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A Resonance Raman Spectral Study of Bis[(dithionitrito-S)amido] nickel(II)*

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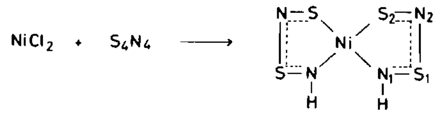
The reaction of tetrasulfurtetranitride with anhydrous nickel(II) chloride in methanol has been shown to yield the planar species bis[(dithionitrito-S) amido] nickel(II) as the major product [1–3]:



(1)

We have recently reported on the vibrational spectrum and a normal coordinate analysis (NCA) on the title compound [4]. These data have been used to support an infrared and NCA study of *trans*-Ni($S_2N_2CH_3$)$_2$ [5] as well as a ^{1}H and ^{13}C NMR study of several bridged condensation products of Ni(S_2N_2H)$_2$ [6]. A recent X-ray study of the title compound has reaffirmed its square planar structure of C_{2v} symmetry [7].

In this paper we report the resonance Raman spectrum and excitation profiles of Ni(S_2N_2H)$_2$ which were used to assign bands in its electronic spectrum [10].

Experimental

The complex, Ni(S_2N_2H)$_2$ was prepared as previously reported [3, 8, 9]. The electronic and resonance Raman spectra were measured using the KBr pellet technique. The electronic spectrum was recorded on a Cary Model 14 spectrophotometer. The resonance Raman spectra were measured by using a Spex Model 1401 double monochromator, while detection was made with a cooled RCA C31034A photomultiplier tube in the DC amplification mode. Exciting lines were provided by a Spectra-Physics Model 164 Argon-ion laser (457.9, 476.5, 488.0, 496.6, 501.8 and 514.5 nm) and by a Spectra Physics Model 365 CW dye laser employing Rhodamine 6G (556.8, 571.8, 578.0, 603.4, 609.8 and 620.1 nm). Relative intensities of the bands were measured against the 984 cm^{-1} band of the internal standard, K_2SO_4, which was mixed homogeneously with the sample in KBr pellet. All the intensities plotted in the excitation profiles were corrected for the ν^4 dependence and detector response. Infrared spectral data on Ni(S_2N_2H)$_2$ were taken from reference 4.

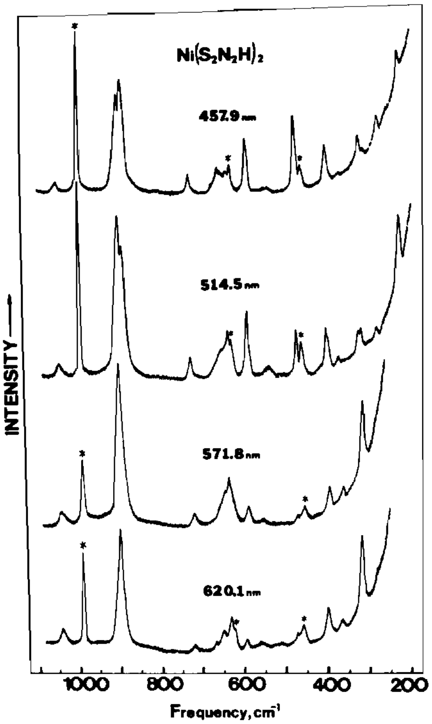


Fig. 1. Resonance Raman spectra of Ni(S_2N_2H)$_2$ in the solid state. The bands marked by asterisk are due to the internal standard (K_2SO_4).

Results and Discussion

The electronic spectrum of Ni(S_2N_2H)$_2$ in ethanol gave bands of increasing intensity [λ_{max}(nm)(ϵ)] at 560 (2170), 400 (4710), 310 (11.470) and 277 (16.500) which are in agreement with those reported by Piper [3]. The 560 and 400 nm bands are slightly shifted to 570 and 410 nm respectively, when the spectrum is recorded in the solid state (KBr pellet). Figure 1 shows the resonance Raman spectra of Ni(S_2N_2H)$_2$ taken in a KBr pellet with laser excitations at 457.9, 514.5, 571.7 and 620.1 nm. The spectral bands marked with asterisks (984, 623, 454 cm^{-1}) are due to the internal standard, K_2SO_4.

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*This compound is also referred to as bis(disulfurdinitride)nickel(II), bis(mercaptosulfurdiimidato-N,$S^{N'}$)nickel(II) and bis[S-(thionitroso)thiohydroxylaminato] nickel(II).

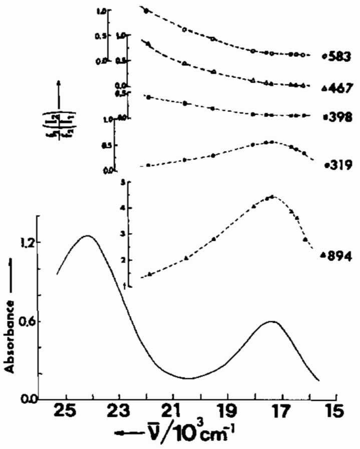

Fig. 2. Excitation profiles of $Ni(S_2N_2H)_2$ in the solid state. Note that the ordinate scale for each fundamental may differ. *I* is the measured intensity; *f* is the ν^4 correction factor.

Fig. 2 shows the excitation profiles for the 894, 583, 467, 398 and 319 cm^{-1} bands.

According to NCA [4], the bands at 984 and 319 cm^{-1} are predominantly the $N_1\text{---}S_1$ stretch (81%) and $Ni\text{---}S_2$ stretch coupled with an in-plane ligand bending mode, respectively. Figs. 1 and 2 show that both of these bands are most strongly enhanced when the exciting frequency is tuned in the electronic band near 570 nm. Similar trends are also seen for the weak bands at 1032 [$S_2\text{---}N_2$ stretch] and 715 cm^{-1} [$S_1\text{---}N_2$ stretch].

These results clearly indicate that the electronic band at 570 nm originates in the $Ni\text{–}S_2$ charge-transfer transition. Since the S_2 atom belongs to the π-conjugated chelate ring system, such a transition also involves electron drift to the $S_2\text{–}N_2$, $N_2\text{–}S_1$ and $S_1\text{–}N_1$ bonds although its exact character can be determined only by rigorous M.O. calculations. A very similar observation was made previously [11] for the resonance Raman spectrum of the $[Ni(DTO)_2\text{-}(SnI_4)_2]^{2-}$ ion [DTO: dithiooxalato ion]; the Ni–S (335 cm^{-1}) and the $C\text{---}C$ coupled with $C\text{---}S$ stretching modes (1151 cm^{-1}) were most strongly enhanced when the exciting frequency was tuned in the Ni–DTO charge-transfer band [12].

According to NCA [4], the bands at 583, 567 and 398 cm^{-1} are due to the $Ni\text{–}N_1$ stretch (35 ~ 40%) coupled with ligand bending modes. As is seen in Fig. 2, the intensities of these vibrations increase monotonically as the exciting frequency is shifted to the UV region. It was not possible, however, to observe the maxima in their excitation profiles due to the lack of the UV laser sources. Thus, it is not certain whether the electronic band at 400 nm is mainly responsible for the resonance enhancement of these vibrations.

The intensity behavior of the 225 cm^{-1} [$Ni\text{–}S_2$ stretch coupled with $Ni\text{–}N_1$ stretch] is not clear since the steepness of the background Rayleigh lines obscured this band when the exciting wavelength was 571.7 and 620.1 nm.

Finally, as seen from Fig. 1 the Raman spectra of $Ni(S_2N_2H)_2$ are dependent on the exciting frequency used and the spectra are dominated by bands which arise from skeletal stretching vibrations of the ligand (L). This indicates that the M–L CT band at 570 nm (and possibly the band at 400 nm) involves the transfer of an electron which is delocalized over the ring system. In fact the CNDO/2 calculation of the free ligand HSNSNR (R is H, CH_3) in the same conformation as in $Ni(S_2N_2H)_2$ suggests much delocalization in the π system [13].

Acknowledgments

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