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Single Crystal Electronic and EPR Spectra of $CaCuSi_4O_{10}$, a Synthetic Silicate Containing Copper(II) in a Four-coordinate, Planar Ligand Environment

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The electronic structure of planar metal complexes is of considerable interest, both because such compounds have been the subject of numerous theoretical calculations [1] and because evidence has recently been accumulating which suggests that simple bonding model cannot adequately explain all the energy levels of complexes with this particular stereochemistry [2–4]. Moreover, recent investigations have shown that the low temperature electronic spectra of the planar ions $CuCl_4^{2-}$, $PdCl_4^{2-}$ and $PtCl_4^{2-}$ show extensive vibrational fine structure [5, 6]. A compound which has been the subject of numerous investigations [7–11] is the rare mineral gillespite, $BaFeSi_4O_{10}$, which contains iron(II) in a four-coordinate, square planar ligand environment. The present study involves the isomorphous copper(II) complex, egyptian blue (cuprorivaite), $CaCuSi_4O_{10}$. The spectral properties of this are reported and compared with those of gillespite and other related compounds. The *d*-orbital energies have been deduced and interpreted using the angular overlap model of the bonding in metal complexes.

Experimental

Crystals of $CaCuSi_4O_{10}$ large enough for spectral measurements were grown by a modification of the method of Pabst [12] using $CaCO_3$, CuO and powdered SiO_2 as constituents with 10% borax added to act as flux. These were mixed in a Spex mixing mill for one hour and then pressed into a compact pill 2.5 cm in diameter at a pressure of 10 tonnes. The sample was placed in a graphite crucible, heated for one day at 800 °C and then subsequently cooled at 100 °C per day for five days. The product was found to consist of a mesh of fine-grained platey blue crystals. At one point the specimen had come into contact with the furnace tray and larger crystals approximately 1 mm square had developed. The platey habit was due to the preferred growth of (001) but this was always terminated by suppressed (111) faces. The crystals were qualitatively checked for purity using a JEOL-JXA50 electron probe fitted with an Edox system. An X-ray diffraction trace showed a pattern similar to that given by Pabst; however the intensities of the diffraction peaks differed due to preferred orientation of the plates in the sample preparation. The ω (ordinary ray) refractive index for the complex was determined as lying between 1.634 and 1.638 at 20 °C for the NaD line. This was established by matching the crystal refractive index with immersion oils and measuring these with a Zeiss Abbe high dispersion refractometer. This compares with the value of 1.636 reported by Pabst [12].

Egyptian blue crystallizes in the tetragonal space group *P4/ncc* with the (001) face well developed. The electronic spectrum of this face was obtained using a Cary 17 spectrophotometer by mounting the largest crystal which could be grown (dimensions ~ 1 X 1 X 0.035 mm) on a mask of aluminium foil. The crystal was cooled using a C.T.I. cryodyne 21 cryostat. A section containing the [001] direction was obtained by grinding an aggregate of crystals mounted with the appropriate orientation on a microscope slide with glue. The electronic spectrum of this face was measured with the electric vector of polarized light parallel and orthogonal to the [001] direction. Although of poorer quality, the latter spectrum was found to be identical in all essential features to that of the (001) crystal face. The EPR spectra were obtained at room temperature with a JEOL JES-P-10 X-band spectrometer using an experimental procedure described elsewhere [13].

Results and Discussion

Electronic Spectrum

The copper(II) in egyptian blue is truly four-coordinate, with a centrosymmetric, planar ligand environment of D_{4h} symmetry [12]. The metal and ligand oxygen atoms lie in the (001) crystal plane and the electronic spectra with the electric vector in this plane (the *xy* spectrum) measured at 10K and 295K, and along the [001] *z* molecular direction measured at 10K are shown in the Figure. The intensities of all three '*d–d*' transitions are much greater in *xy* than in *z* polarization; this seems to be a general feature of many copper(II) complexes with planar or tetragonally elongated octahedral geometries [5, 14, 15].

The overall band intensities in $CaCuSi_4O_{10}$ are quite similar to those observed recently for planar $CuCl_4^{2-}$ [5] and are considerably greater than those of centrosymmetric copper(II) aquo complexes [15] or $BaFeSi_4O_{10}$ [7]. Unlike planar $CuCl_4^{2-}$, no vibrational fine structure was observed in the electronic

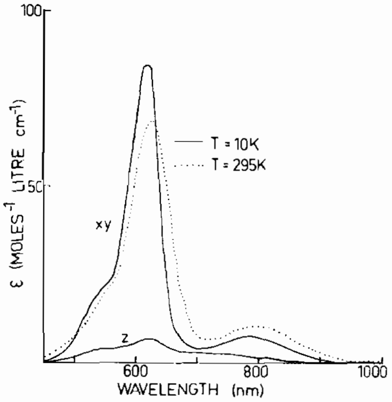

Figure. Electronic spectrum of $CaCuSi_4O_{10}$ with the electric vector of light parallel to the z and xy molecular axes.

TABLE. Measured g-Values of $CaCuSi_4O_{10}$ for Various Angles of the Magnetic Field with the [001] Direction.

Data Set 1		Data Set 2	
Angle°	Value of g^2	Angle°	Value of g^2
−27.65	5.1749	−29.34	5.1171
−12.65	5.3255	−14.34	5.2951
2.35	5.3685	0.66	5.3792
17.35	5.2882	15.66	5.3082
32.35	5.0769	30.66	5.1357
47.35	4.8079	45.66	4.8554
62.35	4.5188	60.66	4.5770
77.35	4.3318	75.66	4.3493
92.35	4.2783	90.66	4.2634
107.35	4.3698	105.66	4.3324
122.35	4.6070	120.66	4.5369
Best-fit g^2 *values:*		*Best-fit* g^2*-values:*	
5.3891	4.2823	5.3887	4.2716
Standard error: 0.0073		*Standard error:* 0.0066	

spectrum of $CaCuSi_4O_{10}$ at low temperature. Indeed, at least for the xy spectrum, the bands in egyptian blue show little or no decrease in intensity on cooling from 295 to 10 K (the very weak z spectrum was not well enough resolved to warrant a study of its variation with temperature). This suggests that the intensity in each transition is derived from coupling with comparatively high energy ungerade vibrational modes. This is in marked contrast to the behavior of other copper(II) complexes with oxygen donor ligands [15, 16] and to planar $CuCl_4^{2-}$ [5], where a large decrease in intensity occurs on cooling.

The vibronic selection rules suggest that only a single transition is forbidden for a copper(II) complex with D_{4h} symmetry, ${}^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$ in z polarization. The very weak intensity of the z spectrum makes an unambiguous application of the selection rules difficult. However, theory suggests that the ${}^2B_{2g}(xy) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition should occur at lower energy than ${}^2E_g(xz, yz) \leftarrow {}^2B_{1g}(x^2-y^2)$. As the middle peak is the most intense in the spectrum, this implies that the lowest energy transition must be to the ${}^2B_{2g}(xy)$ state, with the middle and highest energy peaks being to the ${}^2E_g(xz, yz)$ and ${}^2A_{1g}(z^2)$ states, respectively. This assignment agrees with that proposed by Burns *et al.* [7] and the band maxima yield the following values for the excited state energies: ${}^2B_{2g}(xy) = 12740$ cm^{-1}, ${}^2E_g(xz, yz) = 16130$ cm^{-1}, ${}^2A_{1g}(z^2) = 18520$ cm^{-1}.

Molecular g*-Values*

The molecular g-values were obtained by measuring the EPR spectra of several crystals of $CaCuSi_4O_{10}$ with the magnetic field making various angles with the crystal axes. The data were analysed using a least-squares technique, and to minimize errors due to the mounting of the crystals two sets of data were treated (see Table). The overall g-values were found to be $g_z = 2.3214$ (0.0015) and $g_{xy} = 2.0681$ (0.0016) with the possible errors indicated in parentheses. These differ somewhat from those reported previously by Hathaway *et al.* [17] from powder data ($g_z = 2.326$, $g_{xy} = 2.054$).

The shifts from the free electron g-value (2.0023) are related to the excited state energies $E(B_{2g})$ *etc.* by the expressions:

$$\Delta g_z = -8\lambda k_\parallel^2/E(B_{2g})$$

$$\Delta g_{xy} = -2\lambda k_\perp^2/E(E_g)$$

where λ is the spin–orbit constant (−828 cm^{-1} for Cu^{2+}) and $k_\parallel$ and $k_\perp$ are the orbital reduction parameters. Substitution of the relevant numbers in these equations produces the values $k_\parallel^2 = 0.61$ (0.01), $k_\perp^2 = 0.65$ (0.01). Although the quantitative interpretation of orbital reduction parameters is problematical [18] there is considerable evidence that these tend to decrease as the covalency of metal–ligand bonds increases [19]. The parameters in $CaCuSi_4O_{10}$ are very similar to those observed for a series of three copper(II) acetylacetonate complexes ($k_\parallel^2 = 0.61$, $k_\perp^2 = 0.59$, with a maximum deviation of 0.05) [20], being considerably greater than those in planar $CuCl_4^{2-}$. ($k_\parallel^2 = 0.41$, $k_\perp^2 = 0.33$) [21], but somewhat less than those in the $Cu(H_2O)_6^{2+}$ ion (mean values from six salts $k_\parallel^2 = 0.67$, $k_\perp^2 = 0.75$) [13]. This seems in keeping with the covalency expected in a planar copper(II) silicate. It is noteworthy that the alternative assignment of the electronic spectrum of egyptian blue, with $B_{2g}(xy)$ at 16130 cm^{-1} and $E_g(xz, yz)$ at 18520 cm^{-1}, would imply the values $k_\parallel^2 = 0.78$ and $k_\perp^2 = 0.74$ which seem far less reasonable.

Interpretation of the d*-Orbital Energies*

There has been considerable controversy over the ordering of the d-orbitals in planar metal complexes [1]. The above assignment of the electronic spectrum of $CaCuSi_4O_{10}$ suggests the sequence $d_{x^2-y^2} \gg d_{xy} >$

$d_{xz,yz} > d_{z^2}$ in this complex. Truly 4-coordinate, planar copper(II) complexes are rare [14], but the same sequence has been reported recently in planar $CuCl_4^{2-}$ [4] and also for 4-coordinate complexes with nitrogen donor atoms [3]. One of the most useful ways of interpreting the *d*-orbital energies of metal complexes is the angular overlap model (AOM) of Jørgensen and Schäffer [21]. This relates the energy *e* by which a *d*-orbital is raised upon interaction with a ligand orbital to the square of the diatomic overlap integral *S*:

$$e = KS^2 \tag{1}$$

where *K* is a constant dependent on the nature of the metal and the ligand. The total energy of each *d*-orbital *E* is obtained by summing over all the ligand orbitals using the angular overlap matrix appropriate to the complex in question. Both σ and π-interactions are included, and for a 4-coordinate, planar complex the *d*-orbital energies are given by:

$$E(x^2 - y^2) = 3e_\sigma \tag{2a}$$

$$E(z^2) = e_\sigma \tag{2b}$$

$$E(xy) = 4e_\pi(e) \tag{2c}$$

$$E(xz, yz) = 2e_\pi(a) \tag{2d}$$

where e_σ represents the sigma interaction with one ligand, and $e_\pi(e)$ and $e_\pi(a)$ represent the π-interactions with the ligand orbitals parallel and perpendicular to the plane of the complex. Substitution of the transition energies observed for $CaCuSi_4O_{10}$ into the above equations 2a–d yields the values e_σ = 9260 cm^{-1}, $e_\pi(a)$ = 5825 cm^{-1} and $e_\pi(e)$ = 3745 cm^{-1}, while the substitution of the overlap integrals S_σ = 0.09378, S_π = 0.05427 appropriate to the Cu–O bond length of 192 pm observed in $CaCuSi_4O_{10}$ into equation 1 gives the metal–ligand bonding parameters $K_\sigma = 10.5 \times 10^5$ cm^{-1}, $K_\pi(e) = 12.7 \times 10^5$ cm^{-1} and $K_\pi(a) = 19.8 \times 10^5$ cm^{-1}. These values imply a very strong π-interaction, particularly with the out-of-plane ligand π-orbitals (for a ligand in which the σ- and π-bonding orbitals are degenerate, simple theory suggest $K_\sigma = K_\pi(a) = k_\pi(e)$). However, recently evidence has been accumulating that simple models which consider just the interaction between the ligands and the *d*-orbitals cannot adequately explain all of the energy levels in a truly four-coordinate, planar complex. The discrepancy apparently lies in the $a_{1g}(d_{z^2})$ orbital, which is depressed in energy by ~ 5000 cm^{-1} from the value predicted by simple bonding models such as the AOM. The reason for this is thought to be the configuration interaction with the metal $a_{1g}(4s)$ orbital which occurs in a complex of D_{4h} symmetry. This interaction is proportional to the difference in metal ligand bonding along the *z* and (*xy*) axes, and because of the diffuse nature of the 4*s* orbital, this is significant only in a truly four-coordinate complex [2]. Evidence for this effect has now been observed for several planar copper(II) [4], nickel(II) [3] and cobalt(II) [22] complexes as well as for $BaFeSi_4O_{10}$ [11], so that it seems to be a general feature of square planar complexes. It is interesting to note that in compounds such as bis(acetylacetonato)copper(II), which might be expected to behave in a manner similar to $CaCuSi_4O_{10}$. it seems likely that no depression of the d_{z^2} orbital occurs [23]. However, these complexes apparently invariably crystallize with the central carbon atom of the acetylacetonate groups ~ 310 pm above and below each copper(II) ion [24], so that it is possible that the interaction with the π-system of the neighbouring molecules diminishes the configuration interaction between the metal 4*s* and $3d_{z^2}$ orbitals.

If it is assumed that in $CaCuSi_4O_{10}$ the d_{z^2} orbital is depressed in energy by ~ 5000 cm^{-1} (that is, that the energy of the $^2A_{1g}(z^2)$ state would be ~ 13520 cm^{-1} in the absence of this interaction), then equations 1 and 2 suggest the following AOM bonding parameters: $e_\sigma \simeq 6760$ cm^{-1}, $e_\pi(a) \simeq 2075$ cm^{-1}, $e_\pi(e) \simeq 1870$ cm^{-1}; $K_\sigma \simeq 7.7 \times 10^5$ cm^{-1}, $K_\pi(a) \simeq 7.0 \times 10^5$ cm^{-1}, $K_\pi(e) \simeq 6.4 \times 10^5$ cm^{-1}. These appear much more reasonable than those derived ignoring the configuration interaction, both in the similarity of K_σ to $K_\pi(a)$ and $K_\pi(e)$, and when compared with the bonding parameters observed for similar compounds (for instance, the values $K_\sigma = 8.8 \times 10^5$ cm^{-1}, $K_\pi(a) = 8.5 \times 10^5$ cm^{-1}, $K_\pi(e) = 6.5 \times 10^5$ cm^{-1} have been estimated [23] for the acetylacetonate anion towards copper(II)). The values e_σ = 7500 cm^{-1}, $e_\pi(a) \simeq 2250$ cm^{-1}, $e_\pi(e)$ = 2700 cm^{-1}, $K_\sigma = 5.8 \times 10^5$ cm^{-1}, $K_\pi(a) = 4.7 \times 10^5$ cm^{-1}, $K(e) = 5.6 \times 10^5$ cm^{-1} have recently been estimated for $BaFeSi_4O_{10}$ [11], also assuming a depression of ~ 5000 cm^{-1} in the energy of the $a_{1g}(d_{z^2})$ orbital. The parameters are quite similar to those of $CaCuSi_4O_{10}$. Despite the longer bond lengths (Fe–O = 199.5 pm [25] compared with Cu–O = 192 pm [12]) the interaction with the *d*-orbitals is somewhat stronger in the iron (II) complex. This results from the larger overlap integrals associated with the more extended Fe^{2+} 3*d* orbitals. As expected [20], the parameters K_σ *etc.* are smaller for iron(II) than copper(II), because of the greater energy separation between the metal and ligand orbitals for the former metal ion.

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