Resonance-Raman Spectra of Copper(II) and Nickel(II) Diethyldithiocarbamates

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Copper(II) and nickel(II) diethyldithiocarbamates display a resonance-Raman spectrum when excited with laser lines at wavelengths approaching that of the first allowed charge-transfer (c.t.) transition. Both spectra show the preferential intensity enhancement of four bands in the M–S stretching and SCS, SCN, MSC, and SMS bending region at 157—367 cm^{-1}. Except for one deformation mode, all the bands are polarized. Assignments of these bands have been made by comparison with normal-co-ordinate analysis data for dithiocarbamato-complexes. The experimental intensity dependence on Albrecht frequency factors suggests a Raman activity derived from mixing between one c.t. and one ligand transition. The two electronic transitions involved have been assigned by taking into account depolarization ratios and using polarized absorption data and molecular-orbital calculations from the literature.

RESONANCE-RAMAN (r.r.) spectra have been extensively used to identify metal-ligand stretching modes in metalloenzymes. In particular, the Raman spectra of blue copper proteins have shown the preferential intensity enhancement of approximately five resonance Raman peaks in the 260—470 cm^{-1} region [1-3] which have been assigned to metal–ligand vibrations. The region concerned corresponds to CuO, CuN, or CuS stretching modes and, although there is much evidence to support the presence of at least one sulphur ligand co-ordinated to copper,[4-6] the assignment of the CuS stretching mode has been only tentative.[1-3]

The r.r. spectra of copper(II) complexes containing sulphur ligands upon excitation into the band contour of a Cu–S charge-transfer (c.t.) transition should enable a better understanding of the enhancement mechanism taking place as the exciting wave approaches the absorption maximum and permit a more precise assignment of metal–ligand modes. Copper(II) diethyldithiocarbamate appears to be a good simple model with which to study the copper(II)–sulphur interaction by means of r.r. spectra. Its absorption spectrum has a very strong peak at 435 nm which has been assigned to a ligand–metal c.t. transition.[7,8] Furthermore, molecular-orbital calculations based on e.s.r. data [9] and polarized optical-absorption studies [8] should allow a precise assignment of transitions.

A preliminary report on the r.r. spectra of [Cu(S$_2$CNEt$_2$)$_2$] has been published previously.[10] In this paper we present a more complete study of the r.r. spectra of copper(II) and nickel(II) diethyldithiocarbamates.

EXPERIMENTAL

The diethyldithiocarbamates of Cu^{II}, Ni^{II}, and Zn^{II} were prepared by the methods reported in the literature.[11] Sodium diethyldithiocarbamate was of analytical grade and was recrystallized from ethanol for Raman measurements.

Optical-absorption measurements were made using a Cary 14 spectrometer. Raman spectra were recorded with a

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Coderg PHO spectrometer equipped with holographic gratings, using the exciting lines of a Spectra Physics argon-ion laser. The rotating-sample technique was employed[12] using 90° viewing optics. Spectra were recorded in chloroform and benzene solutions for the copper, nickel, and zinc complexes and in water for the sodium salt. Raman intensities were measured using the bands of chloroform at 261 cm^{-1} or of benzene at 606 and 850 cm^{-1} as internal standards. The peak areas were determined by using the trace, cut, and weigh technique or by using the product of peak height and half-band width. When using benzene solutions the Raman spectrum of the quartz rotating cell was observed superimposed on that of the complexes. Therefore the spectrum of quartz was always deducted from that of the sample. Decomposition of the absorption spectra into guassian components was made by means of a Dupont de Nemours 310 curve resolver.

RESULTS AND DISCUSSION

In Figure 1 are reported typical r.r. spectra of [Cu(S_2CNEt_2)$_2$] and [Ni(S_2CNEt_2)$_2$] in benzene. In the spectra of the copper complex an intense band is observed at 157 cm^{-1} and three weaker ones at 325 (plus a shoulder at 312 cm^{-1}), 367, and 426 cm^{-1}. Considerably less-intense bands at 172 (observed in $CHCl_3$ only), 315, 334, 363, and 421 cm^{-1} are observed in the spectra of the nickel complex (see Table 1). Except that at 315 cm^{-1}, all the bands are polarized. The depolarization ratio for the shoulder at 312 cm^{-1} is difficult to ascertain. In fact, this shoulder is detected only as the laser wavelength approaches the maximum of absorption of [Cu(S_2CNEt_2)$_2$]. At wavelengths far away from this maximum only a very broad band is observed at ~318 cm^{-1}. However, taking into account the similarities between the copper and nickel complexes, one can assume that the band at 312 cm^{-1} is also depolarized.

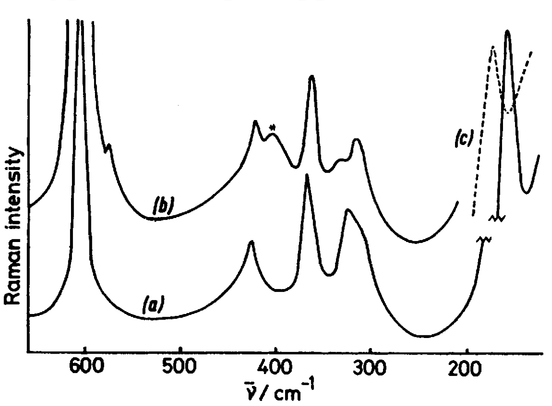

FIGURE 1 Resonance-Raman spectra of [Cu(S_2CNEt_2)$_2$] and [Ni(S_2CNEt_2)$_2$] using 100-mW 454.5-nm argon-ion laser excitation: (*a*) [Cu(S_2CNEt_2)$_2$], 1.44 × 10^{-3} mol dm^{-3} in C_6H_6; (*b*) [Ni(S_2CNEt_2)$_2$], 1.62 × 10^{-2} mol dm^{-3} in C_6H_6; (*c*) [Ni(S_2CNEt_2)$_2$], 1.05 × 10^{-2} mol dm^{-3} in $CHCl_3$. Slit width, 3 cm^{-1}; time constant, 2 s, 50 cm^{-1}/min. The asterisk indicates a C_6H_6 band

The band of [Cu(S_2CNEt_2)$_2$] at 426 cm^{-1} {421 cm^{-1} for [Ni(S_2CNEt_2)$_2$]} is a ligand vibration and appears as a rather strong polarized band at 430 cm^{-1} in the Raman spectra of Na[S_2CNEt_2] in water. It can be tentatively assigned to a totally symmetric NEt deformation mode. A depolarized peak at 306 cm^{-1} is also observed in the spectrum of Na[S_2CNEt_2] in water and, in a normal-co-ordinate study of platinum dithiocarbamates, a band at the same frequency has been assigned to a SCN bending mode (calculated at 297 cm^{-1}).[13] Another weak and depolarized Raman band appears at 352 cm^{-1} in the spectra of the sodium salt and might be assigned to a SCN or SCS out-of-plane bending mode. Hence, the bands originating from complex formation are those at 367 (363), 325 (334), and 157 (172) cm^{-1}. A band at 375 cm^{-1} (357 cm^{-1} in the methyl derivative) has been assigned to a pure Pt–S stretching mode in the platinum dithiocarbamate (calculated at 378 cm^{-1}) by the normal-co-ordinate analysis referred to previously.[13] So it seems reasonable to assign the bands at 363 and 367 cm^{-1} to the Ni–S and Cu–S totally symmetric stretching modes respectively. The band at 325 (334) cm^{-1} can be assigned to a SCS bending mode that might contain some contribution from the MS stretch. Finally, the band at 157 (172) cm^{-1} can be assigned to a bending mode containing contributions from SMC and SMS deformations.

In Figures 2 and 3 are presented the excitation profiles of these Raman bands. The strong asymmetric band of Figure 2 can be decomposed into gaussians at 23 250, 21 600, and 19 500 cm^{-1}. The spectrum contains two additional bands, not seen in the Figure, at 34 700 and 37 000 cm^{-1} which are ligand transitions. As the excitation profile shows, the maximum enhancement follows the general contour of the peak at 23 250 cm^{-1}. The experimental intensity dependence on Albrecht frequency factors suggests a Raman activity derived

TABLE 1

Raman bands (cm^{-1}) and depolarization ratios of the diethyldithiocarbamates of Cu^{II}, Ni^{II}, Zn^{II}, and Na

[Cu(S_2CNEt_2)$_2$] in C_6H_6		[Ni(S_2CNEt_2)$_2$] in C_6H_6		[Zn(S_2CNEt_2)$_2$] in C_6H_6		Na[S_2CNEt_2] in water		
	ρ		ρ		ρ		ρ	Assignment
426	p	421	p			430s	p	δ[NCC(Et)]
						352w	dp	
367	0.3—0.4	363	0.3—0.4					ν(MS)
325	0.3—0.4	334	0.3—0.4	330vw	?			δ(SCS) + ν(MS)
312 (sh)	?	315	dp			306m	dp	δ(SCN)
157	0.33 ± 0.02	172 *	0.33 ± 0.05	147w	p			δ(SMS) + δ(MSC)

* In $CHCl_3$. s = strong, m = medium, and w = weak.

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mainly from mixing between one c.t. and one ligand transition,[14] ν_e at 23 250 and ν_s at 34 600 or 37 000 cm^{-1}, the F_B factor being insensitive to the choice of the latter.

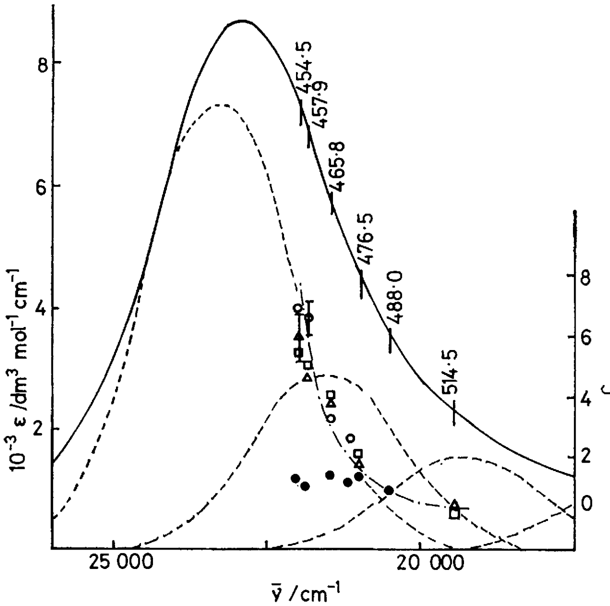
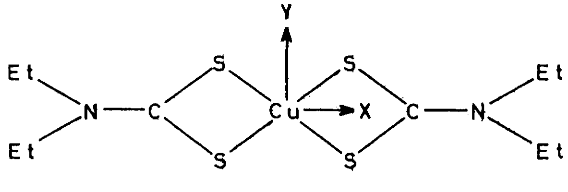


FIGURE 2 Raman excitation profile of $[Cu(S_2CNEt_2)_2]$. I_R^c is the molar Raman-intensity ratio of the band in question relative to the band at 606 or 850 cm^{-1} of C_6H_6, corrected for sample self absorption, instrumental spectral response, and ν dependence. (——) Absorption spectrum of $[Cu(S_2CNEt_2)_2]$ in C_6H_6, laser wavelengths used for Raman excitation being indicated; (– – – –) Gaussian components; (— · — · —) F_B^2/ν^4 frequency factors calculated for mixing between the transitions at 23 250 and 34 700 cm^{-1}, scaled to unity at 20 492 cm^{-1} (488.0 nm). Standard deviations are indicated by vertical bars. Experimental points are scaled to unity at 20 492 cm^{-1}: (○) 157; (△) 367; (□) 325; and (●) 426 cm^{-1}

The absorption spectrum of the nickel complex is slightly different, presenting two c.t. bands at 23 000 and 25 500 cm^{-1} (see Figure 3). The spectrum of this complex also displays two bands at 31 000 and 40 500 cm^{-1} which are those of the free ligand but strongly perturbed.[15] It is more difficult to ascertain the type of resonance behaviour responsible for the intensity enhancement in the nickel complex. The electronic transition at 25 500 cm^{-1} is certainly involved but the experimental points are too far away from the absorption maximum to enable a distinction to be made between an F_A or an F_B factor. By analogy with the copper complex we have assumed an intensity dependence on F_B.

The copper and nickel complexes have D_{2h} symmetry, as indicated in (1). The copper atom is slightly raised above the *xy* plane in the crystal with a sulphur atom of another molecule in an axial position.[16] However, the complex is known to be monomeric in solution [17] and it has presumably the same structure as the nickel complex (D_{2h}) [18] as the similarity of their Raman spectra suggests. Within our experimental errors, and except for the band at 315 cm^{-1}, the depolarization ratios (ρ) of Table 1, measured throughout the whole laser excitation range, are close to the theoretical limit of 0.33 for a single dominant tensor component [19] in D_{2h} symmetry.



(1)

A recent polarized optical-absorption study on single-crystal $[Cu(S_2CNEt_2)_2]$ shows one strong band at 21 830, a much weaker band at 25 640, and a shoulder at 18 600 cm^{-1} which are polarized perpendicular to the *z* axis of Figure 4.[8] The shoulder at 18 600 cm^{-1} corresponds to the band at 19 250 cm^{-1} obtained by gaussian analysis and has been already assigned to a *d–d* transition.[8] The band at 21 830 cm^{-1} must correspond to the peak at 23 250 cm^{-1} of Figure 2. It therefore follows that the dominant tensor element in the Raman spectra of

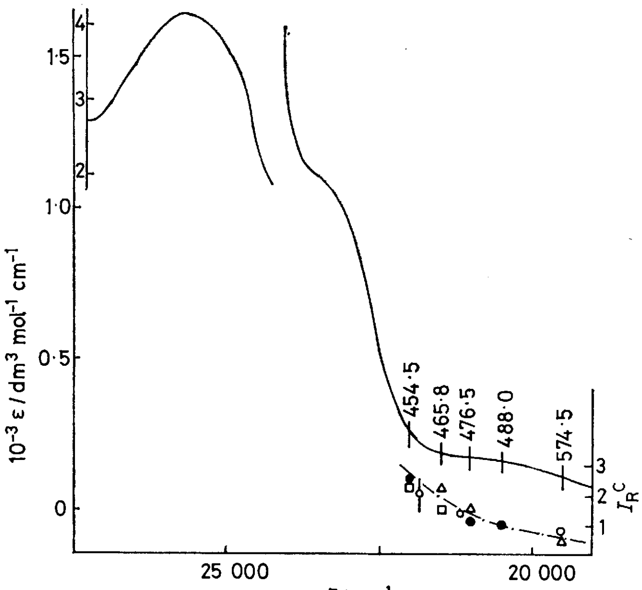


FIGURE 3 Raman excitation profile and absorption spectrum of $[Ni(S_2CNEt_2)_2]$. I_R^c as in Figure 2 except for the band at 172 cm^{-1} which was measured relative to the band of $CHCl_3$ at 261 cm^{-1}. (——) Absorption spectrum of $[Ni(S_2CNEt_2)_2]$ in C_6H_6, laser wavelengths being indicated; (— · — · —) F_B^2/ν^4 frequency factors for mixing between the transitions at 25 500 and 31 000 cm^{-1}, scaled to unity at 20 492 cm^{-1} (488.0 nm). Standard deviations are indicated by vertical bars. Experimental points are scaled to unity at 20 492 cm^{-1}: (○) 172; (△) 363; (□) 334; (●) 315 cm^{-1}

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$[\mathrm{Cu(S_2CNEt_2)_2}]$ must be α_{xx} or α_{yy} since one of the transitions concerned is x or y polarized. On the basis of these findings and taking into consideration the energy-level scheme of Figure 4 derived from e.s.r. data by Keijzers *et al.*,[9] the assignments of the transitions involved in the r.r. process can be made. As the previous workers have shown, the unpaired electron in $[\mathrm{Cu(S_2CNEt_2)_2}]$ is strongly delocalized, being, at most, 0.5 d_{xy} in character. As indicated in Figure 4 and Table 2, there are two orbitally allowed ligand-to-metal c.t. transitions with almost the same energy: $^2B_{1g}\rightarrow{}^2B_{2u}$ and $^2B_{1g}\rightarrow{}^2B_{3u}$ which are respectively x and y polarized, and another which is z polarized at higher energy, $^2B_{1g}\rightarrow{}^2A_u$. Furthermore, the two orbitally allowed ligand transitions $^2B_{1g}\rightarrow{}^2B_{3u}$ and $^2B_{1g}\rightarrow{}^2A_u$ are polarized along y and z respectively. Thus, the two transitions that interact in the resonance-enhancement process should be polarized along y. The assignments are shown in Table 2. Neither molecular-orbital calculations nor polarized optical spectra are available for the c.t. transition region of the nickel complex. The shoulder at 23 000 cm^{-1} has been assigned to an orbitally forbidden metal-to-ligand transition and the intense band at 25 500 cm^{-1} to an allowed transition $^1A_g\rightarrow{}^1B_{2u}$ or $^1A_g\rightarrow{}^1B_{3u}$ polarized along y or x respectively.[15] These assumptions are consistent with our results and they imply that at least one of the ligand transitions is also y or x polarized.

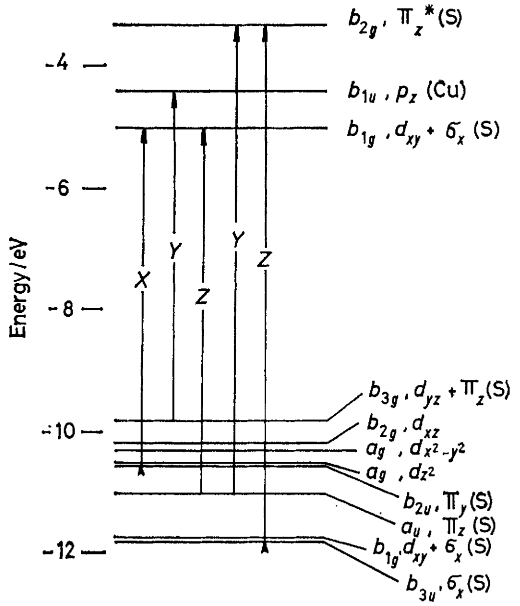

FIGURE 4 Energy-level scheme for the $[\mathrm{Cu(S_2CNEt_2)_2}]$ complex derived by Keijzers *et al.*[9] The arrows indicate allowed transitions

TABLE 2

The charge-transfer spectrum of $[\mathrm{Cu(S_2CNEt_2)_2}]$

Band (cm^{-1})	Assignment	
21 600	$^2B_{1g}\rightarrow{}^2B_{2u}(b_{2u}\rightarrow b_{1g})$	(x)
23 250	$^2B_{1g}\rightarrow{}^2B_{3u}(b_{3g}\rightarrow b_{1u})$	(y)
34 700	$^2B_{1g}\rightarrow{}^2B_{3u}(a_u\rightarrow b_{2g})$	(y)
37 000	$^2B_{1g}\rightarrow{}^2A_u(b_{3u}\rightarrow b_{2g})$	(z)

From the above results it appears that mixing of the two excited states is favoured not only by the metal–sulphur stretch but also by bending of angles that include sulphur and metal atoms such as SMS, MSC, and SCS, probably because this enables extensive orbital overlapping which provides the passage from one excited state to the other. The enhancement of the SCN bending may be due to the fact that this vibration is strongly coupled to all the other deformation modes of the dithiocarbamate chelate ring.

In a previous study on the r.r. spectra of ceruloplasmin we assigned bands at 340 and 360 cm^{-1} to the CuS stretching modes of the two type I copper ions of this protein.[3] Our present results corroborate this assignment. The relatively high frequency of this mode in $[\mathrm{Cu(S_2CNEt_2)_2}]$ is explained by the strong delocalization of the unpaired electron in this complex and this might also be the case in ceruloplasmin. The difference in frequency between the two CuS modes can be ascribed to the different environments of the two type I copper sites.[13]

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