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Crystal Spectrum of Bis-trimethylbenzylammoniumtetrachlorocuprate (II)

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On the basis of the X-ray structure determination presented in the preceding paper [8], the polarized absorption spectrum of single crystals of bis-trimethylbenzylammonium tetrachlorocuprate (II) is interpreted, and detailed evidence for the ordering of ligand-field energy levels is achieved. Predictions of the electrostatic theory of complexes and acceptability of the ionic model are briefly discussed.

Sur la base de la détermination de structure à l'aide des rayons X de l'article précédent, le spectre d'absorption polarisée de cristaux singles de tétrachlorocuprate de bis-trimethylbenzylammonium est interprêté et des arguments détaillés en faveur du rangement des niveaux d'énergie du champ des ligandes sont obtenus. On discute brièvement des prédictions de la théorie électrostatique des complexes et de la convenance du modèle ionique.

Mit Hilfe der röntgenographischen Strukturbestimmung von Vaciago et al. [8] wird das mit polarisiertem Licht erhaltene Absorptionsspektrum von Einkristallen des Bis-trimethylbenzylammonium-tetrachlorocuprat (II) interpretiert. Darüber hinaus werden die Vorhersagen der elektrostatischen Theorie der Komplexe sowie die Anwendbarkeit des ionischen Modells auf den vorliegenden Fall diskutiert.

The ligand-field spectrum of tetrahalogenocuprates (II) has been recently discussed by several authors [1—7]. X-ray structure determinations of $[CuX_4]^{2-}$ in $Cs_2(Cu,Zn)X_4$, as well as the basic features of the ligand-field spectrum point to a flattened tetrahedral structure, with polar angle of the ligand positions between approx. 60° and 68°; it is therefore firmly established, or at least generally accepted, that the broad band in the near infrared between ~5 and 10 kK is the envelope of at least two or three *d-d* transitions from a groundstate $^2B_2\,(d_{xy}^{-1})$ of D_{2d}. Knowledge of the crystal structure should allow thorough and unequivocal assignment of all components, and as a matter of fact we have now good reasons to believe that the ordering of energy levels is as quoted by Ferguson [7], and similar to that proposed by Karipides and Piper for $[CuBr_4]^{2-}$ [2] (Fig. 1).

Nevertheless, some doubts still exist. So e.g., purely electrostatic calculations [1, 3, 5] place $(xz, yz)^{-1}$ above $(x^2 - y^2)^{-1}$ rather than below, in contrast with the results of single-crystal polarized spectra by Ferguson [7] and by Karipides and Piper [2]; actually, this difficulty can be partly overcome by the use of an improved electrostatic model, as we shall discuss in a next section of this paper, and the choice of the system of energy levels depicted in Fig. 1 is further supported by

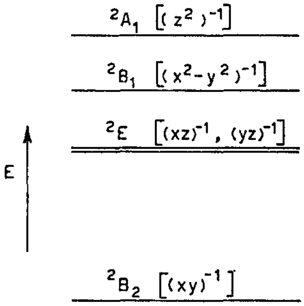

Fig. 1

the results of recent M.O. calculations [6]. On the other hand, Morosin and Lawson [5] present a rather different assignment, where the peak at ~9 kK of $[CuCl_4]^{2-}$ is not regarded as a *d-d* transition, thus producing an improbable spectrochemical inversion between $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$.

In order to settle the question on experimental grounds, we measured the crystal spectrum under polarized light of $(TMBA)_2CuCl_4$*, whose structure has been solved recently by X-ray diffraction [8], and report here further evidence for the assignment of the *d-d* bands of $[CuCl_4]^{2-}$, as presented in Fig. 1. Since one of us had measured previously [3] both the absorption spectrum in solution and the remittance spectrum of the same substance in the solid, from the crystal spectrum we also got conclusive evidence that the same chromophore, substantially unchanged, is responsible for the absorption both in the solid state and in solution. Besides, the orientation of $[CuCl_4]^{2-}$ units in the crystals of $(TMBA)_2CuCl_4$ [8] is somewhat simpler than in the corresponding cesium salt investigated by Ferguson [7] and by Morosin and Lawson [5]: unlike Cs_2CuCl_4, the S_4 axes of all $[CuCl_4]^{2-}$ units in $(TMBA)_2CuCl_4$ lie practically parallel [8], and this fact allows a clearer assignment of the bands of its crystal spectrum.

Single Crystal Spectral Measurements on $(TMBA)_2CuCl_4$

Preparation. $(TMBA)_2CuCl_4$, prepared according to Furlani and Morpurgo [3], crystallizes from acetonitrile in monoclinic, and from absolute ethanol in rhombic, prisms or plates. The unit cell dimensions of both forms are quite similar [8], as are also the densities (~1,36 g/ccm). Monoclinic plates with (001) particularly well developed can be grown at the interface between an acetonitrile solution and ethyl ether, and have been used throughout this work for measurement of crystal spectra, under light incident on face (001).

*Morphology and Optical Analysis of the Monoclinic Crystals***. Orange-red monoclinic crystals of $(TMBA)_2CuCl_4$ belong to $P2_1/n$ with $(a:b:c)_{gm} = 1.053:1:3.125$ and $\beta_{gm} = 92° 45' \pm 5'$. Their morphology is fundamentally characterized by the dominant development of the pinacoid $c\{001\}$, that yields a peculiar tabular habit to most crystals. In case this doesn't occur crystals show a clear tendency to assume a slender prismatic habit, whose elongation may indifferently be along X or Y axis.

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* $TMBA^+ = [C_6H_5CH_2 - N(CH_3)_3]^+$.

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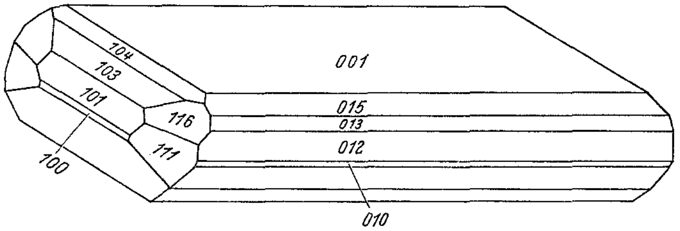

Fig. 2

Observed forms are: $c\{001\}$, $b\{010\}$, $a\{100\}$.
$w\{015\}$, $w'\{013\}$, $w''\{012\}$.
$d\{104\}$, $d'\{103\}$, $d''\{101\}$.
$r\{116\}$, $r'\{111\}$.

As a single-circle horizontal goniometer was used throughout the whole work, measurements are given only in terms of values between couples of real faces:

$c\{001\}: a\{100\} = 92°40'$
$c\{001\}: w\{015\} = 31°29'$
$c\{001\}: w'\{013\} = 46°8'30''$
$c\{001\}: w''\{012\} = 57°21'30''$
$c\{001\}: d\{104\} = 31°27'$
$c\{001\}: d'\{103\} = 46°32'$
$c\{001\}: d''\{101\} = 72°15'$

$c\{001\}: r\{116\} = 40°20'$
$c\{001\}: r'\{111\} = 89°18'$
$a\{100\}: r'\{116\} = 67°26'$
$a\{100\}: r'\{111\} = 67°25'45''$
$b\{010\}: r\{116\} = 66°10'$
$b\{010\}: r'\{111\} = 66°11'15''$

Goniometric measurements generally are not very poor, and acceptable angular readings could be made. Most of the faces are present on the crystals as fine strips $\{012\}$, $\{013\}$, $\{015\}$, or very fine lines $\{100\}$, $\{010\}$, while the $\{hkl\}$ faces show as tiny points. Form $c\{001\}$ is the only one which constantly gives excellent reflections. The drawing (Fig. 2) represents a complete crystal.

Occasionally, couples of faces formed well developed acute prisms, well fit for measuring indexes of refraction; using a monochromatic source of light the following results were achieved:

$$\alpha_{Na} = 1.6198, \beta_{Na} = 1.6334, \gamma_{Na} = 1.6522 .$$

From these values the interior optic axial angle was calculated: $V = 68°$ ($2V = 136°$), too large indeed to be measured under the usual polarizing microscope.

The plane of the optic axes coincides with the unique plane of symmetry, that is $\{010\}$. Optical orientation: $X = c$, $Y = a$, $\sphericalangle Zb = 4°$.

Crystals are pleochroic with

α = yellow
β = pale yellow
γ = orange .

Dispersion: $r > v$.

Spectral measurements. On the basis of the results of the X-ray analysis of the structure of $(TMBA)_2CuCl_4$ [*8*] and of the morphological and optical data reported above, it was possible to perform spectrophotometric measurements on single crystals of $(TMBA)_2CuCl_4$ using polarized light with the electric vector in selected orientations with respect to the direction of the S_4 axis of the $[CuCl_4]^{2-}$ chromophores.

Single monoclinic crystal of $(TMBA)_2CuCl_4$, approximately 40—50 μ in thickness, and of linear dimension about 3—4 mm (*a*) × 2—3 mm (*b*) were easily grown, and could be measured spectrophotometrically as such, since their surfaces were of rather good quality; crystals were mounted on a double goniometric head equipped with two holders bearing a hole of approx. 2 mm diameter in both the reference and the sample channel. Total attenuation of light was sufficiently low in order for ratio-recording system of the spectrophotometer (Beckman DK2) to work properly. Light was incident on $\{001\}$ and crystals were slightly tilted around either axis *a* or *b*; spectra reported here are corrected for increase in light path thickness resulting from tilting of the specimens and for losses due to reflection in tilted specimens. Polarized spectra were taken with a Glan-Thompson prism type polarizer in each channel.

X-ray structure determination [*8*] confirms that in each $[CuCl_4]^{2-}$ group, the polar angle ϑ or π-ϑ is 66,0° ± 0,6° for all four Cl; three Cu-Cl distances fall within ± 0,005 Å of 2,268 Å, the fourth one is 2,228 Å, with a difference from the other three distances which is slightly larger than the standard deviation; therefore the true microsymmetry is probably C_s, but very close to D_{2d}. Flattening of the tetrahedron is slightly more pronounced, and deviations from D_{2d} symmetry are much smaller, than reported for other tetrahalocuprates (II) [*2, 5, 7*]. It also turns out that the alternant axes S_4 of all $[CuCl_4]^{2-}$ units are approximately parallel in the crystal, lying all practically in the (*a c*) or glide planes and making an angle of 54°39′ with *a*. Therefore, for light incident on $\{001\}$, *z*-transitions (electric vector parallel to S_4) are expected to be polarized only $\|$ *a*, while *x*, *y*-transition will appear both $\|$ *a* and $\|$ *b*, with slightly higher intensity in the latter case. Slight clockwise rotation of the crystal around *b* will let *z*-transitions still polarized $\perp$ *b*, whereas *x*, *y*-transitions will tend to appear more and more $\|$ *b*; on the other side, rotating by a small counterclockwise angle α around *b* will bring S_4 towards the direction of propagation of light, eventually letting S_4 coincide (for $\alpha = -54°39'$) with the latter direction, therefore making *z*-transitions inactive under any polarization, while *x*, *y*-transitions would appear equally intense $\|$ *b* and $\perp$ *b*. Rotations around *a* would produce less evident spectral changes, letting *x*, *y*-transitions appear in both polarization planes, only with slightly different intensities; *z*-transitions will always appear strongly $\|$ *a*, and very weakly $\perp$ *a*, except for no tilting, where they would completely vanish under polarization $\perp$ *a*.

Results

Absorption spectra. $[CuCl_4]^{2-}$ anions of microsymmetry D_{2d} are known to exhibit a complex crystal-field band between ~4 and ~10 kK, and some charge-transfer bands from ~25 kK upwards. Our measurements were primarily concerned with the crystal-field band, for which good spectra could be obtained, whereas only indicative data for the much more intense charge-transfer band around 25 kK are presented here. The unpolarized absorption spectrum of our crystal specimens agrees perfectly with already reported absorption spectra of $[CuCl_4]^{2-}$ in organic solvents and with reflection spectra [*2, 3, 7*]. There are two maxima in the *d-d* band, at $8{,}8_5$ kK ($\delta_{\mp} = 1{,}5$ kK) and $5{,}9_2$ kK ($\delta_{-} \sim 1{,}3$ kK). The resolution of both maxima is slightly better in the crystal than in the solution spectrum; to this regard, we note that the position of the short-wave maximum is somewhat influenced by overlapping with the lower-band maximum and appears therefore at slightly higher wavenumbers in the crystal ($\sim 8{,}8_5$ kK) than in the solution spectrum ($8{,}5_0$ kK), and at even higher frequencies in the polarized spectra, when the neighboring bands are extinct ($9{,}2_0$ kK). The maximum intensity of the *d-d* band of the crystal can be only approximately estimated because of uncertainty in the measurement of thickness; our data point to a molar extinction coefficient $E_{\mathrm{mol}} = (1{,}3 \pm 0{,}2) \times 10^2$ at $1{,}13\ \mu$, in substantial agreement with previous reports of solution spectra [*3*].

In the charge-transfer region, we observed a much more intense band at 25,0 kK (with shoulder at 22,7) followed by a minimum at 27,0 kK and by another band at 29,4 kK, again in qualitative agreement with previous reports [*3*], except for the fact that the latter band appears only as a shoulder in solution spectra [*3*].

Assignment of d-d bands. The diagnostic criteria for band assignment are evident from the above discussion of the crystal structure of $TMBA_2CuCl_4$ and from the selection rules for dipole-allowed transitions in D_{2d} (we neglect here vibronic mechanisms, since they are presumably of minor relative importance in systems of undefined parity).

In the point group D_{2d} we have to distinguish only between x,y and z-transitions, i.e., from a groundstate B_2, between E and A_1 excited states, transitions to A_2 and B_1 being dipole-forbidden. To this regard, a first hint as to the assignment can be gained from the polarization of absorption of light propagating perpendicularly to {001}, where, as stated above, z-allowed transitions should vary in intensity between zero and a maximum on rotating the polarization plane, while x, y-transitions are at least partly allowed under any polarization. As shown in Fig. 3, the band at ~9 kK behaves in the former, and the band at ~6 kK in the latter way, thus suggesting $^2B_2 \rightarrow {}^2E$ at ~6 kK, and $^2B_2 \rightarrow {}^2A_1$ at ~9 kK.

This assignment is further supported by the spectral changes observed when tilting the crystal specimens. As shown in the same Fig. 3, a rotation about the direction of the a axis does not change drastically the relative intensities of both bands when observed under light polarized $\parallel a$: under polarization $\perp a$ the x, y-transition at ~6 kK remains allowed practically unchanged, while the z-band at 9 kK, which is not observed for no tilting, begins to appear very weakly on rotation in both senses. The behaviour for rotations around b under polarization $\parallel b$ is rather similar, as in shown in the left part of Fig. 3; again, the band at ~9 kK

Table. *Selection rules for dipole absorption in* D_{2d}

	A_1	A_2	B_1	B_2	E	
A_1	—	—	—	z	x, y	(z^2)
A_2	—	—	z	—	x, y	
B_1	—	z	—	—	x, y	$(x^2 - y^2)$
B_2	z	—	—	—	x, y	(xy) (z)
E	x, y	x, y	x, y	x, y	z	(x, y) (xz, yz)

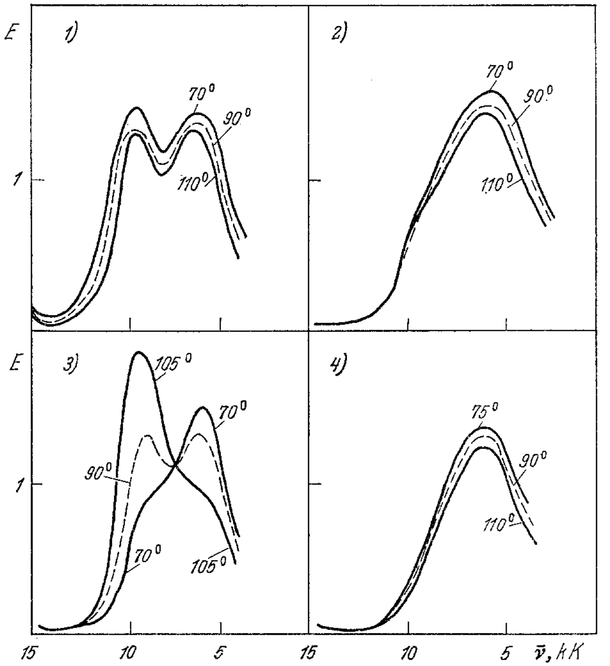

Fig. 3. Polarized absorption spectra of a crystal of $TMBA_2CuCl_4$ of ~45 μ thickness under light incident on {001}, for different incidence angles (marked on the curves)

1. Crystal rotated around *a*, electric vector of light || *a*
2. Crystal rotated around *a*, electric vector of light ⊥ *a*
3. Crystal rotated around *b*, electric vector of light ⊥ *b*
4. Crystal rotated around *b*, electric vector of light || *b*

remains totally inactive, a result which is compatible only with assignment to a *z*-transition.

Far more evident spectral changes are brought about by rotation of the crystal specimens by a small angle α around *b*, under polarization ⊥ *b*. Whereas for $\alpha \sim 0°$ both bands appear with nearly equal intensity, for positive α the 9 kK band increases, and the 6 kK band decreases markedly in intensity; conversely, for negative α the former band decreases and the latter increases (Fig. 3, right). We did not reach complete extinction of either band, since this would require too large rotation angles (the direction of propagation of light should be brought to make an angle of ~54°, respectively 36° with *a*), but the trend is unmistakable.

Of the charge-transfer visible bands, the peak at 25,0 kK behaves very much like a *x*, *y*-transition, which suggests a $^2B_2 \rightarrow {}^2E$ (π-non-bonding) transition: the shoulder at 22,7 kK becomes slightly less evident under polarization || *b*, but this could be due in part to lower-symmetry effects.

Ordering of energy levels-Electrostatic calculations. There is now ample evidence from previous literature reports [*2*, *7*] and from the polarized absorption spectra discussed in the preceding section that the ligand-field band at ~6 kK is due to $^2B_2 \rightarrow {}^2E$ and that the band at ~9 kK is due to $^2B_2 \rightarrow {}^2A_1$ (3*d*). Ligand-field theory predicts a third transition, $^2B_2 \rightarrow {}^2B_1$, in the same spectral region; such transition

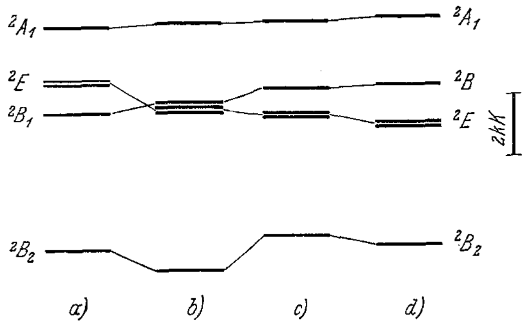

Fig. 4. Electrostatic calculations of the system of energy levels of $(3d)^9$ under a field of symmetry D_{2d} with different choices of the parameters of the crystal-field model:
a) Perturbing charges, $f_{Cu} = 2.10$, $R = 3.70$ u.a., $\vartheta = 62°$ ($\Delta_{oct.} = 8.1$ kK);
b) Perturbing dipoles ($\mu = 0.81$ at. u.), $f_{Cu} = 2.10$, $R = 3.70$ u.a. ($\Delta_{oct.} = 8.1$ kK), $\vartheta = 65°$;
c) Perturbing dipoles ($\mu = 0.93$ at. u.), $f_{Cu} = 2.10$, $R = 3.70$ u.a. ($\Delta_{oct.} = 9.3$ kK), $\vartheta = 62°$;
d) Perturbing dipoles ($\mu = 1.00$ at. u.), $f_{Cu} = 1.72$, $R = 4.18$ u.a. ($\Delta_{oct.} = 9.9$ kK), $\vartheta = 62°$.
The choice of coordinate axes is as in Ref. [*3*]

is dipole-forbidden in D_{2d}, and is therefore expected to be of much smaller intensity than the former two bands: actually, we have found no experimental evidence for such a band in our crystal spectra (which may be in part due to poor resolution of room-temperature spectra), so we have no direct indication as to the position of this transition; however, by analogy with the situation of $[CuBr_4]^{2-}$ as interpreted by KARIPIDES and PIPER [*2*] and accepting FERGUSON's low-temperature results, we can assume that $^2B_1$ lies very probably between ^2E and $^2A_1$, as is shown in Fig. 1. Now, preliminary electrostatic calculations done by one of us [*3*] suggested rather an ordering $^2A_1 > {}^2E > {}^2B_1$, and this fact has been taken for a demonstration of inherent inadequacy of the electrostatic model [*7*]. We can however show that it is possible, under suitable assumptions, to bring the correct ordering $^2A_1 > {}^2B_1 > {}^2E$ in accordance with an electrostatic model.

While no doubt exists that the highest state of the partly field shell is $(d_{z^2})^{-1}$ because of the smallest covalent bonding ability of d_{z^2}, and that the lowest one is $(d_{xy})^{-1}$ because of the good σ-antibonding character of d_{xy}, the relative position of $(d_{xz})^{-1}$, $(d_{yz})^{-1}$ and $(d_{x^2-y^2})^{-1}$ is much more uncertain; in an electrostatic model, it depends upon the ligand-field perturbation strength, upon the degree of flattening of the coordination tetrahedron, and upon a delicate balance of multipole interactions of the d-electron distributions with the perturbing ligands. Thus, if we consider the perturbing ligands as point charges, the predicted ordering of levels is $^2B_1 > {}^2E$ for small distortions from T_d and small ligand field strength, but is $^2E > {}^2B_1$ for more pronounced flattening of the tetrahedron and stronger ligand perturbation (the latter situation corresponds to the tentative interpretation of Ref. [*3*]). If we however assume that the electrostatic perturbation is mainly caused by ligand dipoles (namely if we put more weight on the induced dipole than on the negative charge of the chloride ligands, partly following FELSENFELD's [*1*] arguments), then ^2E is markedly stabilized with respect to $^2B_1$, and remains lower than the latter level even under relatively strong tetragonal perturbations. Fig. 4 gives diagrammatically the results of crystal-field calculations according to different choices of the parameters of the perturbing entities in a $[CuX_4]^{2-}$ complex of the same geometry as is experimentally known for $(TMBA)_2CuCl_4$: it is seen that, for the observed geometry, $^2B_1$ lies invariably above ^2E if the perturbing ligands are regarded as dipoles rather than as point charges. Thus, the crystal-field or electrostatic model, despite its approximate character and its inability to settle unequivocally the ordering of *d*-levels, is at least not unavoidably bound to predict a wrong ordering of levels and can still be used with some confidence as an aid to classification of the energy levels within the partly filled shell of Cu (II) in its pseudotetrahedral complexes of not too strong tetragonality.

References

[1] FELSENFELD, G.: Proc. Roy. Soc. **A 236**, 506 (1965).
[2] KARIPIDES, A. G., and T. S. PIPER: Inorg. Chem. **1**, 970 (1962).
[3] FURLANI, C., and G. MORPURGO: Theoret. chim. Acta **1**, 102 (1963).
[4] BRATERMAN, P. S.: Inorg. Chem. **2**, 448 (1963).
[5] MOROSIN, B., and K. LAWSON: Molecular Spectroscopy **12**, 98 (1964).
[6] LOHR, L. L., and W. N. LIPSCOMB: Inorg. Chem. **2**, 911 (1963).
[7] FERGUSON, J.: J. chem. Phys. **40**, 3406 (1964).
[8] BONAMICO, M., G. DESSY, and A. VACIAGO: Theoret. chim. Acta **7**, 367 (1967).

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