# The Resonance Raman Study on the Visible Absorption Spectrum of Tris(dithiooxalato-*S,S*)cobaltate(III)

Kan KANAMORI,* Akiko ONO, Sonomi INO, Isao KANESAKA, Kiyoyasu KAWAI, and Jinsai HIDAKA†
Faculty of Science, Department of Chemistry, Toyama University, Gofuku, Toyama 930
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
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**Synopsis.** The Raman bands due to the totally symmetric $\nu$(C-C)+$\nu$(C-S) and $\nu$(Co-S) modes of tris(dithiooxalato-*S,S*)cobaltate(III) exhibit resonance enhancements with excitation lines in the visible region. The resonance Raman excitation profiles of the two modes reveal the presence of a charge-transfer transition in the visible absorption spectrum of the complex.

The electronic structure of a transition metal complex with dithiooxalate ($dto^{2-}$: $C_2S_2O_2^{2-}$) has been a subject of interest because of the considerably delocalized $\pi$-orbital system of the ligand. The electronic spectral properties of planar divalent metal complexes with $dto^{2-}$ were studied in several ways. For example, Kida et al.[1] reported the electronic absorption spectra of $[M(dto)_2]^{2-}$ (M=Ni(II), Pd(II), and Pt(II)). Latham et al. assigned the electronic absorption bands of the above-mentioned complexes on the basis of a molecular orbital treatment.[2] The visible absorption feature of $[Ni^{II}(dto)_2]^{2-}$ was investigated in detail by the use of Raman excitation profiles.[3] For octahedral trivalent metal complexes with $dto^{2-}$, Carlin and Canziani[4] investigated the visible absorption spectra of $[M(dto)_3]^{3-}$ (M=Cr(III), Co(III), and Fe(III)) and Hidaka and Douglas[5] discussed the circular dichroism spectra of $[M(dto)_3]^{3-}$ (M=Cr(III), Co(III), and Rh(III)). Two shoulders at 17000 and 21800 $cm^{-1}$ of $[Co^{III}(dto)_3]^{3-}$ were assigned to the d-d transitions.[4,5] However, the absorption coefficient ($\log\varepsilon$=3.5) of the 21800-$cm^{-1}$ band seems to be large for a Laporte-forbidden d-d transition, even if the d-d transitions are allowed to occur, to some extent, by orbital mixing (covalency) between the sulfur donor and cobalt(III). Here, we report the resonance Raman excitation profiles of $[Co^{III}(dto\text{-}S,S)_3]^{3-}$ as well as the property of absorption bands in the visible region. The application of the resonance Raman effect to the electronic absorption spectral study of transition metal complexes has been reviewed.[6]

## Experimental

**Preparation of Complexes.** $CaK[Co^{III}(dto\text{-}S,S)_3]\cdot 6H_2O$ was prepared according to a method described in the literature[7] and was identified by its electronic absorption spectrum.

**Measurements.** Samples for Raman measurements were provided as disks containing an appropriate amount of $K_2SO_4$ (8 to 12 times of the complex in weight) as an intensity standard. Disks were spun in order to avoid thermal decomposition. Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer using a Spectra Physics 164 $Ar^+$ laser (514.5, 501.7, 496.5, 488.0, 476.5, 465.8, and 457.9 nm) and a Coherent Radiation model CR599 dye laser employing Rhodamine 6G dye (632.8, 610.0, 588.0, and 567.8 nm). The laser power was below 100 mW. The spectral band width was set to 5 $cm^{-1}$. Intensity measurements were made relative to the totally symmetric S-O stretching of the sulfate incorpolated in the sample. Corrections of the observed intensity were applied to the fourth power of the wavenumber of scattered radiation and the instrumental response. Intensities were averaged over more than three measurements.

Electronic absorption spectra were measured with a Hitachi 220 spectrophotometer.

## Results and Discussion

Figure 1 shows the resonance Raman spectrum of $CaK[Co^{III}(dto\text{-}S,S)_3]$. The band at 1113 $cm^{-1}$ can be assigned to the $\nu$(C-C)+$\nu$(C-S) mode and the band at 349 $cm^{-1}$ to the $\nu$(Co-S) mode in comparison with the

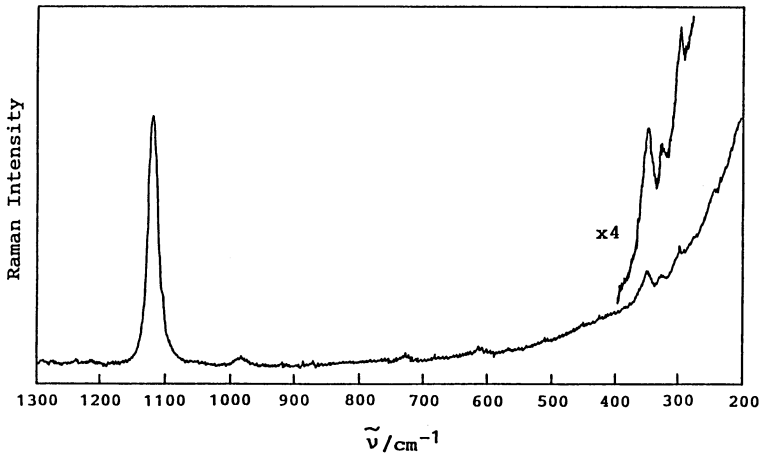


Fig. 1. Resonance Raman spectrum of $CaK[Co^{III}(dto\text{-}S,S)_3]$ (KBr disk, 488.0-nm excitation).

results of the normal coordinate analysis of $[Ni(dto\text{-}S,S)_2]^{2-}$,[3] where the $\nu$(C-C)+$\nu$(C-S) and $\nu_s$(Ni-S) modes were assigned to the bands at 1085 and 317 $cm^{-1}$, respectively. The 1113-$cm^{-1}$ band of $[Co^{III}(dto\text{-}S,S)_3]^{3-}$ is polarized in the solution Raman spectrum and can be assigned to the totally symmetric mode. The depolarization ratio of the 349-$cm^{-1}$ band could not be determined precisely because of difficulty in observing the band of appropriate intensity in solution. This band, however, is the most intense band observed in the Co-S stretching region, and is reasonably assigned to the totally symmetric mode, since a totally symmetric metal-ligand stretching mode generally gives a far more intense Raman band than that of a non-totally symmetric mode as has been observed for the tris(chelate) complexes, $[Co^{III}(en)_3]^{3+}$ and $[Co^{III}(tn)_3]^{3+}$.[8]

Figure 2-A shows the visible absorption spectrum of $[Co^{III}(dto\text{-}S,S)_3]^{3-}$. The broad and unusually intense spectrum indicates that the d-d and charge-transfer transitions overlap each other. Low-energy metal-to-ligand charge-transfer transitions occur with high probability for complexes with $dto^{2-}$ which have a low-energy $\pi^*$-orbital.[2]

Resonance Raman excitation profiles (that is, Raman intensities as a function of the excitation wavelength) have been successfully applied[3,9-13] to resolve overlapping absorption bands, especially those consisting of different types of transitions, such as d-d and charge-transfer transitions. This is because of the following features of resonance enhancements: (1) Excitation profiles are highly structured compared with electronic absorption spectra. (2) The extent of resonance enhancement greatly depends on the nature of resonant transitions. Resonance enhancement

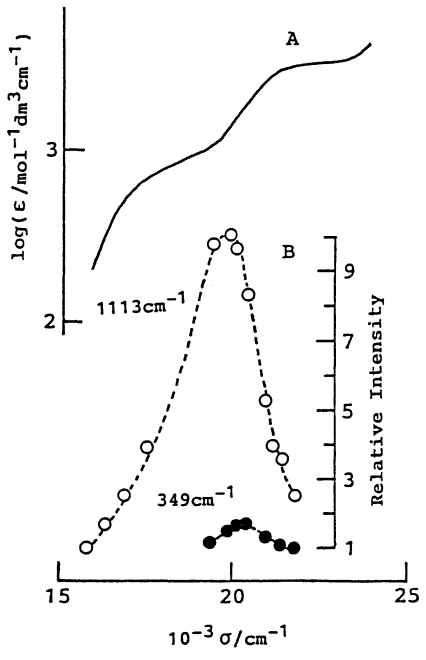


Fig. 2. A: Electronic absorption spectrum of $[Co^{III}(dto)_3]^{3-}$. B: Excitation profiles of the totally symmetric $\nu$(C-C)+$\nu$(C-S) and $\nu$(Co-S). The weakest intensity was normalized to unity.

through an "A-type" interaction,[14] which concerns a single excited state, could hardly be expected within a Laporte-forbidden d-d transition.[15]

The strong resonance-enhancement was observed for the totally symmetric intra-ligand mode, $\nu$(C-C)+$\nu$(C-S), while the weak enhancement was observed for the totally symmetric metal-ligand mode, $\nu$(Co-S).[16] The resonance-enhancement was not observed for the bands due to the non-totally symmetric modes. This observation indicates that the resonance-enhancement found in the present complex is the "A-type" which causes an intensity enhancement for the totally symmetric mode, but not for the non-totally symmetric mode. Therefore, the resonant transition must be a purely allowed transition, namely a charge-transfer transition. Figure 2-B illustrates the excitation profiles of the totally symmetric $\nu$(C-C)+$\nu$(C-S) and $\nu$(Co-S) modes. The excitation profiles for both modes maximize at ca. 20000 $cm^{-1}$. This fact reveals that a charge-tansfer transition is situated at ca. 20000 $cm^{-1}$ and overlaps with the two d-d transitions.

Coucouvanis and Piltingstrud[17] studied the absorption spectra of polynuclear complexes of the $[M(Ph_3P)_2]_3[M'(dto)_3]$-type (M=Cu(I), Ag(I); M'= Co(III), Al(III), Rh(III), and Cr(III)). They presumed that the band at ca. 20000 $cm^{-1}$ of $[Co^{III}(dto)_3]^{3-}$ is due to a charge-transfer transition on the basis of the spectral change caused by the formation of an adduct with $[Cu^{I}(Ph_3P)_2]^{+}$. The present result is consistent with their suggestion.

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15) Resonance enhancement of totally and non-totally symmetric modes was observed within the d-d absorption bands of nitrocobalt(III) complexes. This phenomenon was interpreted as a result of "B-type" interaction that concerns two excited states, namely the partly allowed d-d

and charge-transfer states. K. Kanamori, A. Shimizu, H. Sekino, S. Hayakawa, Y. Seki, and K. Kawai, *J. Chem. Soc., Dalton Trans.*, **1988**, 1827.

16) This is similar to the case of $[Fe^{II}(bpy)_3]^{2+}$ and $[Fe^{II}(phen)_3]^{2+}$ complexes of which the electronic configuration is same as that of the present complex (low spin $d^6$) and the visible absorption arises from a metal-to-ligand charge-transfer transition. Ref. 9.

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