# Resonance Raman Spectra of Copper(I) Complexes with α-Di-imine Ligands

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The resonance Raman spectra of [Cu(ebba)$_2$]ClO$_4$ [ebba = *NN'*-ethane-1,2-diylidenebis(t-butylamine)], [Cu(pmba)$_2$]ClO$_4$ [*N*-(2-pyridylmethylene)-t-butylamine], and [Cu(bquin)$_2$]ClO$_4$ (bquin = 2,2' biquinolyl) have been measured in the region of the metal to ligand charge-transfer absorption between 457 and 600 nm. The interpretation of the resonance Raman enhancement allows a detailed description of the structural and electronic changes upon electronic excitation. This interpretation is in agreement with the results of molecular orbital calculations previously published.

The $d^6$ transition-metal ions Fe$^{2+}$, Ru$^{2+}$, and Os$^{2+}$ form octahedral 1 : 3 complexes with α-di-imine ligands, such as bipyridine and phenanthroline.[1] The absorption spectra in the visible region, characterized by strong metal to ligand charge-transfer (m.l.c.t.) bands, and the electronic structure of these complexes have been studied by different methods during the last few years.[2] The reason for this interest is that these complexes, especially those of Ru$^{II}$, undergo photo-induced redox reactions,[3] which might be used for solar energy conversion. It has been known for more than 30 years that Cu$^{I}$,[4] a $d^{10}$ system, forms 1 : 2 complexes with α-di-imine ligands, which show strikingly similar absorption spectra in the visible region.[5,6] These complexes have been used by analytical chemists for colorimetric determination of copper ions in solution.[7] There is no doubt that in the Cu$^{I}$ complexes too, a m.l.c.t. transition gives rise to the strong absorption band in the visible region. The latter band is structured as in the 1 : 3 complexes of the $d^6$ ions. This structure of the m.l.c.t. absorption band has not been assigned in detail so far. In this paper we report the resonance Raman spectra of the copper(I) complexes, which allow an interpretation of the structure of the m.l.c.t. band.

## Experimental

*Preparation of the Complexes.*—The ligands *NN'*-ethane-1,2-diylidenebis(t-butylamine)[8] (ebba) and *N*-(2-pyridylmethylene)-t-butylamine [9] (pmba) were prepared by published methods. 2,2'-Biquinolyl (bquin) was purchased from Fluka AG, Buchs, Switzerland. [Cu(CH$_3$CN)$_4$]ClO$_4$ was prepared by reaction of [Cu(H$_2$O)$_6$][ClO$_4$]$_2$ with Cu powder in CH$_3$CN. The Cu$^{I}$ complexes were prepared by the method of Ayranci *et al.*[6] for [Cu(ebba)$_2$]ClO$_4$.

*Analyses.* [Cu(ebba)$_2$]ClO$_4$ (Found: C, 48.0; H, 8.05; Cu, 12.7; N, 11.3. Calc. for C$_{20}$H$_{40}$ClCuN$_4$O$_4$: C, 48.1; H, 8.05; Cu, 12.7; N, 11.2%). [Cu(pmba)$_2$]ClO$_4$ (Found: C, 49.4; H, 5.9; Cu, 13.0; N, 11.55. Calc. for C$_{20}$H$_{28}$ClCuN$_4$O$_4$: C, 49.3; H, 5.8; Cu, 13.05; N, 11.5%). [Cu(bquin)$_2$]ClO$_4$ (Found: C, 63.95; H, 3.65; Cu, 9.45; N, 8.5. Calc. for C$_{36}$H$_{24}$ClCuN$_4$O$_4$: C, 64.0; H, 3.6; Cu, 9.4; N, 8.3%).

*Resonance Raman Spectra.*—The resonance Raman spectra were measured on a Spex Ramalog 4 Raman spectrometer, using back scattering of the solid samples in a spinning cell.[10] The solid complexes were mixed with KClO$_4$ in a ratio of 1 : 10. An argon ion laser (Spectra Physics 164) and a dye laser (Spectra Physics 375; Rhodamin G, 570—650 nm, and Coumarine 6, 525—550 nm) were used as exciting source. The Raman intensities, the product of amplitude and linewidth at half-height, were measured relative to $\tilde{\nu}_1$ of ClO$_4^-$ (internal standard) and are corrected for the $\tilde{\nu}^4$ dependence of the scattered intensity, the absorption of the sample, the spectrometer, and the photomultiplier response. The latter was determined by measuring the intensity ratio of Stokes and anti-Stokes lines of CCl$_4$ with different exciting wavelengths. The depolarization ratios were measured on 10$^{-3}$ mol dm$^{-3}$ solutions in ethanol using the same set-up. The absorption spectra of the complexes in acetone have been measured on a Zeiss DMR-21 spectrometer.

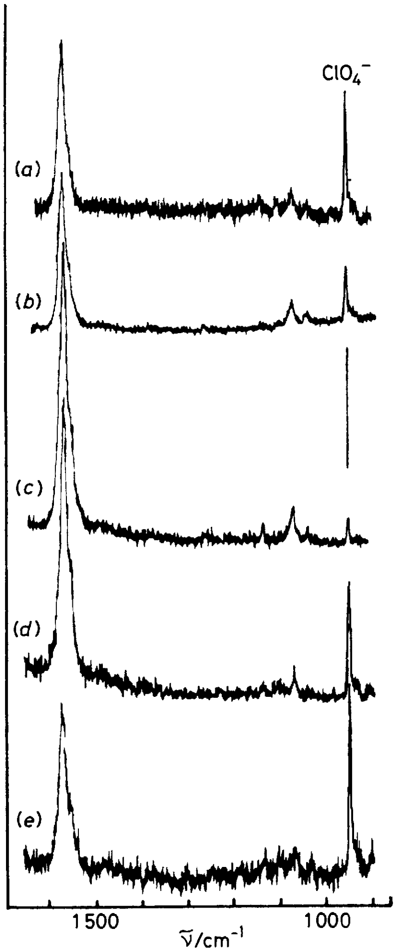

**Figure 1.** Raman spectra of [Cu(ebba)$_2$]ClO$_4$ in KClO$_4$: $\tilde{\nu}_0$ = 16 456 (*a*), 17 515 (*b*), 19 430 (*c*), 20 487 (*d*), and 20 987 cm$^{-1}$ (*e*)

## Results and Discussion

*Raman Spectra of* $[Cu(ebba)_2]ClO_4$.—Figure 1 shows the Raman spectra of $[Cu(ebba)_2]ClO_4$ solid in the region 1 600—800 $cm^{-1}$ using exciting light of different wavelengths. The spectra show three bands of the complex in this spectral region, an intense one at 1 544 $cm^{-1}$ and two weaker ones at 1 055 and 1 030 $cm^{-1}$. The band at 932 $cm^{-1}$ is due to $\tilde{\nu}_1$ of $ClO_4^-$ and is used as an internal standard. Figure 1 clearly shows that the intensities of the two Raman bands at 1 544 and 1 055 $cm^{-1}$ are strongly dependent on the exciting wavelength. The relative Raman intensities and the depolarization ratios of these transitions measured in solution at 594 and 514 nm ($\nu_0$ = 16 824 and 19 430 $cm^{-1}$) are given in Table 1. The band at 1 030 $cm^{-1}$ is too weak to measure the excitation profile. Outside the spectral region shown in Figure 1 only two other bands were observed, the first overtone of the 1 544 $cm^{-1}$ vibration at 3 082 $cm^{-1}$, and a combination band (1 055 + 1 544 $cm^{-1}$) at 2 599 $cm^{-1}$. In the region of the Cu–N stretching vibrations no Raman bands were observed. The fundamentals have been assigned, based on their depolarisation ratio to the totally symmetric $\tilde{\nu}$(C=N) (1 544 $cm^{-1}$), $\tilde{\nu}$(C–C) (1 055 $cm^{-1}$), and $\tilde{\nu}(C–H_{wag})$ (1 030 $cm^{-1}$) vibrations of the ligand. In free glyoxal the analogous vibrations are reported at 1 729 [$\tilde{\nu}$(C=O)], 1 078 [$\tilde{\nu}$(C–C)], and 1 055 $cm^{-1}$ [$\tilde{\nu}(C–H_{wag})$].[11] Upon deuteriation they are shifted to 1 709, 944, and 908 $cm^{-1}$ respectively. In the deuteriated complex $[Cu([^2H_2]ebba)_2]ClO_4$, prepared from $[^2H_2]$glyoxal, similar isotope shifts are observed. The fundamentals are found at 1 534, 920, and 830 $cm^{-1}$, with the overtone at 3 056 $cm^{-1}$.[12] The large isotope shift of $\tilde{\nu}$(C–C) indicates a considerable coupling with the $\tilde{\nu}$(C–H) wagging vibration. Staal *et al.*[13] reported the resonance Raman enhancement of the same two ligand modes in $[M(CO)_4(ebba)]$ (M = Cr, Mo, or W). In these mixed complexes a resonance Raman enhancement of $\tilde{\nu}$(C≡O), $\tilde{\nu}$(M–C), and $\tilde{\nu}$(M–N) vibrations is also observed. Based on the $^{14}N/^{15}N$ isotope shifts the coupling between $\tilde{\nu}$(C=N) and $\tilde{\nu}$(C–C) is manifest, which is probably due to structural constraints within the chelate ring.[13]

Table 1. Excitation profiles of $[Cu(ebba)_2]ClO_4$

| $\tilde{\nu}_0/cm^{-1}$ | $I_{rel.}$ [a] (1 544 $cm^{-1}$) | $I_{rel.}$ [a] (1 055 $cm^{-1}$) | $I_{rel.}$ [a] (3 082 $cm^{-1}$) |
|---|---|---|---|
| 16 824 | 1.61 ± 0.10 | 0.23 ± 0.10 | |
| | 0.16 ± 0.08 [b] | 0.20 ± 0.08 [b] | |
| 17 153 | 2.38 | 0.46 | |
| 17 515 | 3.74 | 0.64 | |
| 17 883 | 4.98 | 1.39 | |
| 18 218 | 7.13 | 1.65 | |
| 18 779 | 10.03 | 1.95 | |
| 19 430 | 10.96 | 2.00 | 2.40 ± 0.20 |
| | 0.32 ± 0.04 [b] | 0.37 ± 0.06 [b] | |
| 19 926 | 7.17 | 0.87 | 3.00 |
| 20 135 | 6.12 | 0.49 | 3.10 |
| 20 487 | 4.27 | 0.29 | 5.00 |
| 20 981 | 3.85 | 0.12 | 4.92 |
| 21 150 | 2.12 | 0.18 | 2.80 |
| 21 643 | 2.91 | | 2.20 |
| 21 831 | 2.19 | 0.10 | 1.90 |

[a] Intensities relative to $\tilde{\nu}_1$ of $ClO_4^-$ as internal standard. [b] Depolarisation ratio ($10^{-3}$ mol $dm^{-3}$ solution in EtOH).

Figure 2 shows the absorption spectrum and the excitation profile of the Raman fundamentals at 1 544 and 1 055 $cm^{-1}$, and the overtone at 3 082 $cm^{-1}$ of $[Cu(ebba)_2]ClO_4$. The excitation profile of $[Cu([^2H_2]ebba)_2]ClO_4$ is identical within experimental error. The Raman band of the first harmonic is considerably broader than the bands of the fundamentals. It is, therefore, mandatory to consider the peak area if the relative Raman intensities of the fundamental and the first harmonic are compared. The excitation profile of the combination band could not be measured with reasonable accuracy because the former band is too broad. The maximum in the excitation profile of the fundamentals is close to the maximum of the m.l.c.t. absorption band, the one of the overtone is in the spectral region of the shoulder on the high-energy side of this band. The shape of the excitation profile, no indication of a Mortensen[14] doublet, and the depolarization ratio clearly indicate a resonance enhancement by a Frank–Condon mechanism (A-Type),[15] due to interaction with one non-degenerate excited electronic state.[16] In this case the potential minimum of the excited state is shifted along the totally symmetric normal co-ordinate, which gives rise to the enhanced Raman bands. This causes the coupling of the electronic and vibrational transition. This effect is quantified by the parameter $B_i$, defined in equation (1):[16] $\nu_{mi}$ is the vibrational

$$B_i = \left[\frac{2\,\nu_{mi}\nu_{gi}}{\nu_{mi} + \nu_{gi}}\right]^{\frac{1}{2}}[Q_{im} - Q_{ig}] \qquad (1)$$

frequency of the *i*th normal vibration in the excited state; $\nu_{gi}$ is the vibrational frequency of the *i*th normal vibration in the ground state; $Q_{im}$ is the position of the potential minimum of the excited state along the *i*th normal co-ordinate; and $Q_{ig}$ is the position of the potential minimum of the ground state along the *i*th normal co-ordinate ($Q_{ig}$ = 0 in general, by convention).

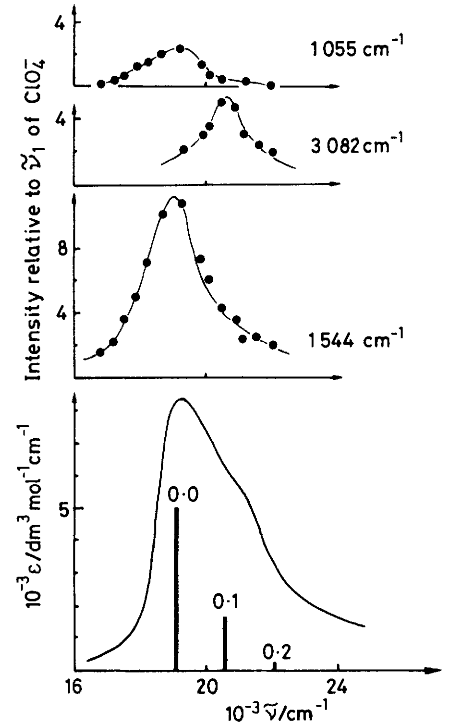

Figure 2. Absorption spectrum and excitation profiles of the Raman bands of $[Cu(ebba)_2]ClO_4$

If the high-frequency shoulder in the absorption spectrum is assigned to the second component of a vibronic progression in $\tilde{\nu}$(C=N), the relative maxima of the excitation profile of the fundamental and the first harmonic allow the determination of the parameter $B_{C=N}$ as being ±0.80 ± 0.10 (the sign of $B_{C=N}$ is not defined), by the formulae for the Frank–Condon overlap integrals given by Siebrand and Zgierski.[17]

This assignment of the high-frequency shoulder can be checked because the parameter $B_{C=N}$ also determines the relative intensities of the components of the vibronic progression in the absorption spectrum.[17] The relative intensities calculated with $B_{C=N} = \pm 0.80$, obtained from the excitation profiles, are indicated as vertical bars in Figure 2. This shows that the calculated intensities are in reasonable agreement with those observed. The ratio of the resonance Raman enhancements of the C=N and the C–C stretching vibrations allow an estimation of the absolute value of $B_{C-C}$ as $\pm 0.23 \pm 0.05$. $B_{C=N}$ and $B_{C-C}$ are directly correlated with the structural change upon electronic excitation by equation (2) ($\tilde{\nu}_i$ is the

$$B_i \approx 1.218 \times 10^{-3}\,.\,\tilde{\nu}_i^{\frac{1}{2}}\,.\,\Delta Q_i\,.\,\mu_i^{\frac{1}{2}} \qquad (2)$$

vibrational frequency in cm$^{-1}$; $\Delta Q_i$ is the shift along the normal co-ordinate $i$ in pm; and $\mu_i$ is the reduced mass in atomic units), which follows from equation (1) under the assumptions of equal vibrational frequencies in the ground and excited states. This assumption is justified, because it has been shown that the corresponding frequencies between ground and excited state in $[Ru(bipy)_3]^+$ (bipy = 2,2′-bipyridyl) differ only by a few cm$^{-1}$.[18]

The shifts along the normal co-ordinate $Q_{CN}$ upon m.l.c.t. excitation are estimated to be $\pm 6.7$ pm, and along $Q_{CC}$ to be $\pm 2.4$ pm, by equation (2). Assuming localized normal co-ordinates, the absolute changes in internal co-ordinates upon excitation are $\pm 3.35$ pm for the C=N bond, and $\pm 1.7$ pm for the C–C bond. Bond length and bond order are related by equation (3):[19,20] $r_i$ is the length of the bond $i$ in pm; $b_i$ is

$$r_i = c_{i0} - c_{i1}\,.\,b_i \qquad (3)$$

the bond order of the bond $i$; $c_{i0}$ and $c_{i1}$ are empirical constants. The constant $c_{i1}$ is 18 pm per unit bond order for C–C and C–N bonds.[19,20] The changes in bond order are, therefore, $\pm 0.186$ for the C–N bond and $\pm 0.094$ for the C–C bond. In this way the excitation profiles of the resonance Raman active vibrations of $[Cu(ebba)_2]ClO_4$ allow a direct insight into the redistribution of electrons upon m.l.c.t. excitation. The result of this interpretation is in accordance with the proposed electronic structure for this complex.[21] A detailed analysis of the m.l.c.t. excited states (Table 2) arising from excitation of a $d$ electron in the lowest unoccupied ligand orbital, which is formed by the $\pi_3$ orbital of the RN=CH–CH=NR (R = alkyl) systems (irreducible representation $e$), shows four symmetry-allowed transitions. To include excited states with one electron in the $\pi_4$ orbital of the ligand in the discussion, as in the interpretation of the electronic spectra of $[M(bipy)_3]^{2+}$ (M = Fe, Ru, or Os) [2] is not reasonable, because the energy difference between $\pi_3$ and $\pi_4$ orbitals in RN=CH–CH=NR is of the order of 20 000 cm$^{-1}$. Of the four allowed transitions, only the $z$-polarized $A_1 \longrightarrow B_2$ carries intensity because transfer of electrons is only possible along the $S_4$ axes in these complexes. Hence, only one m.l.c.t. transition with a large transition moment is predicted in the visible region. This is in accordance with the interpretation of the resonance Raman effect. In this excited state one electron is transferred from a metal-centred $d$ orbital to the $\pi_3$ orbital of the RN=CH–CH=NR system. The latter is antibonding with respect to the C=N bond and bonding with respect to the C–C bond. Hence, the relative signs of the changes in internal co-ordinates not defined by the interpretation of the excitation profile are negative for $\Delta r_{C-C}$ and positive for $\Delta r_{C=N}$. The changes in the bond orders estimated by an extended Hückel calculation are $-0.195$ for the C=N bond and $+0.185$ for the C–C bond,[21] which is in reasonable agreement with the values deduced from resonance Raman spectroscopy.

**Table 2.** Metal to ligand charge-transfer transitions in $[Cu(\alpha\text{-di-imine})_2]^+$ complexes (symmetry $D_{2d}$)

| Electronic transitions | Corresponding states |
|---|---|
| $a_1(d_{z^2}) \longrightarrow e(\pi_3)$ | $A_1 \longrightarrow E(x,y)$ * |
| $b_1(d_{x^2-y^2}) \longrightarrow e(\pi_3)$ | $A_1 \longrightarrow E(x,y)$ * |
| $b_2(d_{xy}) \longrightarrow e(\pi_3)$ | $A_1 \longrightarrow E(x,y)$ * |
| $e(d_{xz}),(d_{yz}) \longrightarrow e(\pi_3)$ | $A_1 \longrightarrow A_1,A_2,B_1,B_2(z)$ * |

* Symmetry-allowed transition (polarisation in parentheses).

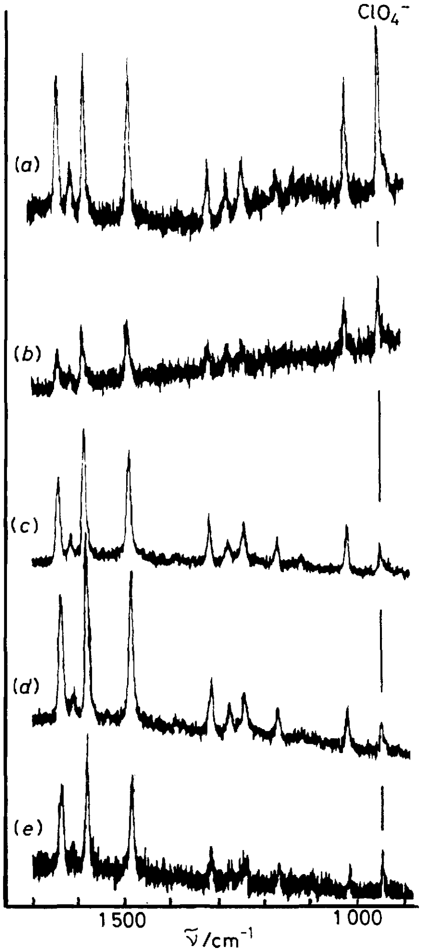

**Figure 3.** Raman spectra of $[Cu(pmba)_2]ClO_4$ in $KClO_4$: $\tilde{\nu}_0$ = 17 690 (*a*), 18 542 (*b*), 19 430 (*c*), 20 487 (*d*), and 21 150 cm$^{-1}$ (*e*)

*Raman Spectra of* $[Cu(pmba)_2]ClO_4$.—Figure 3 shows the Raman spectra of $[Cu(pmba)_2]ClO_4$ using different exciting wavelengths. There are nine bands observed in the region between 1 700 and 1 000 cm$^{-1}$ which show resonance enhancement in the spectral region of the m.l.c.t. absorption. The depolarisation ratios of these bands reveal that they are all due to totally symmetric vibrations. The Raman band at the highest energy (1 619 cm$^{-1}$) is assigned to the C=N vibration of the imine group of the ligand. The other bands are probably due to vibrations within the pyridine moiety. One of the bands between 1 000 and 1 200 cm$^{-1}$ is due to the C–C vibration of the α-di-imine chelate ring. A definite assignment of this mode is not possible. Balk *et al.*[22] observed resonance Raman enhancement of the same ligand modes in their study of $[M(CO)_4(pmba)]$ (M = Cr, Mo, or W). In addition, they found

**Table 3.** Excitation profiles of $[Cu(pmba)_2]ClO_4$

| | $I_{rel.}$[a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\tilde{\nu}_0$/cm$^{-1}$ | (1 619 cm$^{-1}$) | (1 594 cm$^{-1}$) | (1 565 cm$^{-1}$) | (1 472 cm$^{-1}$) | (1 303 cm$^{-1}$) | (1 265 cm$^{-1}$) | (1 233 cm$^{-1}$) | (1 160 cm$^{-1}$) | (1 014 cm$^{-1}$) |
| 17 690 | 0.74 ± 0.10 | 0.22 ± 0.10 | 0.85 ± 0.10 | 0.89 ± 0.10 | 0.27 ± 0.10 | 0.17 ± 0.10 | 0.25 ± 0.10 | 0.13 ± 0.10 | 0.58 ± 0.10 |
| | 0.07 ± 0.03[b] | | 0.12 ± 0.04[b] | 0.16 ± 0.02[b] | 0.18 ± 0.05[b] | | | | |
| 18 544 | 0.82 | 0.18 | 0.90 | 0.90 | 0.38 | 0.29 | 0.32 | 0.20 | 0.73 |
| 19 430 | 3.12 | 0.92 | 4.97 | 4.03 | 1.50 | 0.77 | 1.29 | 0.97 | 1.41 |
| 19 926 | 4.55 | 1.31 | 7.43 | 6.22 | 2.22 | 1.01 | 1.75 | 1.10 | 2.18 |
| 20 135 | 5.31 | 1.32 | 7.92 | 6.66 | 2.38 | 1.18 | 1.97 | 1.21 | 1.50 |
| 20 487 | 5.26 | 0.96 | 7.80 | 6.23 | 2.07 | 1.03 | 0.95 | 0.97 | 1.45 |
| | 0.41 ± 0.06[b] | | 0.36 ± 0.03[b] | 0.25 ± 0.05[b] | 0.41 ± 0.08[b] | | | | |
| 20 981 | 3.20 | 0.56 | 4.18 | 3.08 | 0.97 | 0.43 | 0.59 | 0.52 | 0.56 |
| 21 150 | 2.26 | 0.34 | 3.61 | 2.56 | 0.75 | 0.20 | 0.50 | 0.30 | 0.49 |
| 21 831 | 1.32 | | 1.84 | 1.41 | 0.34 | 0.17 | 0.30 | 0.21 | 0.34 |

[a] Intensities relative to $\tilde{\nu}_1$ of $ClO_4^-$ as internal standard. [b] Depolarisation ratio ($10^{-3}$ mol dm$^{-3}$ solution in EtOH).

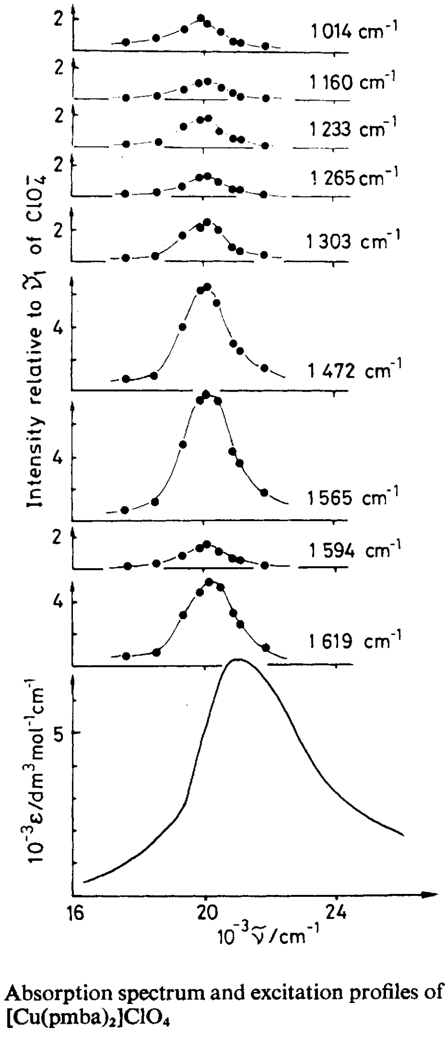

Figure 4. Absorption spectrum and excitation profiles of the Raman bands of $[Cu(pmba)_2]ClO_4$

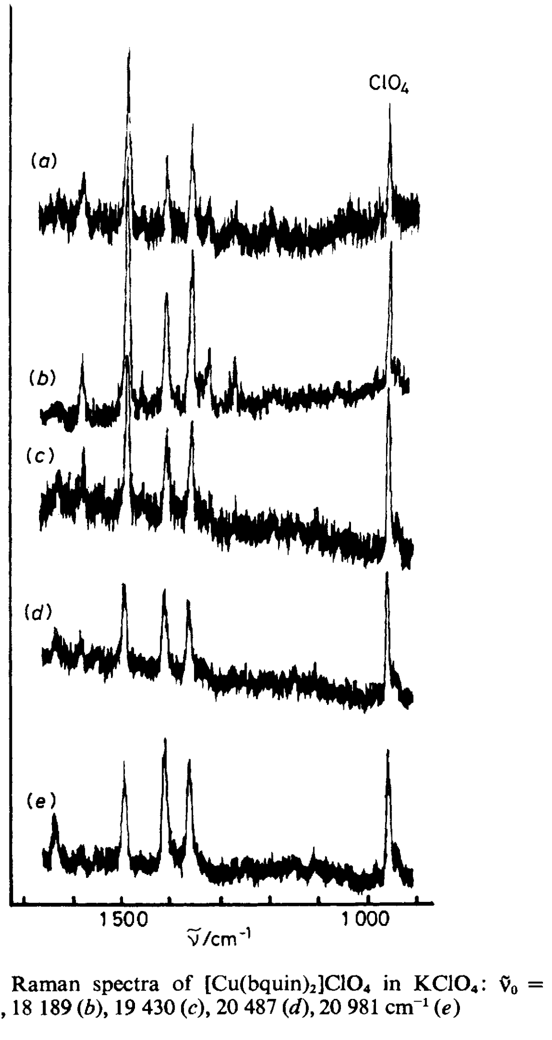

Figure 5. Raman spectra of $[Cu(bquin)_2]ClO_4$ in $KClO_4$: $\tilde{\nu}_0$ = 17 515 (*a*), 18 189 (*b*), 19 430 (*c*), 20 487 (*d*), 20 981 cm$^{-1}$ (*e*)

resonance active bands due to metal–ligand vibrations. None of these modes could be observed in the resonance Raman spectrum of any of the copper(I) complexes. This indicates that there are only minor structural changes in the co-ordination sphere of the copper(I) ions upon m.l.c.t. excitation. The absorption spectrum and the excitation profile of the resonance Raman active bands are shown in Figure 4. The relative Raman intensities are listed in Table 3. The maxima in the excitation profiles (20 000 cm$^{-1}$) are shifted to lower energies by 1 300 cm$^{-1}$, compared to the absorption maximum (21 300 cm$^{-1}$). This is in contrast with the situation observed in $[Cu(ebba)_2]ClO_4$. Furthermore, the m.l.c.t. absorption band is much broader in the spectrum of $[Cu(pmba)_2]ClO_4$ than in $[Cu(ebba)_2]ClO_4$. It is possible to rationalize these differences with the interpretation of the resonance Raman spectra of $[Cu(ebba)_2]ClO_4$. In $[Cu(pmba)_2]ClO_4$, seven vibrations at 1 619, 1 565, 1 472, 1 303, 1 265, 1 233, and 1 160 cm$^{-1}$ are strongly resonance enhanced. All these vibrations are

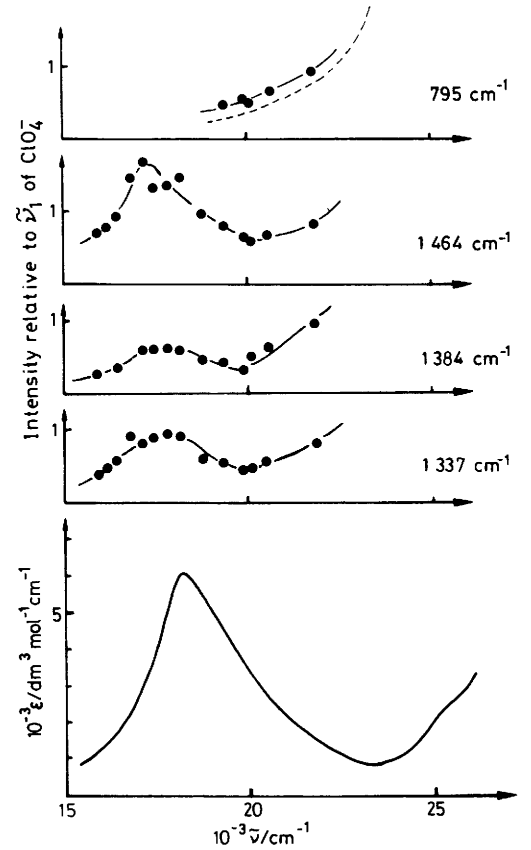

**Figure 6.** Absorption spectrum and excitation profiles of the Raman bands of $[Cu(bquin)_2]ClO_4$

totally symmetric, and probably give rise to an onset of a similar vibronic progression as the C=N vibration in $[Cu(ebba)_2]ClO_4$. Superposition of the absorption lines of the 0–0 transition and the 0–1 transitions of the seven vibrational modes will lead to a broad unresolved absorption band, with the maximum shifted to higher energies than that of the 0–0 transition. A detailed quantitative interpretation of the resonance Raman effect is not possible for $[Cu(pmba)_2]ClO_4$, due to the high complexity of the problem if seven totally symmetric strongly coupled vibrations are involved. Resonance enhancement of vibrations localised within the pyridine ring and the α-di-imine moiety is observed. This indicates that the transferred electron is delocalized over the whole ligand π system in the excited state. This observation is consistent with extended Hückel theory calculation of pmba, which yields a lowest unoccupied molecular orbital of π symmetry, and which is evenly distributed over the whole ligand.

*Raman Spectra of* $[Cu(bquin)_2]ClO_4$.—Figure 5 shows the Raman spectrum of $[Cu(bquin)_2]ClO_4$ in the range 1 600—900 cm$^{-1}$ using different excitation frequencies. In addition to the five Raman bands in this region, another one at 795 cm$^{-1}$ has been observed. As in the Raman spectra of the copper(I) complexes of ebba and pmba all the observed bands are due to ligand-centred totally symmetric vibrational modes. The three most intense bands at 1 464, 1 384, and 1 337 cm$^{-1}$, which dominate the spectrum, are tentatively assigned to C–C stretching modes; the bands at 1 606 and 1 566 cm$^{-1}$ are assigned to the C–N stretching modes. The bands of the corresponding modes in the free ligand are observed at 1 622, 1 599, 1 440, 1 378, and 1 326 cm$^{-1}$ respectively. Quinoline also shows intense Raman bands in this spectral region, at 1 622, 1 571, 1 433, 1 392, and 1 372 cm$^{-1}$.[23] The band at 795 cm$^{-1}$ is probably due to the breathing mode of the quinoline rings. The corresponding modes in free bquin and quinoline are at 779 and 760 cm$^{-1}$ respectively. No intense Raman bands have been observed in the region of the M–N vibrations. Figure 6 shows the excitation profiles of the four bands at 1 464, 1 384, 1 337, and 795 cm$^{-1}$ in the region of the m.l.c.t. transition. The relative Raman intensities are listed in Table 4. The bands at 1 606 and 1 566 cm$^{-1}$ are too weak for measurement of the excitation profile. Qualitatively, it seems that the resonance enhancement is more pronounced for the band at 1 602 cm$^{-1}$. The relative intensity of the breathing mode at 795 cm$^{-1}$ is continuously increasing when the exciting line shifts towards the blue end of the spectrum. This band is to weak to measure the intensity with reasonable accuracy when the exciting wavelength is larger than 19 430 cm$^{-1}$. This behaviour is typical for a pre-resonance enhancement by an allowed transition in the near-u.v. region. The broken line in Figure 6 indicates the increase of the relative intensity as calculated from the formula of Albrecht and Hutley [24] for an A-Type preresonance enhancement, assuming an electronic transition at 28 000 cm$^{-1}$. The absorption spectrum shows a strong band in this region, which is probably due to an ligand-centred excitation. The bands at 1 464, 1 384, and 1 337 cm$^{-1}$ exhibit resonance enhancement in the region of the m.l.c.t. band. The net effect is, however, considerably smaller than in $[Cu(ebba)_2]ClO_4$ and $[Cu(pmba)_2]ClO_4$. This is not surprising because the absorption coefficient of the m.l.c.t. transition is also smaller. We have, therefore, to assume that the structural changes upon excitation are smaller than in the other complexes. This is expected, because the transferred electron is more delocalized in the large π system of bquin.

**Table 4.** Excitation profiles of $[Cu(bquin)_2]ClO_4$

| | $I_{rel.}$[a] | | | |
|---|---|---|---|---|
| $\tilde{\nu}_0$/cm$^{-1}$ | (1 337 cm$^{-1}$) | (1 384 cm$^{-1}$) | (1 464 cm$^{-1}$) | (795 cm$^{-1}$) |
| 16 054 | 0.37 ± 0.10 | 0.29 ± 0.10 | 0.70 ± 0.10 | |
| 16 207 | 0.49 | 0.31 | 0.82 | |
| 16 455 | 0.56 | 0.33 | 0.93 | |
| 16 764 | 0.83 | 0.56 | 1.50 | |
| 17 071 | 0.81 | 0.58 | 1.52 | |
| 17 328 | 0.87 | 0.61 | 1.67 | |
| 17 516 | 0.83 | 0.54 | 1.31 | |
| 17 883 | 0.90 | 0.58 | 1.33 | |
| | 0.36 ± 0.12 [b] | 0.37 ± 0.10 [b] | 0.34 ± 0.12 [b] | |
| 18 188 | 0.80 | 0.60 | 1.39 | |
| 18 808 | 0.56 | 0.45 | 0.96 | |
| 19 430 | 0.54 | 0.41 | 0.61 | 0.20 ± 0.08 |
| 19 926 | 0.41 | 0.36 | 0.57 | 0.21 |
| 20 135 | 0.45 | 0.51 | 0.57 | 0.21 |
| 20 487 | 0.56 | 0.64 | 0.65 | 0.26 |
| 21 831 | 0.82 | 0.91 | 0.71 | 0.36 |

[a] Intensities relative to $\tilde{\nu}_1$ of $ClO_4^-$ as internal standard. [b] Depolarisation ratio ($10^{-3}$ mol dm$^{-3}$ solution in EtOH).

## Conclusions

These studies show that the copper(I) complexes of α-di-imine ligands, particularly ebba, are good examples for demonstrating the power of resonance Raman spectroscopy in probing experimentally structural and electronic changes upon electronic excitation. This information allows, firstly, a detailed assignment of the electronic transitions, and secondly, a structural description of the excited states, which are important as high-energy intermediates in photochemical reactions.[25]

## Acknowledgements

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## References

1 P. Krumholz, *Struct. Bonding (Berlin)*, 1971, **9**, 139.

2 D. Felix, J. Ferguson, and H. U. Güdel, *J. Am. Chem. Soc.*, 1980, **102**, 4096; C. Daul and J. Weber, *Chem. Phys. Lett.*, 1981, **77**, 593.

3 V. Balzani, F. Bolletta, M. T. Gandolfii, and M. Mestri, *Top. Curr. Chem.*, 1978, **75**, 1.

4 F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 115.

5 R. J. P. Williams, *J. Chem. Soc.*, 1955, 137.

6 H. Ayranci, C. Daul, M. Zobrist, and A. von Zelewsky, *Helv. Chim. Acta*, 1975, **58**, 1732.

7 G. F. Smith and W. H. McCurdy, *Anal. Chem.*, 1952, **24**, 371.

8 P. Clopath and A. von Zelewsky, *Helv. Chim. Acta*, 1972, **55**, 52.

9 G. Bähr and H. G. Döge, *Z. Anorg. Allg. Chem.*, 1957, **292**, 119.

10 D. F. Shriver and J. B. R. Dunn, *Appl. Spectrosc.*, 1974, **28**, 319.

11 H. R. H. Cole and J. R. Durig, *J. Raman Spectrosc.*, 1975, **4**, 31.

12 P. Leupin, Dissertation no. 819, University of Fribourg, Switzerland, 1980.

13 L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 255.

14 O. S. Mortensen, *Chem. Phys. Lett.*, 1975, **30**, 406.

15 A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, 1971, **55**, 4438.

16 W. Siebrand and M. Z. Zgierski, *J. Chem. Phys.*, 1979, **71**, 3561.

17 W. Siebrand and M. Z. Zgierski, ' Excited States,' Academic Press, 1979, vol. 4, p. 8.

18 R. F. Dallinger and W. H. Woodruff, *J. Am. Chem. Soc.*, 1979, **101**, 4391.

19 W. L. Peticolas, D. P. Strommen, and V. Lakshininarayanan, *J. Chem. Phys.*, 1980, **79**, 4185.

20 B. Bak, J. L. Mahleer, L. Nygaard, and S. O. Sorensen, *J. Mol. Spectrosc.*, 1958, **2**, 361.

21 C. A. Daul, C. W. Schläpfer, A. Goursot, E. Penigault, and J. Weber, *Chem. Phys. Lett.*, 1981, **78**, 304.

22 R. W. Balk, P. Y. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1979, **34**, 267.

23 S. C. Wait, jun., and John C. McNerney, *J. Mol. Spectrosc.*, 1970, **34**, 56.

24 A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, 1971, **55**, 4438.

25 B. R. Hollebone, C. H. Langford, and N. Serpone, *Coord. Chem. Rev.*, 1981, **39**, 181.

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