Studies in Eight-co-ordination. Part III.[1] The Single-crystal Electronic Spectrum, Electron Spin Resonance, and Magnetic Anisotropy of, and Crystal-field in, Tetra-(6-aminohexanoic Acid)copper(II) Diperchlorate †

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The single-crystal polarised electronic spectra, e.s.r., and magnetic anisotropy of tetra-(6-aminohexanoic acid)-copper(II) diperchlorate are reported. These properties are interpreted by use of a point-charge crystal-field model and are seen to be consistent with the relative orbital energies, $d_{xy} > d_{x^2-y^2} > d_{z^2} > d_{xz,yz}$. The crystal-field parameters obtained are shown to agree closely with those for $CaCu(AcO)_4,6H_2O$ when allowance is made for the different Cu–O distances involved.

THE crystal structure of tetra-(6-aminohexanoic acid)-copper(II) diperchlorate [$Cu(HA)_4(ClO_4)_2$] has shown[2] the copper to have a very similar co-ordination geometry to that found[3] in calcium copper acetate hexahydrate [$CaCu(AcO)_4,6H_2O$]. This similarity is ideal since it facilitates a study of the detailed effects of co-ordination geometry on the electronic properties of Cu^{II} complexes and thus should test the applicability of the theoretical model chosen to analyse the results. Interpretations of the electronic spectrum and e.s.r. properties of $CaCu(AcO)_4,6H_2O$ in terms of a point-charge crystal-field model[1,4] and also an angular overlap treatment[5] have been reported. Although the two methods agree remarkably well in their predictions for the energy separation of the *d*-orbitals in $CaCu(AcO)_4,6H_2O$ it was suggested[5] that the angular overlap treatment is superior since the parameters involved are readily transferable from one system to another. Based on a limited number of examples it was claimed that this is not the case for the crystal-field model.

As part of a general study of the electronic structures of both eight co-ordinate and mononuclear copper(II) complexes we now report the single-crystal polarised electronic spectra, e.s.r., and magnetic anisotropy of $Cu(HA)_4(ClO_4)_2$.

EXPERIMENTAL AND RESULTS

Crystal Structure.—Single crystals of $Cu(HA)_4(ClO_4)_2$ were supplied by Dr. B. Sjöberg, Department of Medical Biochemistry, University of Göteberg, Sweden. $Cu(HA)_4(ClO_4)_2$ crystallises[2] in the tetragonal space group $P\bar{4}$ with $a = 10{\cdot}60$ and $c = 7{\cdot}72$ Å. The copper occupies the $\bar{4}$ site and is co-ordinated[6] to a slightly distorted square of oxygens at 1·93 Å and an elongated tetrahedron of oxygens at 2·87 Å. The co-ordination geometry about the Cu^{II} is shown in Figure 1 and compared with that in $CaCu(AcO)_6,6H_2O$ in Table 1.

Single-crystal Polarised Electronic Spectra.—These were recorded at room temperature on a Cary 14 spectrophotometer equipped with Nicol prisms. Crystals of $Cu(HA)_4(ClO_4)_2$ were mounted on glass microscope slides in suitable orientations to allow the incident beam to be polarised parallel or perpendicular to the $c(\bar{4})$ axis of the crystal. Also a crystal was mounted such that the *c* axis was parallel to the direction of the incident light, thus allowing polarisation in any direction in the plane perpendicular to the *c* axis, and the spectrum was observed to be independent of the orientation of the Nicol prisms and confirmed that recorded previously. The results of these measurements are summarised in Table 2 and Figure 2.

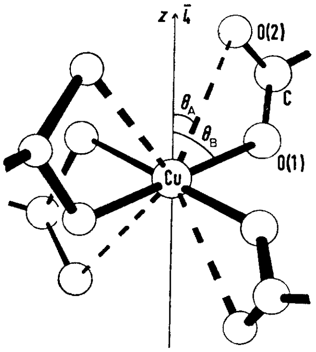

FIGURE 1 Co-ordination geometry of Cu^{II} in $Cu(HA)_4(ClO_4)_2$

TABLE 1

Dimensions of the Cu^{II} environment in $Cu(HA)_4(ClO_4)_2$ and $CaCu(AcO)_4,6H_2O$

	$Cu(HA)_4(ClO_4)_2$ [a]	$CaCu(AcO)_4,6H_2O$
Cu–O(1) [c]	1·932 ± 0·008 Å	1·973 ± 0·002 Å
Cu–O(2)	2·872 ± 0·009 Å	2·790 ± 0·003 Å
O(1)–Cu–O(1′)	179·7 ± 0·8°	168·0 ± 0·1°
O(2)–Cu–O(2′)	79·7 ± 0·4°	65·7 ± 0·1°

[a] Ref. 6. [b] Ref. 3. [c] The co-ordination geometry is as in Figure 1.

TABLE 2

Single-crystal polarised electronic spectral data (cm^{-1}) for $Cu(HA)_4(ClO_4)_2$

Polarisation parallel to *c*-axis (*z*-polarisation)	Polarisation perpendicular to *c*-axis (*xy*-polarisation)
16,300 strong	*ca.* 13,500 shoulder
17,000—18,000 unresolved shoulder	17,500 strong

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† Since this paper was submitted we have been grateful to receive from Dr. B. J. Hathaway a preprint of his publication [*J. Chem. Soc.* (*A*), 1971, 3355]. Where the experimental results overlap, there is good agreement.

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E.s.r. Spectra.—These were recorded at room temperature and *ca*, 160 K on a Varian V4561 instrument system operating at *Q*-band frequencies. Single crystals were mounted on quartz rods in such a manner that the magnetic field was in a plane containing the molecular $g_{\parallel}$ and $g_{\perp}$ axes ($g_{\parallel}$ was taken to be parallel to the *c* axis). Spectra were recorded at 15° intervals in this plane by rotating the magnet. The magnetic fields were measured on a Varian FA8 fluxmeter in conjunction with an internally calibrated crystal frequency meter, and the microwave frequency by use of the direct-reading frequency meter on the Varian V4561 klystron. The spectra at both temperatures consisted of four almost completely resolved lines, when the magnetic field was parallel to the crystallographic $\bar{4}$ axis, which collapsed to a single line as the perpendicular direction was approached. These results are summarised in Table 3. The observation of ^{63}Cu hyperfine splittings in this compound is in contrast to the lack of such splittings in undoped crystals of $CaCu(AcO)_4,6H_2O$.[1,7,8] This difference may be attributed to smaller intermolecular dipolar or exchange interactions in $Cu(HA)_4(ClO_4)_2$ than in $CaCu(AcO)_4,6H_2O$.

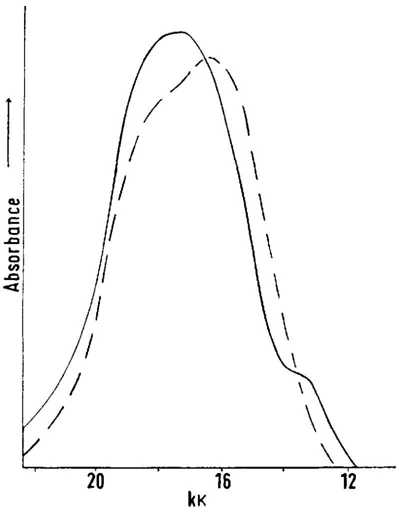

FIGURE 2 Room-temperature electronic spectra of $Cu(HA)_4(ClO_4)_2$; full line, *xy*-polarisation; broken line, *z*-polarisation

Magnetic Susceptibility Measurements.—The average magnetic susceptibilities and the magnetic anisotropies were measured by the Gouy and Krishnan 'critical torque' methods over the temperature range 80—300 K on apparatus described previously.[9] The fibre for the critical torque method was calibrated with triphenylbenzene[10] and Cs_3CoCl_5.[11] The results obtained for $Cu(HA)_4(ClO_4)_2$ are given in Table 4 and Figure 3. The average magnetic susceptibility was measured to an accuracy of 1% at room temperature and the relative values over the temperature range to 0·5%. The magnetic anisotropy was measured on two different crystals, the mean values being given in Table 4. The individual values were within 2% of the mean at all temperatures.

TABLE 3

(1) E.s.r. measurements for $Cu(HA)_2(ClO_4)_2$ at room temperature. $\nu = 3{\cdot}5250 \times 10^{10}$ Hz. The zero for the measurements is perpendicular to the crystallographic *c* axis

Angle (°)	*g*-Value field (G)	^{63}Cu hyperfine splitting (G)
90	10,945	190
75	11,012	185
60	11,214	168
45	11,520	138
30	11,859	—
15	12,138	—
0	12,253	—
−15	12,164	—
−30	11,905	—
−45	11,565	132
−60	11,247	164
−75	11,027	185
−90	10,942	190

Least-squares analysis gives $g_{\parallel} = 2{\cdot}301$, $g_{\perp} = 2{\cdot}055$, $A_{\parallel} = 0{\cdot}0204$ cm^{-1}, $A_{\perp} = 0{\cdot}0087$ cm^{-1}.

(2) E.s.r. measurements for $Cu(HA)_2(ClO_4)_2$ at 160 K. $\nu = 3{\cdot}5310 \times 10^{10}$ Hz. The zero for the measurements is perpendicular to the crystallographic *c* axis

Angle (°)	*g*-Value field (G)	^{63}Cu hyperfine splitting (G)
90	10,990	196
75	11,062	193
60	11,270	173
45	11,572	142
30	11,908	—
15	12,178	—
0	12,288	—
−15	12,185	—
−30	11,928	—
−45	11,593	137
−60	11,284	171
−75	11,068	189
−90	10,987	195

Least-squares analysis gives $g_{\parallel} = 2{\cdot}296$, $g_{\perp} = 2{\cdot}054$, $A_{\parallel} = 0{\cdot}0210$ cm^{-1}, $A_{\perp} = 0{\cdot}0101$ cm^{-1}.

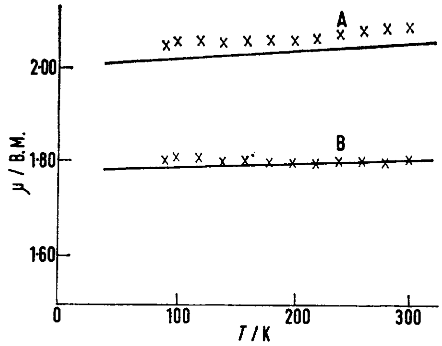

FIGURE 3 Plot of the experimental (× × ×) and calculated (——) μ values of $Cu(HA)_4(ClO_4)_2$. The latter were calculated by use of the eight-co-ordinate model with $Dq = -1260$, $Cp = -4000$, $\lambda = -828$ cm^{-1}, $k_{\parallel} = 0{\cdot}78$, and $k_{\perp} = 0{\cdot}83$; A, $\mu_{\parallel}$; B, $\mu_{\perp}$

Crystal-field Calculation.—We have approached the interpretation of the electronic structure of the complex using the point-charge crystal-field formalism outlined previously.[12] The structural parameters for $Cu(HA)_4(ClO_4)_2$ given in Table 1 were used to calculate the energy

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matrix of the d-functions under the perturbation $V_{D_{2d}} + k\zeta\hat{l}\cdot\hat{s}$ (with $\zeta = -828$ cm^{-1}) for various combinations of the parameters Dq, Cp, $k_{\parallel}$, and $k_{\perp}$, on the Atlas Computer at the University of Manchester. The eigenvalues and eigenfunctions resulting from the diagonalisation of this matrix were then used to calculate the positions of the bands in the electronic spectrum, the g values, and the principal magnetic moments of the complex. A discussion of the approximate and exact methods of calculating the orbital reduction factors is given in the Appendix.

TABLE 4

Magnetic susceptibilities of $Cu(HA)_4(ClO_4)_2$

T/K	c.g.s. units				Bohr Magnetons		
	$10^6\bar{\chi}$	$10^6\Delta\chi$	$10^6\chi_{\parallel}$	$10^6\chi_{\perp}$	$\bar{\mu}$	$\mu_{\parallel}$	$\mu_{\perp}$
300·0	1513	457	1818	1361	1·91	2·09	1·81
280·0	1610	484	1933	1449	1·90	2·08	1·80
260·0	1728	511	2069	1558	1·90	2·07	1·80
240·0	1870	541	2231	1690	1·89	2·07	1·80
220·0	2030	577	2415	1838	1·89	2·06	1·80
200·0	2230	623	2645	2022	1·89	2·06	1·80
180·0	2487	682	2942	2260	1·89	2·06	1·80
160·0	2798	758	3303	2545	1·89	2·06	1·81
140·0	3193	852	3761	2909	1·89	2·05	1·81
120·0	3755	985	4412	3427	1·90	2·06	1·81
100·0	4506	1178	5291	4113	1·90	2·06	1·81
90·0	4945	1293	5807	4514	1·90	2·05	1·80

DISCUSSION

The single-crystal polarised electronic spectra closely resemble those of $CaCu(AcO)_4,6H_2O$,[4,7] except that the bands appear at higher energies. The similarity of the environment of Cu^{II} in the two compounds strongly suggests that the assignment of the spectral bands should be the same for the two compounds. Table 5 shows the predicted [1] electronic transitions based on the orbital functions computed with the inclusion of spin–orbit coupling. The transitions are thus all assumed [1,4,5] to be electronically allowed. The order of orbital energies $d_{xy} > d_{x^2-y^2} > d_{z^2} > d_{xz,yz}$ proposed [1,4] for $CaCu(AcO)_4,6H_2O$, is clearly compatible with the single-crystal polarised spectra of $Cu(HA)_4(ClO_4)_2$, the absorption at 17,500 cm^{-1} representing the mean position of the $(xy) \longrightarrow (xz,yz)$ doublet which is split by spin–orbit coupling. This orbital ordering leads to a satisfactory interpretation of the e.s.r. and magnetic data. The shifts to higher energy compared to $CaCu(AcO)_4,6H_2O$ are compatible with the slightly lower g values and magnetic susceptibilities observed for $Cu(HA)_4(ClO_4)_2$.

TABLE 5

Predicted electronic transitions [a] based on the d-orbital functions after spin–orbit coupling

Transition	Allowability		Assigned energy (cm^{-1})
	z-Polarisation	xy-Polarisation	
$(xy) \rightarrow (x^2-y^2)$	Weakly allowed	Weakly allowed	13,500
$(xy) \rightarrow (z^2)$	Allowed	Weakly allowed	16,300
$(xy) \rightarrow (xz,yz)$	Weakly allowed	Allowed	17,500
$(xy) \rightarrow (xz,yz)'$	Weakly allowed	Allowed	

[a] Ref. 1.

The Dq and Cp parameters which predict the positions of the observed bands in the electronic spectrum of $Cu(HA)_4(ClO_4)_2$ to within *ca.* 1000 cm^{-1} are summarised in Table 6, together with the values of $k_{\parallel}$ and $k_{\perp}$ which, over this range of Dq, Cp, give good agreement with the observed g values. As expected, because the nearest Cu–O distance is slightly shorter, the values of Dq are significantly greater than those for $CaCu(AcO)_4,6H_2O$, although the values of Cp are approximately the same. In view of the similarity between the ligands in these two compounds it seems reasonable to expect that, apart from differences in Cu–O distances, the values of Dq, Cp should be almost identical. In fact it is possible to find a very small range of Dq and Cp values which give reasonable agreement with the electronic spectra of both compounds after allowance [12] has been made for the different Cu–O distances. By standardising the values of Dq, Cp to a Cu–O distance of 2·00 Å it was found that the region of coincidence at this distance was $-Dq = 1040$—1080 and $-Cp =$ 3450—3850 cm^{-1}. Using these values, suitably scaled by the appropriate metal–ligand distances, we have calculated the transition energies and present them in Table 7. For most combinations of the parameters reasonable agreement with the observed spectra is obtained, especially if one bears in mind the low resolution of the room temperature spectra. However, it is noticeable that when the $(xy) \longrightarrow (z^2)$ transition is predicted correctly the position of the $(xy) \longrightarrow (xz,yz)$ doublet is placed too high in energy, particularly in $Cu(HA)_4(ClO_4)_2$. Conversely, when the latter transition is calculated correctly then $(xy) \longrightarrow (z^2)$ is placed too low in energy. A reasonable compromise seems to be the selection of Dq, Cp values in the middle of the range for both compounds. The ratios of Cp/Dq are then 3·21 for $Cu(HA)_4(ClO_4)_2$ and 3·35 for $CaCu(AcO)_4,6H_2O$. This ratio would not be expected to remain constant in systems involving different metal–ligand distances, but to vary as the factor $(a_2/a_1)^2$, where a_i are the metal–ligand distances in the two systems, assuming the point-charge formalism to be correct in this respect.

The values of k required to reproduce the g values in $Cu(HA)_4(ClO_4)_2$ are similar to those found for $CaCu(AcO)_4,6H_2O$, with $k_{\parallel}$ being slightly smaller than the preferred values in the latter system. The interpretation of the k values in either of these systems is not straightforward since it is possible to have contributions from both ligand orbitals and metal d–p orbital mixing. Only if the extent of d–p mixing is the same in each system can more ligand contribution to k be invoked in $Cu(HA)_4(ClO_4)_2$ than in $CaCu(AcO)_4,6H_2O$.

The parameters required to fit the electronic spectrum and also the e.s.r. data are in good agreement with the observed magnetic anisotropy. An example of the degree of agreement is illustrated in Figure 3. The magnetic properties are almost entirely determined by the composition of the ground-state after spin–orbit coupling.

The excited states then only contribute *via* the second-order Zeeman effect giving temperature-independent contributions of *ca.* 90 × 10^{-6} and *ca.* 40 × 10^{-6} c.g.s. units in the parallel and perpendicular directions respectively.

TABLE 6

Parameters required to fit the experimental e.s.r. and electronic spectra with use of an eight-co-ordinate model

						← Calculated values (cm^{-1}) →			
$-Dq/cm^{-1}$	$-Cp/cm^{-1}$	$k_{\parallel}$	$k_{\perp}$	$g_{\parallel}$	$g_{\perp}$	$(xy) \rightarrow (x^2 - y^2)$	$(xy) \rightarrow (z^2)$	$(xy) \rightarrow (xz,yz)$	$(xy) \rightarrow (xz,yz')$
1240	3800	0·78	0·83	2·307	2·057	12,710	15,390	17,220	18,090
1240	4000	0·78	0·83	2·308	2·055	12,710	16,000	17,670	18,570
1240	4200	0·78	0·83	2·308	2·054	12,710	16,580	18,130	19,050
1260	3800	0·78	0·83	2·303	2·057	12,910	15,460	17,360	18,220
1260	4000	0·78	0·83	2·303	2·055	12,920	16,060	17,820	18,700
1280	3800	0·78	0·83	2·298	2·057	13,110	15,540	17,500	18,360
1280	4000	0·78	0·83	2·298	2·055	13,130	16,200	18,050	19,100
1300	3800	0·78	0·83	2·294	2·057	13,320	15,610	17,640	18,490
1300	4000	0·78	0·83	2·294	2·055	13,320	16,200	18,100	18,960

TABLE 7

Crystal-field parameters (cm^{-1}) which simultaneously account for the electronic spectra of $Cu(HA)_4(ClO_4)_2$ and $CaCu(AcO)_4,6H_2O$, with use of an eight-co-ordinate model

2·00 Å		$Cu(HA)_4(ClO_4)_2$		Spectral energies (cm^{-1})			
$-Dq$	$-Cp$	Dq [a]	Cp [a]	$(xy) \rightarrow (x^2 - y^2)$	$(xy) \rightarrow (z^2)$	$(xy) \rightarrow (xz,yz)$	$(xy) \rightarrow (xz,yz')$
				13,500 [b]	16,300 [b]	17,500 [b]	
1040	3450	1236	3826	12,314	15,378	17,221	18,346
1040	3650	1236	4049	12,694	16,038	17,725	18,883
1040	3850	1236	4271	12,700	16,690	18,226	19,419
1060	3450	1260	3826	12,927	15,467	17,380	18,501
1060	3650	1260	4049	12,936	16,127	17,892	19,036
1060	3850	1260	4271	12,943	16,781	18,394	19,591
1080	3450	1283	3826	13,159	15,550	17,551	18,650
1080	3650	1283	4049	13,169	16,212	18,054	19,185
1080	3850	1283	4271	13,175	16,867	18,555	19,718
		$CaCu(AcO)_4,6H_2O$					
				10,800 [b,c]	12,500 [b,c]	14,400 [b,c]	
1040	3450	1112	3590	11,016	11,294	13,498	14,496
1040	3650	1112	3799	11,036	11,751	13,829	14,863
1040	3850	1112	4007	11,052	12,205	14,163	15,229
1060	3450	1133	3590	11,217	11,367	13,643	14,639
1060	3650	1133	3799	11,238	11,824	13,973	14,995
1060	3850	1133	4007	11,255	12,279	14,306	15,300
1080	3450	1154	3590	11,419	11,440	13,789	14,762
1080	3650	1154	3799	11,442	11,898	14,118	15,128
1080	3850	1154	4007	11,459	12,353	14,450	15,492

[a] These are the crystal-field parameters for the four nearest oxygen atoms. The total crystal-field potential includes a small additional contribution from the four furthest oxygens calculated from the particular *Dq* (*Cp*) value weighted by the appropriate distance factor. [b] Observed; all other values calculated. [c] Data from ref. 7.

In view of the long Cu–O(2) distances in both $Cu(HA)_4(ClO_4)_2$ and $CaCu(AcO)_4,6H_2O$ we have also investigated the possibility of ignoring these atoms and used a four-co-ordinate crystal-field model. The parameters required to give a reasonable reproduction of the electronic spectra of these compounds are given in Table 8. A good description of the electronic spectrum of $Cu(HA)_4(ClO_4)_2$ can be obtained with $-Dq$ *ca.* 1280—1340 and $-Cp$ *ca.* 3000—3200 cm^{-1}, whilst for $CaCu(AcO)_4,6H_2O$ the parameters are $-Dq$ *ca.* 1080—1140 and $-Cp$ *ca.* 2200—2400 cm^{-1}. As in the eight-co-ordinate model when the $(xy) \longrightarrow (z^2)$ transition is estimated correctly the position of the transition from (xy) to the (xz,yz) doublet is over-estimated, particularly for $Cu(HA)_4(ClO_4)_2$. On this four-co-ordinate model the $Cp:Dq$ ratio for both complexes is significantly lower than that for the eight-co-ordinate model. One important feature of the four-co-ordinate model is that, in contrast to the eight-co-ordinate model, the parameters deduced independently for each compound cannot be transferred to the other. Although this does not prove the correctness of the eight-co-ordinate model, it does suggest that it will provide a more consistent interpretation of the electronic properties of compounds of this type, and that ligands at *ca.* 2·8 Å from a metal cannot be neglected when considering crystal-field effects.

The angular overlap model has been strongly recommended[5] for the interpretation of the electronic structure of Cu–O systems, on the grounds that the parameters of this model may be transferred from one system to another, particularly where different metal–ligand bond lengths are involved. It was claimed that this was not possible by use of the point-charge crystal-field model. We feel that the work reported here demonstrates that, at least for these two compounds, crystal-field parameters can be transferred in a systematic manner.

However, the angular overlap method as applied by Smith [5] does not appear to cope satisfactorily with the electronic spectra of $CaCu(AcO)_4,6H_2O$ and $Cu(HA)_4(ClO_4)_2$. For the former, the angular overlap method *only* gives good agreement with the spectral data if Cu–O (carboxylate) is assumed to be 2·00 Å. The crystal-structure determination [3] gives Cu–O = 1·973 ± 0·002 Å. If this distance is used the transitions are all predicted at too high an energy, $(xy) \longrightarrow (x^2 - y^2) = 12{,}570$, $(xy) \longrightarrow (z^2) = 14{,}510$, $(xy) \longrightarrow (xz,yz) = 15{,}700$ cm^{-1}, compared with the experimental values of 10,800, 12,500, and 14,400 cm^{-1} respectively. For $Cu(HA)_4(ClO_4)_2$, the details of the co-ordination geometry about the Cu^{II} allow the σ^* and electrostatic parameters to be determined.[13] The π^* parameters are not so readily determined, however, $\pi_1^*(\|) = 0{\cdot}50$, $\pi_1^*(\perp) = 0{\cdot}80$, $\pi_2^*(\|) = 0{\cdot}007$, and $\pi_2^*(\perp) = 0{\cdot}009$ kK appear reasonable values in view of those chosen [5,13] to interpret the spectra of $BaCuSi_4O_{10}$ and $CaCu(AcO)_4,6H_2O$. With these parameters, transitions are predicted at 12,720, $(xy) \longrightarrow (x^2 - y^2)$; 17,130, $(xy) \longrightarrow (z^2)$; and 15,900 cm^{-1}, $(xy) \longrightarrow (xz,yz)$, in poor agreement with the experimental values of 13,500, 16,300, and 17,500 cm^{-1}, respectively, even to the extent that the sequence of the *d*-orbitals is incorrectly predicted. The *d*-orbital ordering suggested by the single-crystal polarised electronic spectra can be obtained by modification of the π^* parameters; however, the predicted transition energies still do not agree well with the experimental values.

TABLE 8

Crystal-field parameters (cm^{-1}) required to fit the electronic spectra of $Cu(HA)_4(ClO_4)_2$ and $CaCu(AcO)_4,6H_2O$, with use of a four-co-ordinate model

$Cu(HA)_4(ClO_4)_2$		Calculated spectral energies (cm^{-1})			
$-Dq$	$-Cp$	$(xy) \rightarrow (x^2 - y^2)$	$(xy) \rightarrow (z^2)$	$(xy) \rightarrow (xz,yz)$	$(xy) \rightarrow (xz,yz')$
1280	3000	12,830	15,470	17,930	18,740
1300	3000	13,020	15,530	18,070	18,880
1320	3000	13,340	15,590	18,200	19,020
1320	3200	13,320	16,380	18,810	19,630
1340	2800	13,410	14,870	17,760	18,540
1340	3000	13,420	15,660	18,360	19,150
1360	2800	13,610	14,930	17,910	18,680
1360	3000	13,620	15,720	18,500	19,290
$CaCu(AcO)_4,6H_2O$					
1080	2400	10,580	12,270	14,130	14,980
1080	2600	10,590	13,020	14,700	15,580
1100	2200	10,760	11,580	13,710	14,510
1100	2400	10,780	12,330	14,270	15,110
1100	2600	10,790	13,080	14,840	15,710
1120	2200	10,960	11,650	13,860	14,660
1120	2400	10,970	12,400	14,410	15,240
1120	2600	10,980	13,150	14,970	15,840
1140	2200	11,150	11,710	13,980	14,770
1140	2400	11,160	12,460	14,540	15,360
1160	2200	11,340	11,770	14,120	14,900
1160	2400	11,350	12,500	14,680	15,490

We feel that the foundation [5,13] of this application of the angular overlap model (not the model itself) may be unsound since (1) it relies upon the assignment [14] of the *d–d* transitions in $BaCuSi_4O_{10}$, $(xy) \longrightarrow (x^2 - y^2) = 12{,}900$; $(xy) \longrightarrow (xz,yz) = 15{,}800$; and $(xy) \longrightarrow (z^2) = 18{,}800$ cm^{-1}, being correct. The reported spectrum [14] of $BaCuSi_4O_{10}$ was unpolarised, the spectral bands being assigned by analogy with the polarised spectra of gillespite, the interpretation of which [15] is not entirely unambiguous.

(2) The scale suggested [13] for σ^* at various atomic distances is based on a Cu–O bond length of 1·91 Å in $BaCuSi_4O_{10}$. In fact the details of the crystal structure of $BaCuSi_4O_{10}$ are not known. The parameters of the isostructural material $CaCuSi_4O_{10}$ have been determined; [16] however, the Cu–O bond length of 1·91 Å is subject to an uncertainty of about ±0·03 to 0·04 Å. Also, (3) the model appears to assume that the effect of all ligand oxygen atoms is the same, apart from the Cu–O distance. Whilst gross changes would not be expected, since oxygen donors are closely grouped in the spectrochemical series, it does seem unlikely that differences in the nature of the ligand can be ignored completely.

Since the environment of Cu^{II} in $Cu(HA)_4(ClO_4)_2$ is so nearly square planar (Table 1) and the *d*-orbital ordering different from that inferred [15] for $BaCuSi_4O_{10}$, the angular overlap model is unlikely to assign the spectrum of the former unless either Cu–O (silicate) and Cu–O (carboxylate) are treated differently or the assignment for $BaCuSi_4O_{10}$ is reconsidered in the light of the results reported here.

APPENDIX

It has been drawn to our attention by a Referee that the *k* values derived from the conventional equations (1) and (2) where $\Delta_1 = E_{d_{xy}} - E_{d_{x^2-y^2}}$ and $\Delta_2 =$

$$g_{\|} = 2 - \frac{8k_{\|}^2\lambda}{\Delta_1} \tag{1}$$

$$g_{\perp} = 2 - \frac{2k_{\perp}^2\lambda}{\Delta_2} \tag{2}$$

$E_{d_{xy}} - E_{d_{xz},d_{yz}}$, are $k_{\|} = 0{\cdot}783$ and $k_{\perp} = 0{\cdot}765$ when $g_{\|} = 2{\cdot}301$, $g_{\perp} = 2{\cdot}055$, $\Delta_1 = 13{,}500$, $\Delta_2 = 17{,}500$, and $\lambda = -828$ cm^{-1}. Not only is the value of $k_{\perp}$ very different from that reported here, but also the relative magnitudes of $k_{\|}$ and $k_{\perp}$ are in the opposite sense. These discrepancies call for some comment.

The differences in the *k* values arise because: (*a*) the approximations made in deriving equations (1) and (2) are not insignificant in this particular case as the subsequent calculations demonstrate. The error in the calculated *k*-value is larger the closer the corresponding *g*-value is to 2·0023.

(*b*) Our method of calculation involves an exact

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[13] D. W. Smith, *J. Chem. Soc.* (*A*), 1970, 176.

[14] M. G. Clark and R. G. Burns, *J. Chem. Soc.* (*A*), 1967, 1034.

[15] R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, 1966, **5**, 1268.

[16] A. Pabst, *Acta Cryst.*, 1959, **12**, 733.

solution of the secular equations resulting from the simultaneous perturbation by crystal-field and spin–orbit coupling effects. This approach results in the ground-state wave functions being of a slightly different composition from those obtained by treating spin–orbit coupling as a small perturbation on the crystal-field levels.

By use of the latter approach, standard perturbation theory leads to the ground state wave functions (3) and (4) where N^2 is given by equation (5). The g-values

$$\varphi_1 = N\left[\frac{1}{\sqrt{2}}(|2,\tfrac{1}{2}\rangle - |-2,\tfrac{1}{2}\rangle) - \frac{k_{\|}\lambda}{\sqrt{2}\Delta_1}(|2,\tfrac{1}{2}\rangle + |-2,\tfrac{1}{2}\rangle) + \frac{k_{\perp}\lambda}{\sqrt{2}\Delta_2}|-1,-\tfrac{1}{2}\rangle\right] \quad (3)$$

$$\varphi_2 = N\left[\frac{1}{\sqrt{2}}(|2,-\tfrac{1}{2}\rangle - |-2,-\tfrac{1}{2}\rangle) + \frac{k_{\|}\lambda}{\sqrt{2}\Delta_1}(|2,-\tfrac{1}{2}\rangle + |-2,-\tfrac{1}{2}\rangle) - \frac{k_{\perp}\lambda}{\sqrt{2}\Delta_2}|1,\tfrac{1}{2}\rangle\right] \quad (4)$$

$$N^2 = \frac{1}{\left[1 + \left(\frac{k_{\|}\lambda}{\Delta_1}\right)^2 + \frac{1}{2}\left(\frac{k_{\perp}\lambda}{\Delta_2}\right)^2\right]} \quad (5)$$

calculated from these wave functions are (6) and (7).

$$\begin{aligned} g_{\|} &= 2\langle\phi_1|k_{\|}\hat{l}z + 2{\cdot}0023\hat{s}_z|\phi_1\rangle \\ &= N^2\left[2{\cdot}0023 + 2{\cdot}0023\left(\frac{k_{\|}\lambda}{\Delta_1}\right)^2 - \frac{2{\cdot}0023}{2}\left(\frac{k_{\perp}\lambda}{\Delta_2}\right)^2 - \frac{8k_{\|}^2\lambda}{\Delta_1} - k_{\|}\left(\frac{k_{\perp}\lambda}{\Delta_2}\right)^2\right] \end{aligned} \quad (6)$$

$$\begin{aligned} g_{\perp} &= 2\langle\phi_1|k_{\perp}\hat{l}_x + 2{\cdot}0023\,\hat{s}_x|\phi_2\rangle \\ &= N^2\left[2{\cdot}0023 - 2{\cdot}0023\left(\frac{k_{\|}\lambda}{\Delta_1}\right)^2 - \frac{2k_{\perp}\lambda}{\Delta^2} + \frac{2k_{\|}k_{\perp}^2\lambda^2}{\Delta_1\Delta_2}\right] \end{aligned} \quad (7)$$

It is usual to assume that terms in $(k\lambda/\Delta)^2$ are negligible, in which case equations (6) and (7) reduce to (1) and (2). (However, it should be noted that even the approximation $2{\cdot}0023 = 2$, can lead to significant errors in the calculated k value when the corresponding g-value is close to 2·0023.) The consequences of this approximation will now be examined by calculating $g_{\|}$ and $g_{\perp}$ from equations (6) and (7) by use of $\Delta_1 = 13{,}500$ and $\Delta_2 = 17{,}500$ cm^{-1}. We find that for $k_{\|} = 0{\cdot}78$ and $k_{\perp} = 0{\cdot}76 - 0{\cdot}83$, $N^2 = 0{\cdot}9973$ and not unity. From $k_{\|} = 0{\cdot}783$ and $k_{\perp} = 0{\cdot}765$ [the values estimated earlier from equations (1) and (2)], equations (6) and (7) give $g_{\|} = 2{\cdot}299$ and $g_{\perp} = 2{\cdot}050$. The agreement for $g_{\|}$ is excellent whilst that for $g_{\perp}$, although good, does show that the effects of terms in $(k\lambda/\Delta)^2$ are not completely negligible. Increase of $k_{\perp}$ to 0·80 leads to $g_{\|} = 2{\cdot}299$ and $g_{\perp} = 2{\cdot}055$, in excellent agreement with the g-values originally taken. Thus, given the g-values of 2·301 and 2·055, a more accurate interpretation than that given by equations (1) and (2) is $k_{\|} = 0{\cdot}783$ and $k_{\perp} = 0{\cdot}800$, *i.e.*, $k_{\|} < k_{\perp}$, whereas equations (1) and (2) give the reverse.

The effect on the ground-state wave functions and the g-values of an exact solution to the secular equations, as opposed to the approximate ones given by equations (3), (4), (6), and (7), can be illustrated by taking the first set of parameters in Table 6. In the absence of spin–orbit coupling, the separation between the ground-state

$$\frac{1}{\sqrt{2}}(|2,\pm\tfrac{1}{2}\rangle - |-2,\pm\tfrac{1}{2}\rangle) \quad (8)$$

$$\frac{1}{\sqrt{2}}(|2,\pm\tfrac{1}{2}\rangle + |-2,\pm\tfrac{1}{2}\rangle) \quad (9)$$

$$|1,\pm\tfrac{1}{2}\rangle, |-1,\pm\tfrac{1}{2}\rangle \quad (10)$$

(8) and the excited states (9) and (10) is 12,687 and 17,428 cm^{-1} respectively. Using these data and equations (3) to (7) we find equations (11) and 12) and

$$\phi_1 = 0{\cdot}7422|2,\tfrac{1}{2}\rangle - 0{\cdot}6702|-2,\tfrac{1}{2}\rangle - 0{\cdot}02785|-1,-\tfrac{1}{2}\rangle \quad (11)$$

$$\phi_2 = 0{\cdot}6702|2,\tfrac{1}{2}\rangle - 0{\cdot}7422|-2,-\tfrac{1}{2}\rangle + 0{\cdot}02785|1,\tfrac{1}{2}\rangle \quad (12)$$

$g_{\|} = 2{\cdot}317$ and $g_{\perp} = 2{\cdot}061$. The analogous quantities derived from the exact solution are equations (13)

$$\phi_1 = 0{\cdot}7411|2,\tfrac{1}{2}\rangle - 0{\cdot}6709|-2,\tfrac{1}{2}\rangle - 0{\cdot}02688|-1,-\tfrac{1}{2}\rangle \quad (13)$$

$$\phi_2 = 0{\cdot}6709|2,-\tfrac{1}{2}\rangle - 0{\cdot}7411|-2,-\tfrac{1}{2}\rangle + 0{\cdot}02688|1,\tfrac{1}{2}\rangle \quad (14)$$

and (14) and $g_{\|} = 2{\cdot}307$ and $g_{\perp} = 2{\cdot}057$. Although the differences between the ground-state wave functions calculated by the two methods are small, they nevertheless lead to significant differences in the calculated g-values. The differences in the ground-state wave functions calculated by the two methods, arises from the fact that in the exact solution the spin-orbit mixing between the excited states (which are within 5000 cm^{-1} of each other) is taken into account, whereas this is not the case in the approximate treatment. This mixing between the excited states is then reflected in small changes in their mixing into the ground-state.

These two examples demonstrate that as far as the calculation of k-values is concerned, even with perfect experimental data, the method of calculation can lead to small but significant differences in the values of k deduced.

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