

Polarized crystal spectrum of bisethylenediamine copper(II) thiosulfate

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Abstract. The polarised single crystal spectrum of bisethylenediamine copper(II) thiosulfate is reported. The three observed absorption bands at 19·10 kK, 15·60 kK and 14·30 kK have been assigned as $d_{xy} \rightarrow d_{xz}, d_{yz}$; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_z^2$ transitions with D_{4h} as the symmetry of the complex ion. However the polarisation of the observed bands can also be accounted by the point group (C_{2h}) of the complex ion. The failure in the detection of all the four bands may be due to bad orientation of the molecules in the unit cell, which also makes the ground state assignment ambiguous.

Keywords. Bisethylenediamine copper(II) ion; polarised electronic spectra; assignments of energy levels.

1. Introduction

In the centrosymmetric copper chelates (Piper and Belford 1962; Belford and Carmichael 1967; Hathaway *et al* 1970; Hitchman and Belford 1971) the polarised crystal spectra are interpreted with reasonable consistency within the oriented gas model although for certain polarisation exciton intensity transfer was suggested. As part of our programme to study the crystal spectrum of transition metal ions (Olson *et al* 1971; Basu 1968, 1969) for assigning the correct energy levels in the presence of crystal field and to find the mechanism of the optical intensity of the forbidden transition to these levels, we report here the crystal spectrum of bisethylenediamine copper(II) thiosulfate where the transition metal complex cations are well separated by the bulky thiosulfate anions.

2. Structure of the compound and the complex ion

Recently the crystal structure and the vibrational analysis of the infrared spectra of bisethylenediamine copper(II) thiosulfate have been reported. It forms monoclinic crystals with four molecule per unit cell (Varand *et al* 1967). The copper ion is in a tetragonally distorted octahedral environment with four nitrogen atoms from the ethylenediamine molecule in an approximately square planar configuration (average Cu-N distance = 2·06 Å). Two sulfur atoms from the

thiosulfate (S_2O_3) group located at two different Cu-S distance (2.71 Å) make up the copper bipyramidal coordination. The thiosulfate ion has a tetragonal configuration but are slightly distorted as compared to the ideal C_{2v} tetrahedron. The $[Cu(en)_2]^{+2}$ complex cations and $S_2O_3^{=}$ anions are joined in the structure by weak $-NH \cdots O$ and $CH \cdots O$ hydrogen bonds.

The infrared frequencies of the six fundamental of the thiosulfate ion (Gabelica 1976) suggest that the thiosulfate ions vibrate as free unperturbed C_{2v} tetrahedron, which do not come under the disturbing influence of the neighbouring ions in the crystal. Any weak coordination through the terminal sulfur has not been revealed in the infrared spectra as that would split the degenerate E modes. Moreover the external sulfur atoms of the two thiosulfate groups are located at different distances from the copper atom. This suggests that if semi-coordination occurs, vibrational pattern characterising two different coordinational $S_2O_3^{=}$ anion would be expected which are not observed.

Thus $[Cu(en)_2]^{+2}$ is a free cation with four equidistance N-atoms around the copper ion which all lie approximately in the same plane. The ethylene-diamine chelate rings are in gauche conformation (Varand *et al* 1967), the carbon atoms being deflected from the NMN planes on opposite sides. Neglecting the hydrogen atoms, the point group of the free complex ion $[Cu(en)_2]^{+2}$ is therefore C_{2h} . The five absorption band in the infrared region of this and many $[M^{II}(en)_2]^{2+}$ ion have been assigned satisfactory on the basis of its C_{2h} symmetry (Omura *et al* 1971; Berg and Rasmussen 1972, 1973).

3. Experimental

Single crystals of this compound were grown by slow evaporation of an aqueous solution of the compound prepared by the method of Varand *et al* (1967) as modified by Gabelica (1976). In a week's time several dark blue plate-like crystals were obtained. Only one face is well developed and this is the cleavage face. Thin sections (below 0.2 mm) of this face were cleaved off and used for recording the spectra on a Unicam SP 700A spectrophotometer with two matched pair of polariser in the optical path. The polarisers were placed before the sample so that the polarised light falls on the crystal face. In order to get the maximum resolution of the instrument, the slit width was always kept below 0.1 mm in the visible region. Spectra of several crystal faces of different thickness were recorded to check the reproducibility of the data. The spectra of the same crystal face in the two polarisation were recorded with the same slit opening. The entire visible region was slowly scanned to check for any missing band or band shoulder. The infrared spectra and copper estimation were used to check the purity of the crystals.

4. Results and discussion

The crystals are dichloric-green when the light vector is perpendicular to the long axis of the crystal face and violet when the light vector is parallel to the long axis. In figure 1 the two polarised spectra and the unpolarised spectra are shown

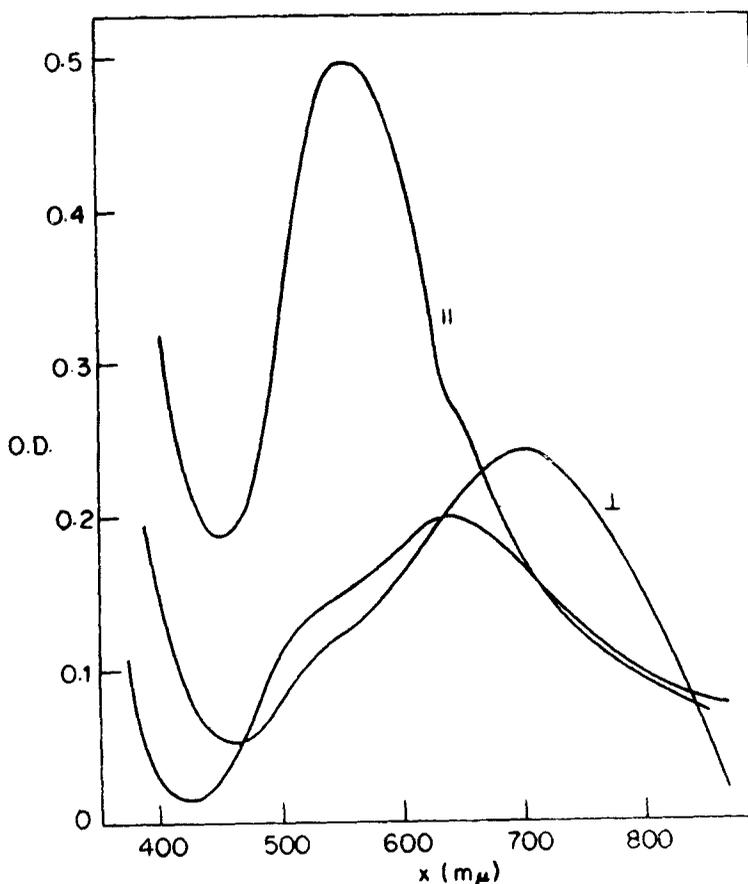


Figure 1. Polarised crystal spectra, [marked (\parallel) and (\perp)] of the cleavage face of bisethylenediamine copper(II) thiosulfate. The un-polarised spectra (un-marked) of a different thick cleavage face is included. O.D. is in arbitrary unit.

at room temperature. The two polarised (\parallel and \perp) spectra are of the same crystal face while the unpolarised spectra is of a different crystal face which is approximately five times thicker than the crystal face used for recording the polarized spectra. The thin crystal used in polarisation study has very little absorption in the visible region with unpolarised light.

Cooling down the crystal to liquid air temperature does not show much change in band shape from the room temperature one. With the unpolarised light the maximum in the optical density appears at 15.60 kK. When the light is polarised perpendicular to the crystal face, the prominent band is at 14.30 kK with asymmetry at 18.10 kK region. In the parallel polarisation, the most intense band appears at 18.10 kK. The inflexion at 15.60 kK region in the parallel polarisation is quite clear when this region is scanned slowly (the region of maximum intensity with unpolarised light). There is no absorption in the near infrared region even with thick crystals.

Although the point group of the complex ion is C_{2h} the crystal field round the copper atom may be considered due to the four nitrogen atoms only and is nearly square planar (D_{4h}). In C_{2h} , the degeneracy of the five d -orbitals will be completely lifted, and four electronic transitions are expected. But only three transitions have been observed in the visible and near infrared region. Thus a higher molecular symmetry, D_{4h} , has been used to analyse the spectra. In D_{4h} symmetry, light can be polarised into two nonequivalent directions along the principal axis (z) and perpendicular to this axis. The selection rules for the $d-d$ transitions in D_{4h} symmetry are given in table 1. The x -axis in the molecule was taken as line passing through the metal ion and parallel to the N_1-N_2 internuclear distance. The y -axis was taken as an axis passing through the origin and the midpoint of the N_1-N_2 distance. Out of the six possible odd vibrational modes which could bring out the vibronic transition, four are of ϵ_u type and one each of a_{2u} and β_{1u} in D_{4h} symmetry. The antisymmetric stretching modes are of ϵ_u type and are usually considered as the main vibronic perturber for the appearance of the forbidden $d-d$ transitions. Thus considering the antisymmetric stretching modes as most effective in bringing about the transition, there should be two bands perpendicularly (\perp) polarised and one doubly degenerate band parallel (\parallel) polarised, if we consider the degenerate state not as the ground state.

The observed polarisation of the bands can be accounted with d_{xy} as the most likely ground state as is used in many other centrosymmetric copper(II) complexes. The most intense band at 18.10 kK can then be assigned as $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition and the band at 14.30 kK as due to transition from d_{xy} to $d_{x^2-y^2}$ ($d_{xy} \rightarrow d_{x^2-y^2}$). The band at 15.60 kK which appears as a weak shoulder (the band of maximum absorption with unpolarised light) corresponds to $d_{xy} \rightarrow d_{z^2}$ transition. The high optical density of 18.10 kK band may be due to transition to a doubly degenerate state.

This assignment offers us little satisfaction because the polarisation of some of the bands can be equally explained by the lower C_{2h} symmetry. The non-resolution of the fourth band may be due to crowdedness of four bands in a small energy

Table 1. Vibrational symmetries which could permit the possible $d-d$ transitions in D_{4h} .

Transition	$z(I)$	$x, y (I)$	Polarisation allowed by vibration		
			Bond stretch ϵ_u	Bend a_{2u}	Bend β_{1u}
$xy \leftrightarrow x^2 - y^2$	B_{2u}	E_u	\perp	—	—
$xy \leftrightarrow z^2$	A_{2u}	E_u	\perp	\parallel	—
$xy \leftrightarrow xz, yz$ $z^2 \leftrightarrow zx, yz$ $x^2 - y^2 \leftrightarrow xz, yz$	E_u	$A_{1u} + A_{2u} +$ $B_{1u} + B_{2u}$	\parallel	—	\perp
$x^2 - y^2 \leftrightarrow z^2$			A_{1u}	E_u	\perp

region with each band having a large halfwidth. The mixed polarisation of the bands may be due to bad orientations of the four molecules in the unit cell where the direction of the x -axis of one molecule may be almost the direction of z -axis of neighbouring molecule in the unit cell. Unfortunately the crystal data in this respect are not available for further analysis of the polarised spectra. Magnetic properties in particular the magnetic anisotropy data together with this optical data may permit to give a better picture of the ground state and molecular symmetry of the complex ion.

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