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The Polarized Absorption Spectra of the Pentacoordinated Complex $[Cu(OH_2)_3NO_3(C_8H_{10}N_4O_2)]NO_3$

M. BIAGINI CINGI,* R. BORROMEI and L. OLEARI**

Istituto di Chimica Generale, Università di Parma and Istituto di Chimica Fisica, Università di Parma**, Italy*

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Single crystal polarized absorption spectra of pentacoordinated triaquanitratocaffeinecopper(II) nitrate have been measured. An interpretation of the spectra is given on the basis of the data from the crystallographic and molecular structure which gives complete explanation of the change of the intensity with different polarizations.

Introduction

The absorption spectroscopy of pentacoordinated compounds of transition metals has been much less investigated with respect to other coordinations. This depends probably on the greater difficulties of the theoretical elaboration due to the lower symmetry.

Nevertheless the importance of this kind of coordination is not smaller. It is worth to remember that pentacoordinated species appear as intermediate state in many reaction paths.

We think that the best way to overcome the difficulties joined to this coordination is to use the most advanced techniques like spectroscopy on single crystal with polarized light at very low temperature. On the basis of this point of view we have examinated the triaquanitratocaffeinecopper(II) nitrate, $[Cu(OH_2)_3 NO_3(C_8H_{10}N_4O_2)]NO_3$, in which the cromophore has a square pyramidal structure. In particular we have measured the polarized absorption spectra at the liquid helium temperature of single crystals in four different orientations with respect to the polarization plane of the light. Hence through a proper elaboration we give an interpretation of the spectra.

Experimental

The crystals of triaquanitratocaffeinecopper(II) nitrate have been prepared by slow evaporation of a solution of copper nitrate and caffeine as described in ref. 1–3.

The crystals are monoclinic (β_{gon} = 102.5(1)°), bright green in colour, tabular {100} somewhat elongated [010], their habit being very similar to the saccharose one; the most extended forms are in the order {100}, {001}, {$\bar{1}$01}, {110} and {1$\bar{1}$0}. The O.A.P. is coincident with (010) and 2V approximates 90°. Pleochroism is strong in the [010]zone, bright blue according to β and grass green in the other directions. The space group is $P2_1$.

The spectra were measured on tabular crystals, roughly 2 × 2 mm, first polished with very fine emery paper and finally with talc to expose the (100) or (001) face. The orientation of the crystals was found from morphology taking structural data into account.[1]

The crystals were mounted over a pinhole in a small copper sheet which was bolted to the base of an Oxford Instruments liquid helium cryostat. Temperature measurement was made by means of a gold/0.03 atomic % iron *vs.* chromel thermocouple.

Spectra were taken using a Cary 14 spectrophotometer, the incident light being polarized by a calcite Glan prism placed in the sample beam.

With purpose of comparison the spectrum of an aqueous solution ($4.27 \times 10^{-3} M$) obtained by dissolving some crystals was also measured.

Description of the Spectra

The polarized spectra are reported in Figure 1 and 2. The spectra of Figure 1 are referring to the crystals smoothed according to the (100) face and those of Figure 2 to the (001) face.

In both cases only one very wide band is observed. In the case of Figure 1, where the electric vector of the polarized light is parallel to the c crystallographic axis, $\vec{E}$//c, the band is more intense (almost twice) and wider than that with $\vec{E}$//b.

In the case of Figure 2 the band substantially does not change with the orientation of the electric vector.

In all cases there is no evidence of a fine vibrational structure.

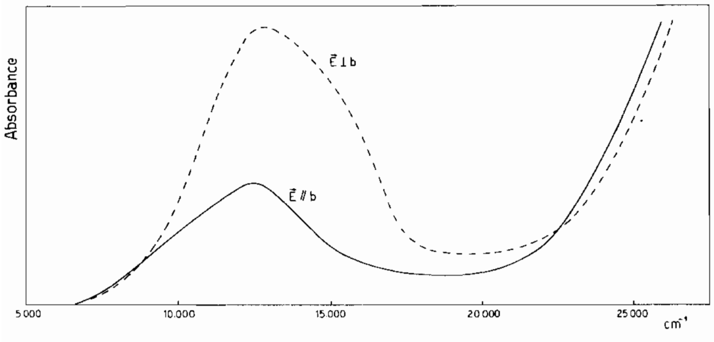

Figure 1. Absorption spectra with incident light on (100)face.

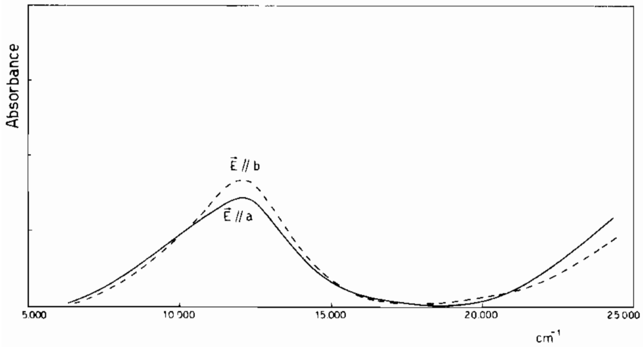

Figure 2. Absorption spectra with incident light on (001)face.

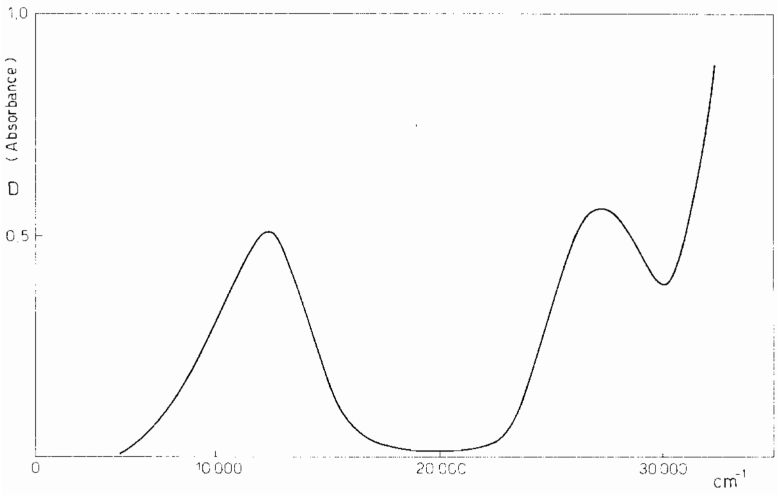

Figure 3. Absorption spectrum of the solution.

In Figure 3 the spectrum of the dissolved crystals is reported. It presents two bands, one at 7500÷16000 cm^{-1} and another at 27000 cm^{-1} with almost the same intensity.

There is no evidence of the second band in the crystal spectra; however it must be pointed out that in such zone the absorbance is so large that it goes out the limits of the instrument also in the case of very thin crystals.

Discussion and Interpretation of the Spectra

As it has been shown by X-ray diffractometric investigation the compound is a complex of copper(II) with a square pyramidal coordination. In particular the chromophore is formed by the oxygen atoms of three water molecules (one at the top and two in *trans* at the base of the pyramid), by an oxygen atom of a nitric group and by a nitrogen atom of a caffeine molecule coordinated to the copper atom. The Cu^{II} atom is not rigorously in the base plane but slightly displaced out of it (0.13 Å) towards the top.

For interpreting the polarized spectra it is first of all necessary to take into account that in the unit cell two molecules are present, with different orientation. Moreover the chromophore, which strictly has no symmetry, can be considered as a first approximation of symmetry C_{4v} and in a more accurate approximation of symmetry C_s, where the symmetry plane is orthogonal to the plane passing through the copper atom and the oxygen atoms of the coordinated water molecules.

In C_{4v} symmetry, Cu^{II} complex having d^9 configuration, the ground state is $^2B_1$. In fact, according to the scheme of the molecular orbital theory, in such system the symmetry of the ground state wave function is the same as that of the singly occupied molecular orbital (m.o.). This m.o. corresponds to the most destabilized one among those of the d set and in particular it derives from the $d_{x^2-y^2}$ atomic orbital, which has the lobes pointing towards the base ligands and belongs to the symmetry B_1.

It follows that, when the electric vector of the polarized light is parallel to the pyramid base ($\vec{E} \perp z$), by assuming only an electric dipole mechanism, only the transitions towards doubly degenerate excited states ^2E are allowed. In particular

1) $^2B_1(d_{x^2-y^2}{}^{-1}) \xrightarrow{\vec{E}//x} {}^2E(d_{xz}{}^{-1})$

2) $^2B_1(d_{x^2-y^2}{}^{-1}) \xrightarrow{\vec{E}//y} {}^2E(d_{yz}{}^{-1})$

When the electric vector is orthogonal to the pyramid base ($\vec{E}//z$) no d–d transitions are allowed. However it must be pointed out that the following transitions

3) $^2B_1(d_{x^2-y^2}{}^{-1}) \longrightarrow {}^2A_1(d_{z^2}{}^{-1})$

4) $^2B_1(d_{x^2-y^2}{}^{-1}) \longrightarrow {}^2B_2(d_{xy}{}^{-1})$

forbidden in C_{4v} symmetry are allowed in C_s symmetry. This is schematically represented in Figure 4 where the y axis is assumed to be orthogonal to the symmetry plane in C_s.

If with $M_{ix} = \langle {}^2B_1|\mu_x|{}^2\Gamma_i \rangle$, $M_{iy} = \langle {}^2B_1|\mu_y|{}^2\Gamma_i \rangle$ and $M_{iz} = \langle {}^2B_i|\mu_z|{}^2\Gamma_i \rangle$ we denote the components of the electric dipole transition moment from the ground state $^2B_1$ to the excited state $^2\Gamma_i$, for the above d–d transitions 1), 2), 3) and 4) we can write Table I.

It must be pointed out that M_{1y}, M_{2x}, M_{2z}, M_{3y}, M_{4x} and M_{4z} are zero in both symmetries C_{4v} and C_s and that M_{1z}, M_{3x}, M_{3z} and M_{4y} are zero in C_{4v} but not in C_s. It is also clear that if the assumption of a C_{4v} symmetry is a good approximation the absolute values of the quantities in parenthesis of Table I must be somewhat smaller than $|M_{1x}|$ and $|M_{2y}|$.

If with $(\alpha_x, \beta_x, \gamma_x)$, $(\alpha_y, \beta_y, \gamma_y)$ and $(\alpha_z, \beta_z, \gamma_z)$ we denote the cosines of the angles of the axes x, y and z for one of the two chromophore groups in the unit cell with respect to the crystallographic axes a, b and c' (being c' an axis orthogonal to the ab plane) and with $(\eta_a, \eta_b, \eta_{c'})$ the cosines of the angles of the electric vector with respect to the crystallographic axes a, b, c', the dipole transition moment is given by the relation:

$$5) \quad \begin{aligned} M_{i\vec{E}} = {} & (\eta_a\alpha_x + \eta_b\beta_x + \eta_{c'}\gamma_x)M_{ix} + \\ & (\eta_a\alpha_y + \eta_b\beta_y + \eta_{c'}\gamma_y)M_{iy} + \\ & (\eta_a\alpha_z + \eta_b\beta_z + \eta_{c'}\gamma_z)M_{iz} \end{aligned}$$

By taking into account that the space group is $P\,2_1$, the cosines of the angles of the x, y, z axes of the second chromophore group are $(-\alpha_x, \beta_x, -\gamma_x)$, $(-\alpha_y, \beta_y, -\gamma_y)$ and $(-\alpha_z, \beta_z, -\gamma_z)$, on the whole we have this expression of the dipole strength:

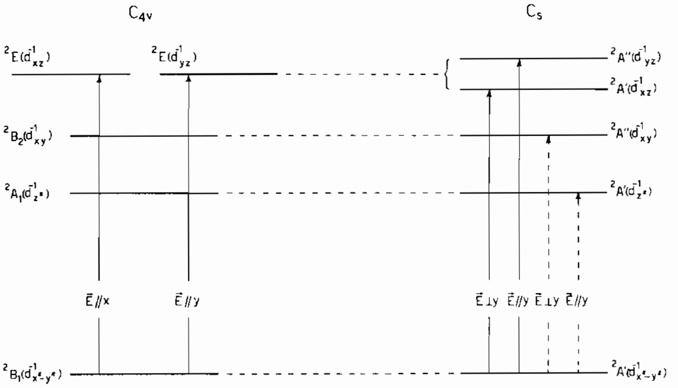

Figure 4. Possible d–d transitions.

TABLE I. Transition Dipole Moment Components.

Transition	Excited State		Dipole moment components		
	in C_{4v}	in C_s	x	y	z
1)	$^2E(d_{xz}^{-1})$	$^2A'(d_{xz}^{-1})$	M_{1x}	0	(M_{1z})
2)	$^2E(d_{yz}^{-1})$	$^2A''(d_{yz}^{-1})$	0	M_{2y}	0
3)	$^2A_1(d_{z^2}^{-1})$	$^2A'(d_{z^2}^{-1})$	(M_{3x})	0	(M_{3z})
4)	$^2B_2(d_{xy}^{-1})$	$^2A''(d_{xy}^{-1})$	0	(M_{4y})	0

$$6)\quad D_i = [(\alpha_x M_{ix} + \alpha_y M_{iy} + \alpha_z M_{iz})\eta_a + (\gamma_x M_{ix} + \gamma_y M_{iy} + \gamma_z M_{iz})\eta_{c'}]^2 + [\beta_x M_{ix} + \beta_y M_{iy} + \beta_z M_{iz}]^2 \eta_b^{\ 2}$$

By means of the least squares method from the coordinates of the atoms we have determined the equation of three orthogonal planes such that: i) one contains, with the least possible deviations, the atoms of the pyramid base (copper has been excluded); ii) the second, again with the least possible deviations, the copper atom and the oxygen atoms of the coordinated water molecules; iii) the third, always with the least possible deviations, the copper atom, the nitrogen atom of coordinated caffeine, the oxygen atom of the coordinated nitric group and the oxygen atom of the apical water molecule.

From these equations we have easily obtained the cosines of the angles of the x, y and z axes relative to the crystallographic ones a, b and c':

$$7)\quad \begin{array}{lll} \alpha_x = 0.675 & \beta_x = 0.729 & \gamma_x = -0.113 \\ \alpha_y = 0.091 & \beta_y = 0.069 & \gamma_y = 0.993 \\ \alpha_z = 0.731 & \beta_z = -0.682 & \gamma_z = -0.019 \end{array}$$

From these data it is evident that the z axis is orthogonal to c' and that the symmetry plane in C_s case is almost parallel to the plane containing the crystallographic axes a and b.

By introducing the above values in eq. 6) and taking properly into account what is reported in Table I, we have the following two relations according to whether the excited state is A' or A'' in C_s:

$$8)\quad \begin{aligned} D_{A'} &= [(0.675M_{ix} + 0.731M_{iz})\eta_a - (0.113M_{ix} + 0.015M_{iz})\eta_{c'}]^2 + [0.729M_{ix} - 0.682M_{iz}]^2 \eta_b^{\ 2} \\ D_{A''} &= [(0.091\eta_a + 0.993\eta_{c'})^2 + 0.005\eta_b^{\ 2}]M_{iy}^{\ 2} \end{aligned}$$

In the specific cases in which the incident light is normal to the face (100) or (001) we have:

a) incident light orthogonal to (100)

$$9)\quad \begin{aligned} &\vec{E}//b \quad \begin{cases} D_{A'} = (0.729M_{ix} - 0.682M_{iz})^2 \\ D_{A''} = 0.005M_{iy}^{\ 2} \end{cases} \\ &\vec{E}//c \quad \begin{cases} D_{A'} = (0.258M_{ix} + 0.178M_{iz})^2 \\ D_{A''} = 0.902M_{iy}^{\ 2} \end{cases} \end{aligned}$$

b) incident light orthogonal to (001)

$$10)\quad \begin{aligned} &\vec{E}//a \quad \begin{cases} D_{A'} = (0.675M_{ix} + 0.731M_{iz})^2 \\ D_{A''} = 0.008M_{iy}^{\ 2} \end{cases} \\ &\vec{E}//b \quad \begin{cases} D_{A'} = (0.729M_{ix} - 0.682M_{iz})^2 \\ D_{A''} = 0.005M_{iy}^{\ 2} \end{cases} \end{aligned}$$

From these relations it is evident that when the incident light is orthogonal to the face (001) the absorption bands for transitions towards A'' states must be much weaker than those for excited states A'. Since we observe in correspondence to the (001) face a rather intense band and its intensity does not change very much by varying the electric vector direction (Figure 2), we can draw the following conclusions:

a) The excited state is certainly A' in C_s symmetry.

b) $|M_{ix}| \gg |M_{iz}|$ or *vice versa,* $|M_{ix}| \ll |M_{iz}|$. However, we must expect values not very much different from those of a C_{4v} symmetry (where $M_{iz} = 0$) and therefore only the first inequality can be accepted.

c) The only one acceptable assignment is $^2B_1(d_{x^2-y^2}^{-1}) \rightarrow {}^2E(d_{xz}^{-1})$ in C_{4v} symmetry or $^2A'(d_{x^2-y^2}^{-1}) \rightarrow {}^2A'(d_{xz}^{-1})$ in C_s symmetry.

When the incident light is orthogonal to the face (100), from relations 9) it results that the observed band corresponds essentially to a transition towards an A' state when $\vec{E}//b$ and corresponds to a transition towards an A'' state when $\vec{E}//c$.

If we take into account that when the symmetry approaches C_{4v} must hold $|M_{ix}| \gg |M_{iz}|$, $M_{iz} \sim 0$ and $|M_{ix}| \sim |M_{iy}|$, we should expect the following ratio of dipole strength:

$$D_{A'}(\vec{E}//b) : D_{A''}(\vec{E}//c) \simeq 1:2$$

This is really observed in Figure 1. It follows that the bands in the two orientations of the electric vector ($\vec{E}//b$ and $\vec{E}//c$) must be assigned to transitions towards two different excited states in C_s (A' and A'') which become degenerate in C_{4v}. Therefore for the d–d transitions the only acceptable assignment is the following:

$$\vec{E}//b: \quad ^2B_1(d_{x^2-y^2}^{-1}) \longrightarrow {}^2E(d_{xz}^{-1})$$
$$\vec{E}//c: \quad ^2B_1(d_{x^2-y^2}^{-1}) \longrightarrow {}^2E(d_{yz}^{-1})$$

This conclusion receives further support by the fact that the two bands differ (besides in the intensity) in the shape (the $\vec{E}//c$ band is wider) and that the $\vec{E}//b$ band is rather similar to that of Figure 2.

With regard to the other possible d–d transitions 3) and 4), forbidden in C_{4v} but allowed in lower symmetries, there is no evidence in the observed spectra. Their intensities are probably too weak with respect to the allowed transitions.

With regard to the band at 27000 cm^{-1} observed in solution we cannot make any consideration because it cannot be observed in the crystal spectra. However, owing to its energy, we think that probably the interpretation has to be found among the charge transfer transitions rather than among the d–d ones.

Conclusions

The main conclusions of the theoretical and experimental work described in this paper may be summarized as follows:

i) The single crystal spectra of triaquanitratocaffeinecopper(II) nitrate measured with incident light orthogonal to the faces (100) and (001) and with electric vector parallel to the crystallographic axes present only one absorption band in the region 8000 ÷ 18000 cm^{-1}.

ii) In spite of the fact that the symmetry of the chromophore is not strictly C_{4v}, the interpretation of the spectra can be done on the basis of such symmetry. In fact, according to this symmetry, only one d–d transition is allowed:

$$^2B_1(d_{x^2-y^2}{}^{-1}) \longrightarrow {}^2E(d_{xz}{}^{-1}),\ {}^2E(d_{yz}{}^{-1})$$

The assignment of the observed band to this transition is supported by the fact that, taking properly into account the orientation of the two chromophore groups in the unit cell, we should have the following ratios of the dipole strength for different orientations of the electric vector:

$$D(\vec{E}//a):D(\vec{E}//b):D(\vec{E}//c) = 1:1.15:2.09$$

This is exactly observed in the spectra.

Acknowledgements

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