Spectroscopic Studies of Metal Complexes containing π-Delocalized Sulphur Ligands. The Resonance-Raman Spectra of the Antitumor Agent [Cu(kts)] and the Related Cation $[Cu(H_2kts)]^{2+}$ †

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The resonance Raman spectra of the antitumor agent [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)-(2−)-*N*¹*N*¹′*SS*′]copper(II), [Cu(kts)], and the related cation $[Cu(H_2kts)]^{2+}$ have been measured. In the spectra of both compounds the bands most strongly enhanced are due to skeletal vibrations (CN and CS stretches and ring deformations), while band intensities of metal–ligand vibrations are only slightly modified. Excitation profiles show that the coupling of these vibrations with two π-delocalized sulphur-to-metal charge-transfer transitions is the mechanism responsible for Raman intensity enhancement.

THE compound H_2kts is a chelating ligand that binds to metal ions giving very stable complexes.[1-3] Its copper(II) complex [Cu(kts)] has been the object of several studies owing to the antineoplastic activity demonstrated *in vivo* against a wide spectrum of rodent tumors.

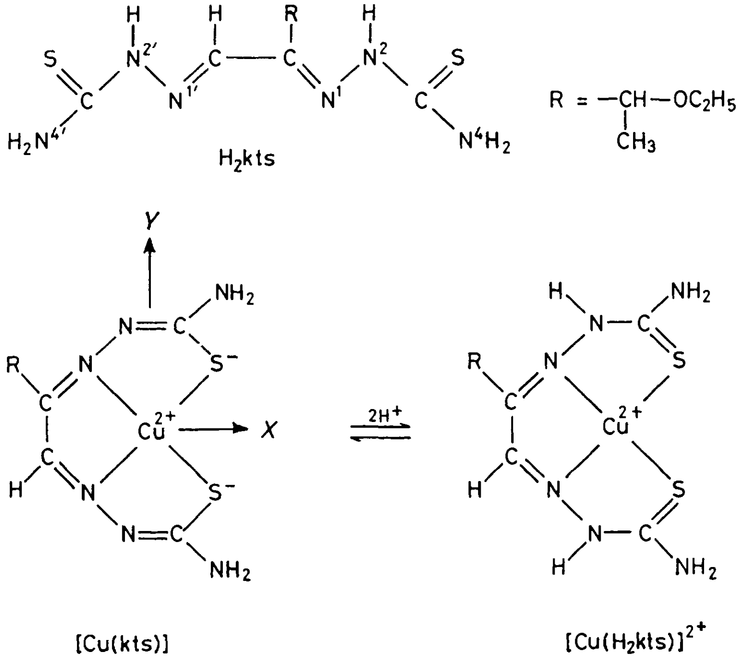

FIGURE 1 Structural formulae of H_2kts, [Cu(kts)], and $[Cu(H_2kts)]^{2+}$ showing the number of atoms for the former

The *X*-ray structure of [Cu(kts)] has been determined and shows that the ligand acts as a tetradentate chelating agent, co-ordinating to the metal *via* two nitrogens and two sulphurs in *cis* position[4] (Figure 1). Three chelating rings are formed with the ligands lying at the corners of a distorted square. The bond distances of this three-ring system indicate considerable electron delocalization as a result of deprotonation at N^2 and $N^{2'}$ in kts.[4] The distances C–S, C–N^4, and C–$N^{4'}$ are lengthened, whereas C–N^2 and C–$N^{2'}$ are shortened[4] (see Figure 1). All atoms, except for the ethoxy and methyl groups of the side chain which is disordered, lie close to the same plane. Each metal ion is six-co-ordinate in the crystal; there are infinite sheets of [Cu(kts)] molecules linked by Cu–S interactions, the Cu–S apical distance being longer than those in the plane.

The complex is lipophilic and very soluble in organic polar solvents. The visible absorption spectra in these media exhibit a strong band at 20 000—21 000 cm^{-1} (ε 6 000—7 000 $dm^3 mol^{-1} cm^{-1}$) with a shoulder at the low-energy side (*ca.* 18 000 cm^{-1}).[5] Peak and shoulder positions are markedly solvent dependent, suggesting axial co-ordination by solvent molecules. As a result of a study on the effect of solvents on the position, shape,

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† Abbreviations; H_2kts = 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone), $[Cu(H_2kts)]^{2+}$ = [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone)-*N*¹*N*¹′*SS*′]copper(II), and [Cu(kts)] = [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)(2−)-*N*¹*N*¹′*SS*′]copper(II).

and intensities of these bands Campbell *et al.*[6] assigned both to sulphur-to-copper l.m.c.t. (ligand-to-metal charge transfer) transitions.

As has been shown by Petering,[5] [Cu(kts)] is soluble in water at concentrations of the order of 10^{-3} mol dm^{-3}. The apparent formation constant of the complex in this medium ($\log K = 18.8$ at pH 7.02) is consistent with the high degree of electron delocalization into the chelate ring referred to above. The visible absorption spectrum of [Cu(kts)] in water differs appreciably from that obtained in polar organic solvents. The strong absorption and shoulder at 20 000 cm^{-1} shift to higher frequencies; both peaks overlap giving rise to a slightly asymmetric band at 21 400 cm^{-1} (469 nm, ε 6 300).[5]

Moreover, titration and spectrometric measurements (electronic and e.s.r.) in water and ethanol show reversible protonation of the ligand, protonation taking place at the N^2 position.[5] The species formed in solution at low pH appears to be that obtained in the solid state by van Giessen and Petering,[7] *i.e.* $[Cu(H_2kts)Cl_2]$. The structures of [Cu(kts)] and $[Cu(H_2kts)]^{2+}$ seem to be fairly analogous as can be inferred by the similarity of their e.s.r. spectra.[5] The absorption spectrum [5] of the cation $[Cu(H_2kts)]^{2+}$ presents an absorption at 24 400 cm^{-1} (410 nm) with much reduced intensity (ε 3 600), see below (Figure 6).

The e.s.r. data of [Cu(kts)] demonstrate the high degree of covalency of copper–ligand bonds, the distinctive feature being a strong metal–sulphur interaction. Cu^{II}–S bonds present a greater degree of covalency as compared with Cu^{II}–N bonds. Moreover, Cu–S and Cu–N bonds behave quite independently.[8] These results corroborate *X*-ray measurements: Cu–S bonds are considerably shorter (2.26 Å) than the sum of the covalent radii.[4]

Resonance-Raman (r.R.) scattering is a particularly appropriate technique to elucidate the origin of the strongly allowed transitions of [Cu(kts)] observed in the visible region. A preliminary communication has been presented previously.[9] We report here r.R. measurements which enable additional insight into the nature of the orbitals involved in l.m.c.t. transitions of [Cu(kts)].

EXPERIMENTAL

3-Ethoxy-2-oxobutyraldehyde was obtained by the method of Tiffany *et al.*[10a] and H_2kts as described by Petering *et al.*;[10b] [Cu(kts)] and $[Cu(H_2kts)Cl_2]$ were prepared according to van Giessen and Petering.[7] The purity of the complexes was checked by thin-layer chromatography on Merck silica gel 60 F_{254} plates. All other chemicals were of the best reagent grade. Demineralized distilled water previously freed of organic contaminants was used throughout.

Raman spectra were measured on a Coderg D800 spectrometer using the exciting lines of Ar^+ and Kr^+ Spectra Physics lasers; 90° scattering was used throughout. For solutions in methanol the spinning-cell technique was employed. Raman intensity measurements were made relative to the intensity of the $\nu_1(SO_4^{2-})$ band used as internal standard in aqueous solution or to one of the solvent bands in methanol solutions. The excitation profiles are reported as the ratio of the area under a band (measured by the product: peak height × half-band width), to the area under the band of the internal standard. The ratios were corrected for sample absorption, instrumental spectral response, and ν dependence (ν = scattered radiation frequency).

Absorption measurements were made on a Cary 219 spectrophotometer equipped with a derivative/log *A* (*A* = absorbance) accessory.

RESULTS

Resonance-Raman Spectrum of [Cu(kts)].—A typical r.R. spectrum of [Cu(kts)] in aqueous solution is illustrated in Figure 2. The frequencies and the vibrational assignments are summarized in the Table. All the Raman peaks are polarized ($\rho = 0.3$—0.4) implying that only symmetric vibrations are resonance enhanced.

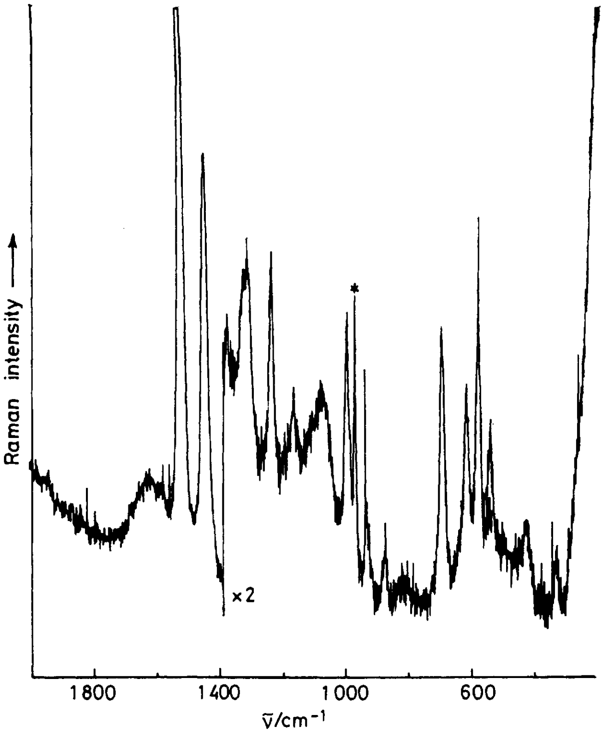

FIGURE 2 Resonance-Raman spectrum of [Cu(kts)] in aqueous solution (0.035 mol dm^{-3} $K_2[SO_4]$): [Cu(kts)] = 2.19×10^{-4} mol dm^{-3}, using the exciting line at 21 155 cm^{-1} (476.5 nm), 100 mW; slit width 5 cm^{-1}, scanning speed 50 cm^{-1} min^{-1}, time constant 1 s. Asterisk indicates the $\nu_1(SO_4^{2-})$ band; left-hand side of spectrum is × 2

The excitation profiles are presented in Figure 3 (for the sake of clarity only those of the most representative bands are reported). With the exception of the bands at 1 322, 1 246, 1 176, and 1 006 cm^{-1} (from this group only that at 1 246 cm^{-1} is presented) which are coupled with one of the ligand transitions lying at 32 500 and/or 39 400 cm^{-1}, all the others are in resonance with two visible transitions at approximately 19 500 and 21 400 cm^{-1}.

We propose to assign the two very strong bands at 1 537 and 1 460 cm^{-1} to skeletal vibrations, mainly the CN stretch of conjugated, delocalized double-bonded C=N. As has been shown, two rather weak bands at 1 531 and 1 499 cm^{-1} are observed in the Raman spectrum of thiosemicarbazide (tsc) and are assigned primarily to ν(CN)[11a,12] and amide II-type modes respectively.[11] The second should contain approximately 60% of N^2H bending;[11b] however, this contribution must be absent in the spectra of [Cu(kts)]. If one disregards the disorder of the lateral chain, the symmetry of the complex is C_{2v}. Thus, the four endocyclic C=N bonds must give rise to two totally symmetric (A_1), in-plane, stretching vibrations which are Raman-active. It must not be ignored, however, that these vibrations may be strongly coupled with the exocyclic CN^4 stretch and the N^4H_2 bending but the largest contribution of the CN^4 stretch might be expected at lower frequencies, in the region 1 200—1 300 cm^{-1}.[13]

As we have remarked above the bands at 1 322—1 006 cm^{-1} are in resonance with one or both u.v. transitions; those at 1 322 and 1 246 cm^{-1} are due mostly to CN^4 and NN stretches, and those at 1 176 and 1 006 cm^{-1} primarily to N^4H_2 in-plane rocking modes.[11,12]

The bands most strongly enhanced are the ones at 714, 632, and 595 cm^{-1} (in Figure 3 the intensity of the peak at 595 cm^{-1}, not shown in the Figure, lies between those of the two others). A band at about 800 cm^{-1} in the i.r. and Raman spectra of tsc, that shifts markedly upon complexation (about 100 cm^{-1}), has been assigned to the CS stretching mode.[14] The vibrational analysis of Ni^{II}–thiosemicarbazide complexes, on the other hand, indicates a strong contribution of this ν(CS) mode at 700 cm^{-1}.[13] We propose a similar assignment for the peak at 714 cm^{-1}. The other three peaks at 632, 595, and 537 cm^{-1} can be ascribed primarily to ring deformation modes; some of them, as we will show below, are strongly coupled with the CS stretch. The enhancement at 949 and 892 cm^{-1} is not impressive, and these bands may be assigned to combinations: 632 + 320, 595 + 320 or 714 plus a metal–ligand deformation at frequencies lower than 250 cm^{-1} not detected by our r.R. measurements.

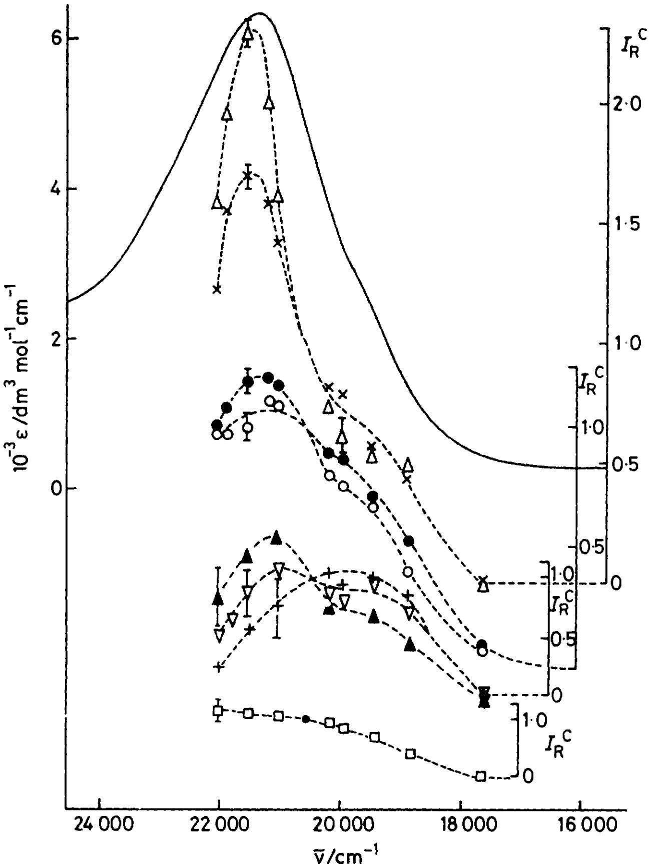

FIGURE 3 Raman excitation profile of [Cu(kts)] in aqueous solution. I_R^c is the molar Raman intensity ratio of the band relative to the $\nu_1(SO_4^{2-})$ band, corrected for sample self-absorption, instrumental spectral response, and ν dependence, scaled to unity at 20 492 cm^{-1} (488.0 nm). (——) Absorption spectrum; Raman bands (○) 1 537 cm^{-1}, (●) 1 460 cm^{-1}, (□) 1 246 cm^{-1}, (×) 714 cm^{-1}, (△) 632 cm^{-1}, (+) 420 cm^{-1}, (▽) 332 cm^{-1}, (▲) 949—892 cm^{-1}. Vertical bars indicate average errors

Resonance-Raman frequencies (cm^{-1}) and assignments * [Cu(kts)] and $[Cu(H_2kts)]^{2+}$

[Cu(kts)]	$[Cu(H_2kts)]^{2+}$	Assignments
	1 620	$\delta(N^4H_2)$
	1 575	$\delta(N^2H_2)$
1 537	1 490	mainly ν(CN)
1 460	1 426	
1 322		$\nu(CN^4) + \nu(NN)$
1 246	1 217	
1 176		$r(N^4H_2)$
1 090		ν(SiO) sample holder
1 006		$r(N^4H_2)$
949		632 + 320
	923	$\nu(CS) + r(N^4H_2)$
892		595 + 320
	843	ν(CS)
714		
632	663	ring deform. + ν(CS)
595		
537	532	ring deform.
	510	δ(NCN) + ν(CS)
420	425	ν(CuN)
332	350	ν(CuS)
	310	ν(CuS) + δ(NCuS)

* Modes are ν = stretching, δ = bending, r = rocking.

In the r.R. spectrum shown in Figure 2 the bands at 420 and 332 cm^{-1} are rather weak and their intensity does not show significant changes. Although both metal–ligand vibrations must be substantially coupled, we propose to assign the band at 420 cm^{-1} mainly to the CuN stretch. A band at approximately 400 cm^{-1} is primarily assigned to this mode in the r.R. spectra of blue copper proteins.[15,16] In these enzymes the ligand of Cu^{II} is the imidazole nitrogen of histidine. A similar value is quite suitable for the CuN mode in [Cu(kts)]. The CuS(thiolate) stretching vibration, on the other hand, has been observed at 360—370 cm^{-1} in the r.R. spectra of (diethyldithiocarbamato)copper(II) [17] and in the copper(II) complex of D-penicillamine.[16] The band at 332 cm^{-1} is a reasonable assignment to this mode which might be also coupled to metal–ligand deformation modes.

The broad band at approximately 1 090 cm^{-1} is due to one of the Raman bands of the cell (SiO stretch [18]) which is enhanced in the presence of the complex. The origin of this enhancement is difficult to ascertain. Larrabee and Spiro [19] have observed a similar band in the r.R. spectra of oxyhemocyanin which they have tentatively assigned to an electronic Raman transition of the antiferromagnetically coupled pair Cu^{II}–Cu^{II}, never observed in the Raman spectra of binuclear Cu^{II} complexes. Our feeling is that this band arises from the interaction of [Cu(kts)] with the silicates of the sample holder at pH ⩾ 7 since it disappears in acid media. The band at 1 090 cm^{-1} is not observed in the spectra of $[Cu(H_2kts)]^{2+}$ (see below).

The r.R. spectra in methanol are impaired by a strong fluorescence band lying at 18 200 cm^{-1} whose position is independent of the excitation frequency. As a result, intensity measurements are restricted to the spectra obtained upon excitation above 20 000 cm^{-1}. In addition, the intensity measurements of some bands are hampered by overlap-

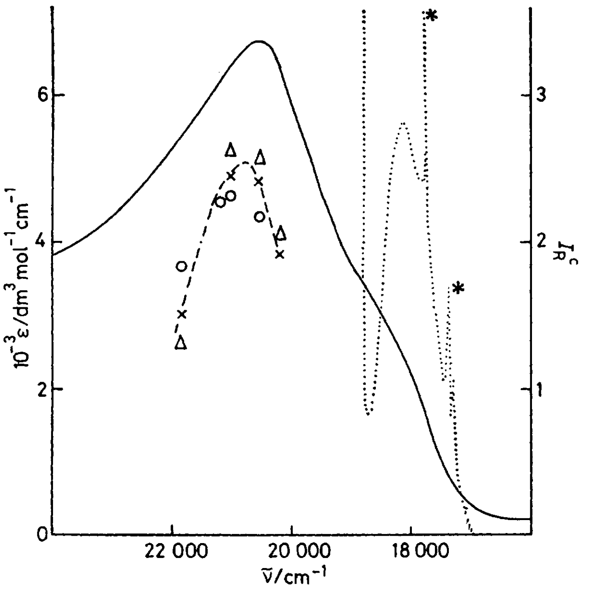

FIGURE 4 Raman excitation profile of [Cu(kts)] in methanol. $I_R{}^c$, as defined in Figure 3, relative to the 1 111 cm^{-1} band of methanol, scaled to unity at 21 468 cm^{-1} (465.8 nm). (——) Absorption spectrum; Raman bands (○) 1 537 cm^{-1}, (×) 714 cm^{-1}, (△) 632 cm^{-1}, (····) fluorescence spectrum, arbitrary units, with λ_0 = 530.8 nm. Asterisks indicate solvent bands

ping with the strong solvent bands at 1 034 and 1 457 cm^{-1}. In Figure 4 are presented the excitation profiles of the most representative bands in the region where intensity measurements could be performed. The fluorescence spectrum upon excitation with the 530.8 nm Kr$^+$ line is also shown.

Resonance-Raman Spectrum of [Cu(H$_2$kts)]$^{2+}$.—Figure 5 presents a characteristic r.R. spectrum of the cation [Cu(H$_2$kts)]$^{2+}$. The frequencies and the vibrational assignments are reported in the Table. As with [Cu(kts)], all the Raman peaks are polarized. The excitation profiles illustrated in Figure 6, in which only the most representative peaks are reported, show that the Raman bands are coupled with the transition at *ca.* 24 600 cm^{-1} assigned to a S(thione) $\longrightarrow$ Cu^{II} l.m.c.t. transition.[6]

The overall pattern of the spectrum of Figure 5 is reminiscent of that of Figure 2, although striking differences are noticeable. The most significant changes occur in the CN and CS stretching regions owing, obviously, to protonation at N^2 and N$^{2'}$. This protonation decreases the double-bond character of the CN^2 and CN$^{2'}$ groups and consequently conjugation. As a result the endocyclic ν(CN) modes are shifted to lower frequencies (47 and 24 cm^{-1} respectively), at 1 490 and 1 426 cm^{-1}. Although one or both of these bands could be considered as arising from an amide II vibration,[11a,b] it seems more reasonable to assign the N^{2}H bending mode to the peak at 1 575 cm^{-1} that was absent in the r.R. spectra of [Cu(kts)]. There is another band in this region becoming r.R. active, at 1 620 cm^{-1}, which may be safely ascribed to the N^{4}H$_2$ in-plane bending.

The region below 1 000 cm^{-1} is also considerably affected by protonation at N^2 and N$^{2'}$. The band at 632 cm^{-1} shifts to higher frequencies (663 cm^{-1}), those at 714 and 595 cm^{-1} decrease considerably in intensity not showing appreciable resonance enhancement (Figure 6), and new strongly resonant bands are noticeable at 923, 843, and 510 cm^{-1}. As has been pointed out, the CS stretching mode is distributed among three strong bands in the vibrational spectra of tsc, at 1 010, 808, and 508 cm^{-1} in the Raman spectra. The band at 808 cm^{-1} arises from a pure ν(CS) mode while other vibrations contribute to the other two peaks, the N^{4}H$_2$ rocking mode to the band at 1 010 cm^{-1} and the NCN deformation to the band at 508 cm^{-1}.[11a,12] As a consequence of the increased double-bond character of the C–S bond in [Cu(H$_2$kts)]$^{2+}$, a similar behaviour of the CS stretch of this compound must be expected. Accordingly, we propose an analogous assignment to the strong peaks at 923, 843, and 510 cm^{-1} that are strongly resonance enhanced (see Figure 6). The band at 632 cm^{-1} in the spectra of [Cu(kts)] that shifts to 663 cm^{-1} in that of [Cu(H$_2$kts)]$^{2+}$ must also contain a significant contribution of ν(CS). From these data, it appears that in the Raman spectra of [Cu(kts)] three bands contain an appreciable contribution of the CS stretch; those lying at 714, 632, and 595 cm^{-1}. As we stated before, the first can be safely ascribed to a pure ν(CS) mode while the two latter are mainly deformations of the tsc ring with some contribution of the NCN bending. The band at 537 cm^{-1}, only slightly sensitive to protonation at N^2, is clearly another ring deformation not associated to the CS stretch.

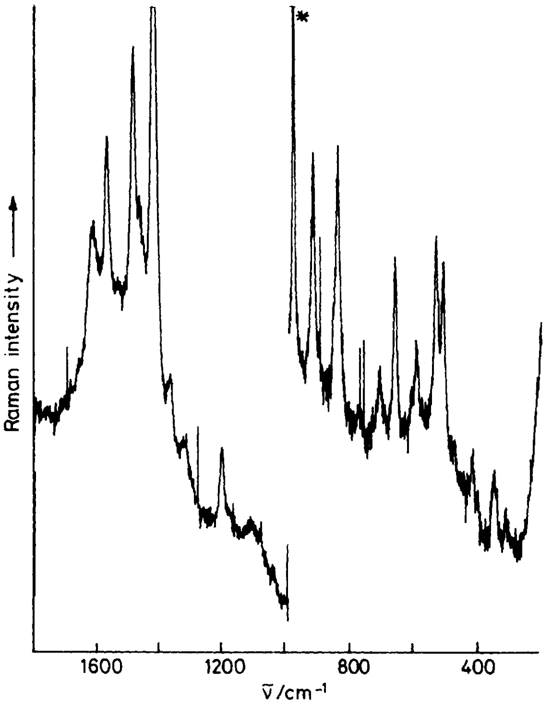

FIGURE 5 Resonance-Raman spectrum of [Cu(H$_2$kts)]$^{2+}$ in aqueous solution (0.05 mol dm^{-3} K$_2$[SO$_4$]); [Cu(H$_2$kts)$^{2+}$] = 5 × 10^{-3} mol dm^{-3}, using the exciting line at 21 839 cm^{-1} (457.9 nm), 100 mW; slit width 5 cm^{-1}, scanning speed 50 cm^{-1} min^{-1}, time constant 1 s. Asterisk indicates the ν_1(SO$_4{}^{2-}$) band

From the group of bands in the range 1 000—1 330 cm^{-1} which were coupled with one or two ligand transitions in the r.R. spectra of [Cu(kts)], only one of low intensity is noticeable which is not appreciably enhanced. The frequency of the peak at 420 cm^{-1} remains practically unchanged and the band at 332 cm^{-1} splits giving rise to two others at 350 and 310 cm^{-1}. These data confirm the assignment of the latter as predominantly a CuS stretch. Changes in C–S bond order

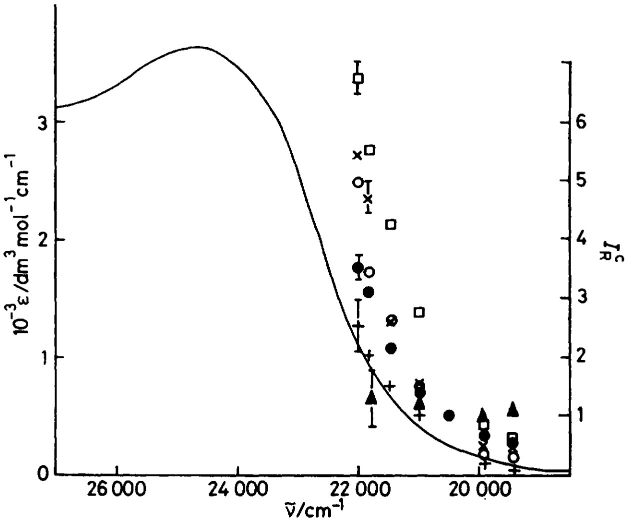

FIGURE 6 Raman excitation profile of $[Cu(H_2kts)]^{2+}$ in aqueous solution. $I_R{}^c$ has the same meaning of Figure 3. (——) Absorption spectrum; Raman bands (○) 1 490—1 426 cm^{-1}, (●) 1 620—1 575 cm^{-1}, (×) 923, 843—663 cm^{-1}, (□) 532—510 cm^{-1}, (+) 425—350 cm^{-1}, (▲) 714—595 cm^{-1}. Vertical bars indicate average errors

must substantially affect ν(CuS) while ν(CuN) is not expected to be perturbed.

DISCUSSION

As we have shown, protonation at the N^2 centre of the thiosemicarbazide ring is responsible for substantial Raman frequency shifts. These changes in vibrational frequencies reflect the distortions occurring in the ground-state structure when the uncharged complex [Cu(kts)] transforms into the cation $[Cu(H_2kts)]^{2+}$. These changes are obviously due to the increased double-bond character of the C=S bond that give rise to less conjugation of the double-bonded C=N.

On the other hand, the intensity enhancement of the ν(CS) and ring-stretching modes at resonance reflect the alterations taking place in the molecular structure during the electronic transition. As has been pointed out by Hirakawa and Tsuboi,[20] if a Raman band is enhanced at resonance it means that the equilibrium conformation of the molecule is distorted along the corresponding normal co-ordinate in the excited electronic state.

The existence of one half-filled *d* orbital in Cu^{II} as well as that of three lone pairs in thiolate may in principle result in three l.m.c.t. transitions in the spectra of [Cu(kts)]; one $\sigma(S) \rightarrow \sigma^*(Cu^{II})$ of higher energy and two $\pi(S) \rightarrow \delta^*(Cu^{II})$ at lower frequencies. If the transition involves a $\pi(S) \rightarrow Cu^{II}$ l.m.c.t. of [Cu(kts)], one of the lone-pair electrons on the sulphur should be brought onto the antibonding orbital of the metal during the transition; *i.e.* the C–S bond length is expected to become longer in the excited state. In addition, the depopulation of the sulphur π orbital would lower the extent of conjugation with the π system of the trichelate ring. Therefore, the vibrations predominantly involved in the transition would be the CS stretching, the ring stretchings, and the ring deformations coupled with the former. These are, in fact, the bands most strongly enhanced in the r.R. spectra of [Cu(kts)] (Figure 3). Furthermore, if the donor orbital in a $S \rightarrow Cu^{II}$ l.m.c.t. is a σ orbital the transition should alter predominantly the Cu–S bond strength; if it is a π orbital the Cu–S bonding should not be significantly perturbed. As a consequence, the intensity of the CuS stretching mode is not expected to be appreciably enhanced, and this is again what is observed in the r.R. spectra of [Cu(kts)].

At this stage it is interesting to compare our results with those obtained in the r.R. studies of metal complexes containing π-delocalized phenolate orbitals, *i.e.* metal transferrins and their model compounds. The absorption spectra of these complexes present a strong absorption assigned to a $p\pi \rightarrow d\pi$ or a $p\pi \rightarrow d\sigma^*$ phenolate-to-metal l.m.c.t. transition. Here, the depopulation of the oxygen *p*π orbital lowers the extent of conjugation with the π system of the phenyl ring during the transition. The Raman bands most strongly enhanced upon excitation into the l.m.c.t. band are the ν(CO) and the ring-stretching modes. The MO stretches, on the other hand, are not always detected and, if present, are not appreciably enhanced.[21]

These spectral features are fairly close to that observed with [Cu(kts)] and $[Cu(H_2kts)]^{2+}$ and give good grounds for the assignment of the electronic transitions to which the Raman modes are substantially coupled. We therefore propose to assign the bands at 19 500 and 21 400 cm^{-1} in the spectrum of Figure 3 to the $\pi(S) \rightarrow Cu^{II}$ l.m.c.t. transitions of [Cu(kts)]. We might then expect to find the σ transitions at higher energy. The separation between the π and σ transitions in ' blue ' copper proteins that contain a thiolate $(CysS^-)$–Cu^{II} bond ($CysS^-$ = cysteinate) in a rather distorted tetrahedral symmetry spans the range 3 800—4 800 cm^{-1}.[22] A comparable splitting for [Cu(kts)] should locate the σ transition at 23 000—24 500 cm^{-1}. The derivative of the absorption envelope of Figure 3 indicates that it is composed of three peaks lying at 19 300, 21 300, and 23 800 cm^{-1} and that gives a quite reasonable splitting between σ and π transitions if the latter is attributed to the $\pi(S) \rightarrow Cu^{II}$ l.m.c.t. One might not rule out the possibility of r.R. scattering from excited-state vibrational levels to explain the excitation profile of Figure 3. Excitation profiles with band progression at regular spacing have been observed with iron transferrin which displays a strong unstructured absorption band assigned to the $p\pi \rightarrow d\pi$ transition mentioned above.[21a] In any case the vibrations dominating the r.R. spectra of [Cu(kts)] strongly suggest that the electronic transitions involved in the process are the $\pi(S) \rightarrow Cu^{II}$ l.m.c.t.

The derivative of the absorption band of Figure 4 indicates again that it is composed of three peaks at 18 500, 20 660, and 22 700 cm^{-1}. The rather strong fluorescence in the region corresponding to the first peak does not prevent the same conclusions being drawn. Here again, the same Raman modes (CS and ring stretches, and ring deformations) are involved in r.R.

enhancement. The study of the fluorescence spectra should give some additional information on the vibrational excited states and might allow the real nature of the two peaks at 18 500 and 20 660 cm^{-1} to be elucidated.

Thione sulphur is less polarizable than thiolate sulphur and has only two lone pairs. Thus, there must be two l.m.c.t. transitions in the spectra of $[Cu(H_2kts)]^{2+}$; one strongly allowed $\sigma(S) \rightarrow \sigma^*(Cu^{II})$ at higher energy and one $\pi(S) \rightarrow \sigma^*(Cu^{II})$ at lower energy. Both should occur at higher frequencies than those of [Cu(kts)] [6,14] and the corresponding absorptions may be located inside the broad envelope of Figure 6. The excitation profiles show that all Raman bands are coupled with a transition lying approximately at 24 000 cm^{-1}. Since the Raman bands that show substantial enhancement are due to CS and CN stretchings, and to ring deformations, we may similarly assign the band at 24 000 cm^{-1} to the π transition.

As we have mentioned previously, contributions from exocyclic deformations are also observed in the r.R. spectra of $[Cu(H_2kts)]^{2+}$, specifically those related to the N^4 and N^2 centres. Enhancement of exocyclic vibrations has been observed in the r.R. spectra of π-delocalized N_4 macrocyclic complexes and has been ascribed to hyperconjugation.[23] An analogous mechanism appears to be possible at N^4 involving the NH_2 group and the trichelate π system.

Further experiments are underway in this laboratory in order to investigate the r.R. spectra of other metal thiosemicarbazonates that will be presented in a future publication.

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