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Resonance Raman Spectra of Bis(dithiooxalato)nickel (II) Ion–Stannic Iodide Adduct

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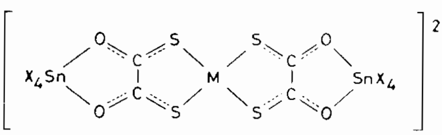
One of the most interesting features of resonance Raman (RR) spectroscopy is the 'selectivity' of resonance enhancement; only those vibrations which are localized on the chromophore are enhanced when the exciting frequency approaches the absorption maximum of this chromophore. In our previous paper [1], we have used this selectivity to assign the V–O (phenolic) charge transfer (CT) band of dibromo-N,N′-bis(salicylidene)propylenediaminato-oxovanadium(V) –copper(I)–methanol. In this paper, we wish to report the RR spectrum of bis(dithiooxalato)nickel (II) ion–stannic iodide adduct which contains two chromophoric groups and to demonstrate the utility of RR selectivity in assigning its electronic spectrum.

Experimental

The stannic iodide adduct of bis(benzyltriphenylphosphonium)bis(dithiooxalato)nickel(II), $[(C_6H_5)_3P(C_7H_7)]_2[(Ni(S_2C_2O_2)_2(SnI_4)_2]$, was prepared by Coucouvanis *et al.* [2]. The RR spectra were measured as KBr pellets. Relative intensities of the bands were measured against the internal standard (KNO_3) which was mixed homogeneously with the sample in a KBr pellet. The spectra were recorded on a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034A photo-multiplier tube in the DC amplification mode. Excitations at 457.9, 488.0 and 514.5 nm were made by a Spectra-Physics Model 164 Ar-ion laser and that at 611.4 nm was made by a Spectra-Physics Model 365 dye laser (Rhodamine 6G) pumped by the above Ar-ion laser. All spectra were measured at low laser powers (typically 30–50 mW) while rotating the sample.

Results and Discussion

In 1973, Coucouvanis *et al.* [2] prepared a series of novel tin halide adducts of nickel(II) and Pd(II) dithiooxalato (DTO) complexes, and determined their structures by X-ray analysis. It was found that the tin halide molecules are coordinated to the oxygen atoms of the dithiooxalato ligands which are already coordinated to the nickel or palladium atom. Such compounds are unique since they contain two chromophoric groups (NiS_4 and SnO_2X_4) in one molecule, and are ideal for testing the selectivity of RR scattering.



According to Coucouvanis *et al.*, the parent compound, $[Ni(DTO)_2]^{2-}$, exhibits three electronic bands at 17.8, 19.9 and 32.7 $\times 10^3$ cm^{-1} in dichloromethane solution. The former two were assigned to the M(d)–DTO(π^*) CT transitions whereas the latter was attributed to the π–π^* transition of DTO itself. When the $[Ni(DTO)_2]^{2-}$ ion forms an adduct with SnI_4, four bands are observed at 15.9, 18.5, 27.9 and 33.0 $\times 10^3$ cm^{-1}. The first two bands were assigned to the M–DTO CT transitions whose energies were reduced by the lowering of the DTO(π^*) orbital energy caused by the adduct formation. However, the nature of the remaining two bands was not clear. As will be shown below, our RR study provides strong evidence for assigning the band at 27.9 $\times 10^3$ cm^{-1} to the CT transition within the SnO_2I_4 moiety. In fact, SnI_4 in CCl_4 solution exhibits a strong CT transition at 27.2 $\times 10^3$ cm^{-1} [3].

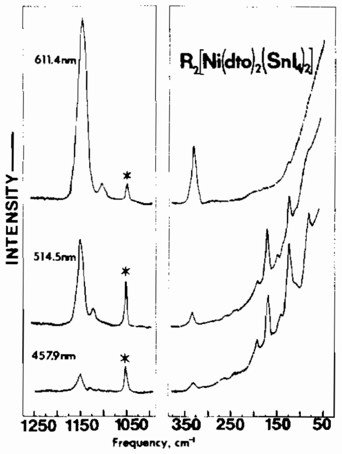


Fig. 1. Resonance Raman spectra of $[(C_6H_5)_3P(C_7H_7)]_2[Ni(DTO)_2(SnI_4)_2]$ in the solid state. Laser power, > 50 mW; slit width, 2–3 cm^{-1}. The band marked by an asterisk is due to the internal standard (KNO_3, 1051 cm^{-1}).

Figure 1 illustrates the RR spectra of the $[Ni(DTO)_2(SnI_4)_2]^{2-}$ ion in the regions of 1250–1000 and 350–50 cm^{-1}. At the 611.4 nm excitation, the spectrum is dominated by two strong bands at 1151 and 335 cm^{-1}. It has been well-established [2] that the former is the ν(CC) coupled with ν(CS) and the latter is the ν(NiS) of the $[Ni(DTO)_2]^{2-}$ moiety. Other weak bands which are not shown in Fig. 1 are the C=O stretch (1516 and 1490 cm^{-1}) and the C–S stretch (630 cm^{-1}). All these frequencies correspond very well with those observed in infrared spectra [2].

At the 514.5 nm excitation (middle trace of Fig. 1), both bands at 1151 and 335 cm^{-1} become weaker, and two new bands appear at 172 and 124 cm^{-1}. The latter frequency is lower than that of the totally symmetric mode of SnI_4 (149 cm^{-1}) [3], and close to that of $(Et_4N)_2[SnI_6]$ (122 cm^{-1} [4]). Thus, it is reasonable to assign it to one of the pseudo-octahedral SnO_2I_4 vibrations which is predominantly the SnI_4 stretch. The other mode at 172 cm^{-1} can be assigned to a similar vibration which is dominated by the Sn–O stretch. The low symmetry (*cis*) SnO_2I_4 moiety is expected to give four more stretching modes in this region. Some of the weak bands observed at 196, 148 and 85 cm^{-1} may be assignable to these modes.

As the exciting frequency approaches the UV region, the $Ni(DTO)_2$ vibrations at 1151 and 335 cm^{-1} become very weak whereas the SnO_2I_4 group vibrations at 200–85 cm^{-1} become very strong. This is dramatically demonstrated by the spectrum obtained with the 457.9 nm excitation (bottom trace of Fig. 1).

These results clearly indicate that two electronic bands of the SnI_4 adduct at 15.9 and 18.5 $\times 10^3$ cm^{-1} (630 and 540 nm, respectively) are due to the Ni–DTO CT transitions as assigned by Coucouvanis *et al.* [2], and that the third band at 27.9 $\times 10^3$ cm^{-1} (358 nm) is due to the CT transition within the SnO_2I_4 unit. The last band at 33.0 $\times 10^3$ cm^{-1} must be due to a π–π^* transition of the $[Ni(DTO)_2]^{2-}$ moiety since the parent complex exhibits a similar band at 32.7 $\times 10^3$ cm^{-1}.

While obtaining the RR spectra, we have noted that the low-frequency spectra change markedly as the laser power is increased. As is shown in Fig. 2, the bands at 196, 172, 124 and 85 cm^{-1} become weaker while the band at 112 cm^{-1} becomes stronger as the laser power is raised from 30 mW (trace 1) to 70 mW (trace 2) to 250 mW (trace 3) at 488.0 nm excitation. In the high frequency region, the band at 1151 cm^{-1} was shifted to 1140 cm^{-1} by laser irradiation. The results were the same for other laser lines. After melting at 135 °C, the sample gave the same RR spectrum as that of trace 3. Its infrared spectrum showed a strong band at 1636 cm^{-1} (free C=O) which was not present in the original sample. These spectral changes definitely indicate the cleavage of the Sn–O bonds by laser irradiation or heating. Although the structure of the resultant compound is not certain, it is possible that such thermal treatment produced a new isomer in which SnI_4 is chelated to the central NiS_4 unit. In any event, our observation demonstrates the need of extreme caution which must be taken in measuring the RR spectra of certain coordination compounds.

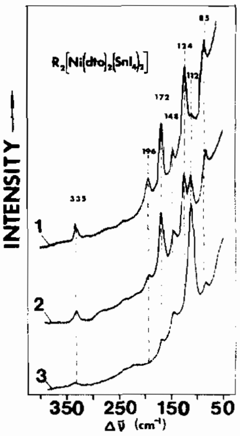


Fig. 2. Resonance Raman spectra of $[(C_6H_5)_3P(C_7H_7)]_2$-$[Ni(DTO)_2(SnI_4)_2]$ in the solid state with 488.0 nm excitation. Laser power used is 30 mW (trace 1), 70 mW (trace 2), and 250 mW (trace 3).

Acknowledgments

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