency components of the doublets must then be attributed to  $\nu(\text{MS}_6)$  and  $\nu(\text{MS}_6)$  of the central metal. Two experimental observations reinforce those assignments. First of all the Ni-S bond lengths in the complex  $[\text{Ni}(\text{NiL}_2)]\text{Cl}_2$  [15] are very close indicating similar bond strengths for both the central and terminal Ni-S bonds. Thus we expect their frequencies to be close to one another. Secondly, the splitting of the higher frequency doublet increases with the increasing softness of the central metal. Namely, soft metals such as Cd(II) or Ni(II) show a band separation of 15–20  $\text{cm}^{-1}$  while harder metals *i.e.* Co(III) and Fe(III) give rise to 9–13  $\text{cm}^{-1}$  separations.

#### Electronic Spectra and Excitation Profiles

Figure 4 shows the electronic spectra of the  $[M(\text{CoL}_3)_2]^{n+}$  ions in aqueous solution. These spectra are essentially the same as those obtained in the solid state except that the band maxima are shifted by *ca.* 10–20 nm to longer wavelength (see Table I). Bands I and II were originally suggested to be d-d transitions [21]. Later Freeh *et al.* [13] assigned them to the metal-ligand CT transitions since they are too strong for d-d transitions. These metal-ligand CT transitions probably involve metal-sulfur CT because metal-nitrogen CT would not occur at such low energies.

We have previously shown that excitation profile studies of metal complexes are extremely useful in

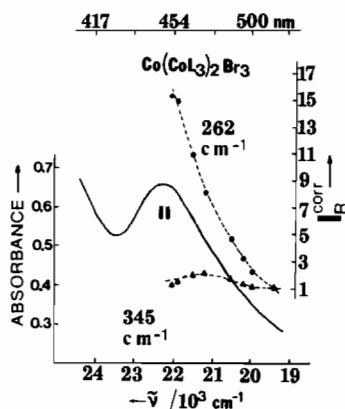


Fig. 5. Excitation profiles for  $\nu(\text{CoS})$  ( $345 \text{ cm}^{-1}$ ) and  $\delta(\text{CoS}_3)$  ( $262 \text{ cm}^{-1}$ ) of  $[\text{Co}(\text{CoL}_3)_2]\text{Br}_3$ .

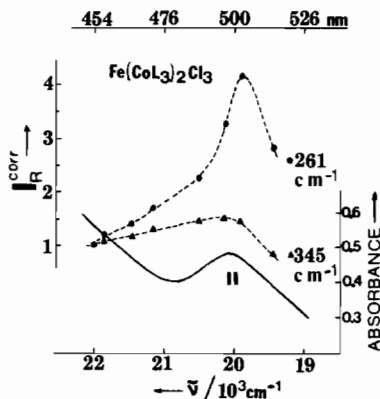


Fig. 6. Excitation profiles for  $\nu(\text{CoS})$  ( $345 \text{ cm}^{-1}$ ) and  $\delta(\text{CoS}_3)$  ( $261 \text{ cm}^{-1}$ ) of  $[\text{Fe}(\text{CoL}_3)_2]\text{Cl}_3$ .

understanding their electronic and vibrational spectra [4, 8, 9]. In almost all cases we have studied, the enhancement was found to be due to interaction with a single electronic transition. This is the so-called A-type resonance [22] which enhances only the totally symmetric modes. The transition involved in the process is typically of the metal  $\rightarrow$  ligand or ligand  $\rightarrow$  metal type. We know of only one reported case of resonance enhancement *via* d-d transitions [23]. In fact, d-d enhancement is not expected at all since the lead terms in the analytical expression for the A-type resonance involve pure electronic transition moments which are zero for d-d transitions.

Figures 5 and 6 show the Raman excitation profiles of the  $\delta(\text{CoS}_3)$  and  $\nu(\text{CoS}_3)$  of the two trinuclear compounds. The intensity of the  $\delta(\text{CoS}_3)$  near  $261 \text{ cm}^{-1}$  maximizes at *ca.* 500 and 450 nm, respectively, for the Fe and Co complexes. These positions correlate nicely with the electronic absorp-

tion maxima (Band II) of the respective complexes and clearly demonstrate that it is of the CT type in each case. The excitation profiles of the  $341\text{ cm}^{-1}$  bands show a slight wavelength dependence in both compounds. Following the suggestion of Tsuboi [24] we can conclude that the intensity of the  $261\text{ cm}^{-1}$  band arises because the vibrational motion (which we have ascribed to a bend) approximates the shape of the first excited state of the molecule. Band I must be largely due to a d-d transition since no resonance enhancement of any mode was noted when the laser wavelength was close to 590 nm. The large  $\epsilon$  which is observed for the 590 nm band may be due to overlap with the tail of higher energy CT transitions.

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