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# Inelastic neutron scattering measurements on [$Cu_4OCl_6L_4$] (L = pyridine or dimethyl sulfoxide). Observation of zero-field splitting of the cluster ground state‡

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Inelastic neutron scattering measurements on the complexes [$Cu_4OCl_6L_4$] (L = pyridine or dimethyl sulfoxide) revealed ground-state zero-field splittings of *ca.* 3 and 6 $cm^{-1}$. The splittings are interpreted as due to the combined effects of exchange and spin–orbit coupling, and suggest a new interpretation of previous magnetic data.

The magnetic properties of the series of compounds $Cu_4OX_6L_4$ (X = Cl or Br, L is a neutral donor or $X^-$) indicate the presence of an exchange interaction between the $Cu^{2+}$ ions, but their detailed interpretation has proved controversial.[1] In those cases where the molecular structure has been determined,[2] it consists of a nearly regular tetrahedron of copper atoms, each bonded in approximately trigonal-bipyramidal geometry to the central O atom, three bridging X atoms, and a terminal ligand L (Fig. 1). In a regular tetrahedron of spin-$\frac{1}{2}$ ions the Heisenberg exchange Hamiltonian, equation (1), with all $J_{ij}$ equal (where

$$H = -2\Sigma_{ij}J_{ij}\boldsymbol{S}_i\cdot\boldsymbol{S}_j \qquad (1)$$

$i,j$ = numbers of the ions) gives rise to three energy levels of total spin $S = 0$, 1 and 2, transforming respectively as ${}^1E$, ${}^3T_1$ and ${}^5A_2$ in $T_d$ symmetry,[3] and with relative energies given by equation (2). Thus, for negative $J$ the energy increases with $S$,

$$E_S = -J[S(S+1)] \qquad (2)$$

causing the magnetic moment to decrease monotonically as the temperature falls, and for positive $J$ the opposite is true. Although some of the compounds behave magnetically in the way expected from equation (1) with an exchange interaction of antiferromagnetic sign ($J < 0$), most do not, showing a maximum in the plot of magnetic moment against temperature.[1] It is difficult to account for such behaviour (which suggests a less regular dependence of energy on total spin) on the basis of the generally small (in some cases unobservable) deviations from tetrahedral symmetry that are revealed crystallographically. Proposed explanations include orbital degeneracy of the individual copper states[1a] and fluxional distortion of the tetrahedron,[1d] but the question is far from settled.

Since in most cases information about the spin energy levels has been obtained somewhat indirectly by fitting a theoretical model to the temperature variation of the bulk magnetic susceptibility, we sought to investigate them more directly by means of inelastic neutron scattering, as has been done successfully for several other cluster complexes.[4] In a preliminary study of a number of the compounds on the IN4 spectrometer at Institut Laue-Langevin (ILL) we failed to observe any of the allowed transitions expected from the models that were used to fit the magnetic data. This may have been due simply to low transition probabilities associated with the low number of unpaired electrons. Three compounds, [$Cu_4OCl_6(py)_4$], [$Cu_4OBr_6(py)_4$] and [$Cu_4OCl_6(dmso)_4$] (dmso = dimethyl sulfoxide), were then examined at much lower energy transfers on the sensitive, high-resolution IN5 and IN6 instruments, scanning the range −1.5 to +1.5 meV (−12 to +12 $cm^{-1}$). The bromo-complex showed no features of interest, but the chloro-complexes both showed two low-intensity transitions of clearly magnetic origin between 2 and 6 $cm^{-1}$.

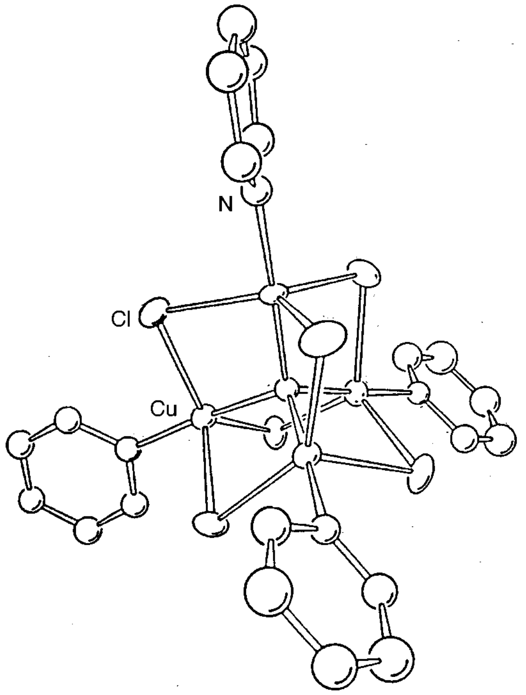

**Fig. 1** Structure of [$Cu_4OCl_6(py)_4$] (py = pyridine) taken from ref. 2(*b*)

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‡ Dedicated to the memory of the late Professor William E. Hatfield. *Supplementary material available* (No. SUP 57250, 8 pp.): calculation of neutron scattering intensities and fitting of magnetic susceptibility data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

*Non-SI units employed*: eV ≈ $1.60 \times 10^{-19}$ J, $\mu_B \approx 9.27 \times 10^{-24}$ J $T^{-1}$.

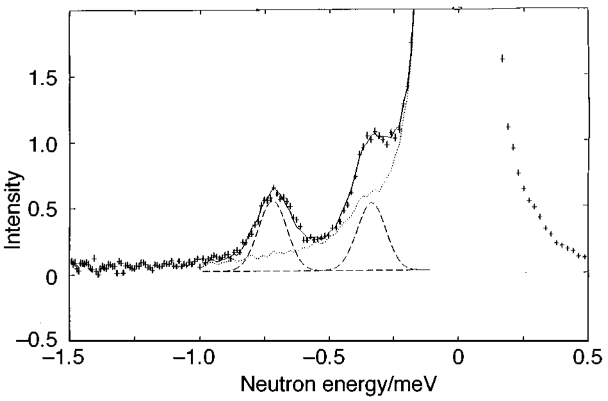

**Fig. 2** Inelastic neutron scattering (INS) spectrum of $[Cu_4OCl_6(py)_4]$ on the IN6 spectrometer at 1.5 K, with a gaussian fit to the two peaks in down scattering

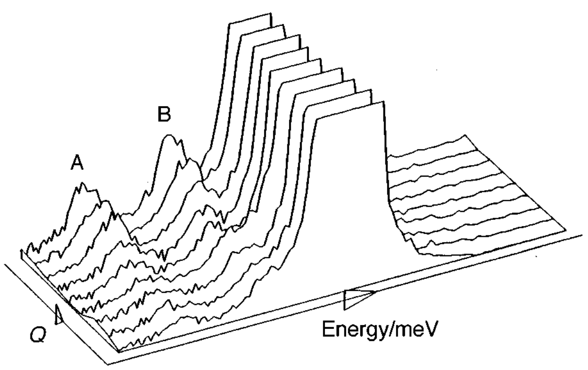

**Fig. 3** *Q* Dependence of the energy-loss peaks in the INS spectrum of $[Cu_4OCl_6(py)_4]$ on IN6 at 1.5 K. Peak energies: A, 0.73 meV; B, 0.34 meV. The variation in the relative scattering intensities (vertical scale) with scattering angle 2θ is shown, with 2θ increasing from 15.3 (back) to 65.4° (front)

## Experimental

The compounds were prepared[5] by reaction of the copper(II) halide with copper(II) oxide in methanol and treatment of the resulting methanol adduct with the appropriate base, and were dried in vacuum. Purity was confirmed by IR spectroscopy and microanalysis (C, H, N).

Neutron inelastic scattering measurements were made on the time-of-flight spectrometers IN5 and IN6 at ILL, Grenoble, France. The samples were placed in flat aluminium cans and oriented so that neutron detection took place in transmission geometry only. The sample thickness was chosen to remove about 5% from the incident beam either through scattering processes or neutron capture. Data were collected over three- to six-hour periods to ensure good statistics, the samples being cooled by use of standard ILL helium-flow cryostats. The neutron wavelengths were 5 Å on IN5 at 2 K and 5.1 Å on IN6 at 1.5 K. The data were corrected for detector efficiency and converted into non-symmetrised $S(Q,\omega)$ form by use of standard ILL programs.

In an attempt to establish both the exact positions and the relative intensities of the two peaks, a gaussian fit was made to the corrected data by means of the program PROFIT available at the ILL. Since the instrumental resolution function was determined from a vanadium run, and it was known that there was a small inelastic feature on the vanadium spectrum at the position of our inner peak, the relative intensities must be treated with caution, especially as the intensity of the peaks was low.

The IN6 spectrum of $[Cu_4OCl_6(py)_4]$ was also run at *ca.* 30 K. As the down-scattered peaks had lost intensity to up-scattering, it was not possible to determine their relative intensities at this temperature. The same two peaks were observed in up-scattering, but were too indistinct to allow intensity determination.

## Results

The spectrum of $[Cu_4OCl_6(py)_4]$ measured on the IN6 spectrometer at 1.5 K (Fig. 2) showed two peaks, at *ca.* 0.35 and 0.73 meV (2.8 and 5.9 $cm^{-1}$) neutron energy loss (down-scattering). Their *Q* dependence (Fig. 3) exhibited the decline in intensity with increasing *Q* characteristic of transitions involving a change of spin rather than vibrational excitation. The two transitions seemed to be of roughly equal intensities, although (as noted in the Experimental section) a precise determination of the intensity ratio was not possible. At a higher temperature (*ca.* 30 K) the same two peaks were also observed in neutron energy gain (up-scattering).

The IN5 and IN6 spectra of $[Cu_4OCl_6(dmso)_4]$ also showed two weak features, of roughly similar intensities and apparently magnetic origin, at *ca.* 0.25 and 0.55 meV (2.0 and 4.4 $cm^{-1}$), but the resolution was poor, and hence only the results for the pyridine complex will be discussed in detail. However, we note that the approximately 2:1 ratio of the energies of the two transitions is similar to that of the pyridine complex. It may also be significant that, of all the $Cu_4OX_6L_4$ complexes studied, this is the one which most closely resembled $[Cu_4OCl_6(py)_4]$ in its magnetic properties.[1b,6] Furthermore, the splitting of the IR spectrum of the dmso complex is not very different from that of the pyridine complex (see below), supporting the idea that the two complexes may be distorted similarly.

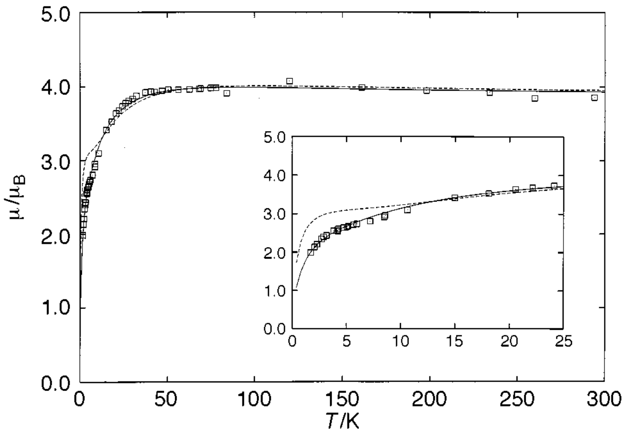

**Fig. 4** Magnetic moment $\mu_{eff}/\mu_B$ of $[Cu_4OCl_6(py)_4]$. □, Data from ref. 6. Curves calculated as described in the text with $d_1$ and $d_2$ (fixed) 3.7 $cm^{-1}$: – – – –, best fit without molecular-field correction; ——, best fit including molecular-field correction. Inset: detail of the 0–25 K region

## Discussion

Any interpretation of these observations must be consistent with the temperature dependence of the bulk magnetic properties, studied earlier by Hatfield and co-workers.[6] The effective magnetic moment $\mu_{eff}$ of $[Cu_4OCl_6(py)_4]$ increases very slightly as the temperature is reduced from 300 to about 70 K, and falls steeply below about 30 K (Fig. 4), behaviour which those workers interpreted as due to ferromagnetic exchange ($J = +7.6$ $cm^{-1}$) in a regular $Cu_4$ tetrahedron giving an $S = 2$ ground state, together with an antiferromagnetic intercluster interaction ($zJ' = -4$ $cm^{-1}$) required to reproduce the decrease in $\mu_{eff}$ at low temperatures. The possibility of such a relatively large intermolecular interaction has been questioned, however.[1a,b,d,7]

This model also does not account for the INS transitions reported here. In principle, zero-field splitting of the $S = 2$ level could occur as a consequence of spin–orbit coupling (and for the analogous triphenylphosphine adduct a 0.5 $cm^{-1}$ splitting has been inferred from ESR measurements[1e]), but since the level is an orbital singlet the splitting is unlikely to exceed a few tenths of a cm$^{-1}$. Such a splitting is far too small to explain the INS spectrum (or, by itself, the decrease in $\mu_{eff}$).

To explain these observations we believe it is necessary to take into account distortion of the complex from $T_d$ symmetry. The room-temperature crystal structure determination showed that there is no crystallographically imposed symmetry. Within experimental error the $N_4Cu_4O$ group conforms to tetrahedral symmetry, and the Cu–Cl–Cu angles are equal, but there is significant variation in the Cu–Cl distances [2.355–2.486; estimated standard deviation (e.s.d.) 0.009 Å] and Cl–Cu–Cl angles (107.9–137.9, e.s.d. 0.3°).[2b] We have observed that the asymmetric Cu–O stretching mode in the IR spectrum at 100 K is split into three peaks, implying a rather low-symmetry structural distortion of the tetrahedron ($C_{2v}$ or lower) at this temperature.[8] There is experimental evidence from vibrational spectroscopy for concealed symmetry lowering, averaged out by dynamic or static disorder, in other complexes of this type,[9] and in view of the well known plasticity of the $Cu^{2+}$ ion in its coordination geometry it has been suggested that dynamical distortion of the $Cu_4O$ system is likely at moderate temperatures, and may be responsible for the anomalous magnetic behaviour.[1d,10] At 1.5 K, however, any fluxional motion would be largely frozen, and the nature and degree of the resulting static distortion in the present case is not known.

Initially we attempted to explain the results on the basis of low symmetry alone. So as not to introduce too many parameters, we examined two cases, in which the exchange Hamiltonian is assumed to retain approximate symmetry $D_{2d}$ and $C_{3v}$, respectively. (Although the IR spectrum suggests lower symmetry, it should be borne in mind that the relationship between superexchange and structure is not simple, and the approximate symmetry of the exchange Hamiltonian need not be close to that of the vibrational one.) We also briefly examined the behaviour expected in the absence of symmetry. We took $g = 2.25$, the value derived from the magnetic susceptibility measurements.[6]

### $D_{2d}$ Distortion

With $J_{13} = J_{23} = J_{14} = J_{24} \equiv J_1$ and $J_{12} = J_{34} \equiv J_2$, the matrix of Hamiltonian (1) is diagonal in $S_{12}$, $S_{34}$ and $S$ (where $\boldsymbol{S}_{12} = \boldsymbol{S}_1 + \boldsymbol{S}_2$, $\boldsymbol{S}_{34} = \boldsymbol{S}_3 + \boldsymbol{S}_4$, $\boldsymbol{S} = \boldsymbol{S}_{12} + \boldsymbol{S}_{34}$), and the spin manifold splits into $^1A_1$, $^1B_1$, $^3A_2$, $^3E$ and $^5B_1$, with relative energies given by equation (3). It is important to note that in this

$$E_S = -J_1[S(S + 1)] - (J_2 - J_1)[S_{12}(S_{12} + 1) + S_{34}(S_{34} + 1)] \quad (3)$$

symmetry the ground state must have either $S = 0$ or $= 2$: neither of the $S = 1$ levels can lie lowest. The behaviour of $\mu_{eff}$ suggests an $S = 0$ ground level with the $S = 2$ level intermediate in energy. Although two pairs of $J_1$, $J_2$ values can be found (+4.3, –2.9 and +1.6, –2.9 cm$^{-1}$) which satisfy this condition and predict two INS transitions at the observed energies, in both cases the calculated ratio of their intensities at 1.5 K (12:1 and 170:1) differs markedly from the approximate equality observed (see SUP 57250). Moreover, these $|J|$ values are much too small to reproduce the observed decrease in $\mu_{eff}$ below 50 K.

### $C_{3v}$ Distortion

With $J_{12} = J_{23} = J_{31} \equiv J_1$ and $J_{14} = J_{24} = J_{34} \equiv J_2$, the matrix of Hamiltonian (1) is diagonal in $S_{12}$, $S_{123}$ and $S$ (where $\boldsymbol{S}_{123} = \boldsymbol{S}_{12} + \boldsymbol{S}_3$) and its eigenstates are of symmetry types $^1E$, $^3A_2$ ($S_{123} = \tfrac{3}{2}$), $^3E$ ($S_{123} = \tfrac{1}{2}$) and $^5A_2$, with relative energies given by equation (4). Depending on the two $J$ values, any one

$$E_S = -J_2[S(S + 1)] + (J_2 - J_1)[S_{123}(S_{123} + 1)] \quad (4)$$

of these may be the ground level. In this case the maximum in $\mu_{eff}$ requires that one of the $S = 1$ levels is lowest and the other highest. Within this limitation, three pairs of $J_1$, $J_2$ values can be found (+1.73, −0.69; −1.90, +2.94; and +2.42, −1.37 cm$^{-1}$) which predict the two INS transitions observed, and their calculated intensity ratio (5:4 in each case) is consistent with observation. However, the $|J|$ values are again too small to reproduce the bulk magnetic behaviour.

### $C_{3v}$ Distortion with spin–orbit coupling

The picture is significantly modified when we include the effect of spin–orbit coupling. For the reason indicated below, we consider only the case of $C_{3v}$ symmetry. Taking the direct products of the spin and spatial representations, we find the irreducible representations (5)–(8) spanned by the complete wavefunctions.

$$^1E \longrightarrow A_1 \times E = E \quad (5)$$

$$^3A_2 \longrightarrow (A_2 + E) \times A_2 = A_1 + E \quad (6)$$

$$^3E \longrightarrow (A_2 + E) \times E = A_1 + A_2 + 2E \quad (7)$$

$$^5A_2 \longrightarrow (A_1 + 2E) \times A_2 = A_2 + 2E \quad (8)$$

The $S = 0$ level ($^1E$) remains degenerate, and although the degeneracy of the $^3A_2$ and $^5A_2$ levels is formally removed the splitting of these spatially non-degenerate levels is zero to first order in spin–orbit coupling. However, the $^3E$ level is subject to first-order splitting, and it is evident that, if this were the lowest energy level arising from equation (1), transitions between its spin–orbit sub-levels might account for the two transitions observed in the INS spectrum. To calculate the splitting pattern we have used a spin-Hamiltonian formalism.

It was shown by Moriya[11] that the first-order effect of spin–orbit coupling on the energy of a pair of exchange-coupled ions can be represented by including in the spin Hamiltonian an antisymmetric exchange term $\boldsymbol{d} \cdot \boldsymbol{S}_1 \times \boldsymbol{S}_2$. The effect of this could be significant in the $Cu_4O$ cluster because the ions are not related by inversion (a necessary condition for non-vanishing antisymmetric exchange) and spin–orbit coupling is relatively strong for $Cu^{2+}$. We therefore consider the general Hamiltonian (9), which, unlike (1), is not diagonal in $S$ or any of the intermediate-spin quantum numbers. Expressions for its matrix elements are given in SUP 57250, where we also discuss symmetry constraints on the directions of the axial vectors $\boldsymbol{d}_{ij}$. In $C_{3v}$, $d_{12} = d_{23} = d_{31} \equiv d_1$ and $d_{14} = d_{24} = d_{34} \equiv d_2$, leaving five parameters: $J_1$, $J_2$, $d_1$, $d_2$ and $g$. The risk of overparametrisation is reduced, however, by the requirement that the model must account quantitatively for the two INS transitions as well as fitting the magnetic data. In particular, $^3E$ must be the ground-level multiplet, which means $J_2$ must be positive and $J_1/J_2 < -\tfrac{1}{3}$. Trial calculations (see SUP 57250) with $J$ values chosen to meet this requirement and with $d_1 = d_2 = ca.$ 4 cm$^{-1}$ confirmed the splitting pattern above, and showed that the $A_1$ and $A_2$ components remain close (<0.2 cm$^{-1}$ splitting) but the two E levels are separated from them by *ca.* 3 and 6 cm$^{-1}$, just the pattern needed to account for the INS transitions. The $^3A_2$ and $^5A_2$ levels undergo very small splittings (<0.3 cm$^{-1}$), and the $^1E$ level is not split. A moderately good fit to the magnetic data and a good fit to the zero-field splittings indicated by the INS spectrum are obtained with $J_1$ *ca.* −20, $J_2$ *ca.* +40, $d_1 = d_2$ *ca.* 4 cm$^{-1}$, as shown in Fig. 4 (broken curve) and Fig. 5. Note that the magnitude of $d$ is consistent with the approximate relationship $|d| \approx |J(g - 2)/g|$.[11] However, the precise magnitudes and signs of $d_1$ and $d_2$ are not determined, since somewhat different choices give similar splittings of the $^3E$ level.

$$H = -2\Sigma_{ij}J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j + \Sigma_{ij}\boldsymbol{d}_{ij} \cdot \boldsymbol{S}_i \times \boldsymbol{S}_j \quad (9)$$

It should be noted that we are not assuming orbital degeneracy in the individual $Cu^{2+}$ states, which, as shown by Lines *et al.*,[1a] leads to an antisymmetric exchange contribution even in

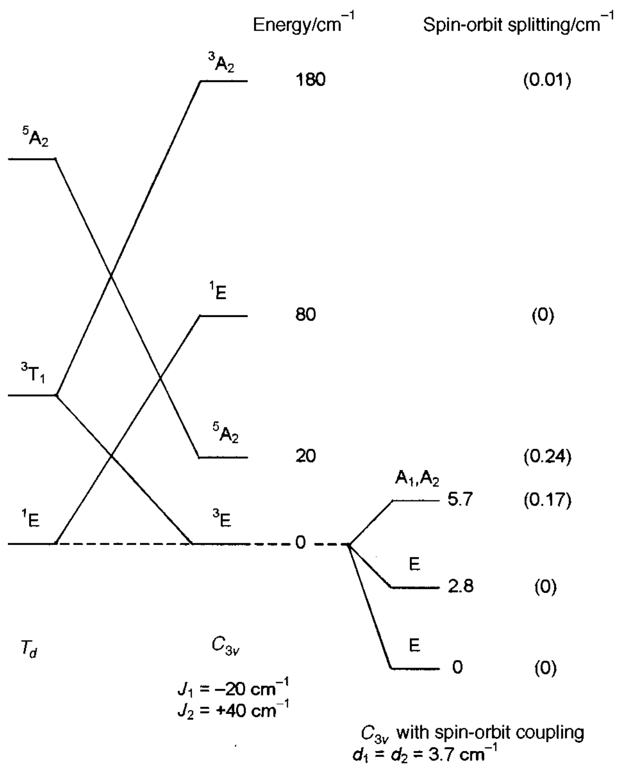

**Fig. 5** Effects of exchange, $C_{3v}$ distortion, and spin–orbit coupling on the zero-field energy levels of [$Cu_4OCl_6(py)_4$], with $J_1$ −20, $J_2$ 40, $d_1$ and $d_2$ 3.7 cm$^{-1}$ (energies not to scale)

the absence of spin–orbit coupling. We believe that an orbitally degenerate ($x^2 - y^2$, $xy$) $Cu^{2+}$ ground state is very unlikely in the case of [$Cu_4OCl_6(py)_4$], where the ligand field along the O–Cu–N axis would be stronger than that in the equatorial plane due to three $Cl^-$ ligands.

We did not investigate the effect of spin–orbit coupling in $D_{2d}$ because, as noted above, the $^3E$ level can never lie lowest in that symmetry. For the same reason, of course, $T_d$ symmetry cannot account for the INS transitions observed.

Since the $^3E$ level is magnetic, the presence of weak intermolecular exchange might be anticipated, and could account for the rather steep decrease in the moment below 5 K. We therefore looked at the effect of including a molecular-field correction,[1a,6] replacing the molar susceptibility $\chi_m$ by $\chi_m/(1 - \alpha)$, where $\alpha = 2zJ'\chi_m/(N_A\mu_B{}^2g^2)$; where $J'$ is the intermolecular exchange parameter and $z$ the number of neighbours coupled to each molecule. Fig. 4 (solid curve) shows the improvement in the fit, with the optimised parameter values $J_1 = -14.3$, $J_2 = 31.4$, $zJ' = -1.1$ cm$^{-1}$, $g = 2.22$, and with $d_1 = d_2 = 3.7$ cm$^{-1}$. The fit index $R = 0.0274$, where $R$ is defined as $[\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}{}^2]^{\frac{1}{2}}$, and the INS transitions are predicted to lie at 2.9 and 5.8 cm$^{-1}$. We realise, of course, that introducing another parameter is bound to improve the fit. Whilst *some* level of intermolecular coupling between magnetic ground states is to be expected, further experimental evidence is needed before we can be sure that this value of $zJ'$ is physically real. Low-temperature magnetisation studies in variable field are also needed to confirm the $S = 1$ ground level postulated here.

It is perhaps worthwhile to comment briefly on the shape of the calculated curve in Fig. 4. The very gradual increase in $\mu_{eff}$ with decreasing temperature to a maximum around 70 K, and its subsequent decrease, reflect the order of the spin levels as determined by $J_1$ and $J_2$. Although the presence of an $S = 1$ ground level might suggest that, as $T$ goes to zero, $\mu_{eff}$ should tend towards the value $g\sqrt{[S(S+1)]}$ = *ca.* 3.14 $\mu_B$, the moment is actually predicted to fall steeply below about 3 K as the Zeeman splittings become comparable with $kT$. The observed downturn in the moment that begins at about 10 K is reproduced in our calculation as a result of two effects: about one-fifth of it is due to the spin–orbit splitting of the $^3E$ ground level, while the intermolecular coupling term $zJ'$ accounts for the remainder.

### Other possible explanations

As a further check we also attempted to fit the data with a model that did not include antisymmetric exchange but assumed that the complex had no molecular symmetry (six independent $J$ values), as suggested by the IR spectrum at 100 K. Although satisfactory fits could be obtained to the magnetic susceptibility with many different values of the parameters, the lowest levels above the ($S = 0$) ground level were invariably predicted to lie at *ca.* 2.5 ($S = 1$) and 25 cm$^{-1}$ ($S = 2$), in disagreement with the two INS transitions observed.

Another possibility might be a structural change below room temperature, like that of [$Cr_3O(O_2CMe)_6(H_2O)_3$]Cl·6$H_2O$, the unit cell of which doubles below 210 K to give two symmetry-inequivalent molecules.[12] Conceivably, the presence of such inequivalent sites in the crystal at 1.5 K could give rise to the two low-energy INS transitions of equal intensities, and it would also not be inconsistent with the IR spectrum. However, we have not been able to fit both the magnetic and neutron scattering data on this assumption. Nevertheless, determination of the crystal structure of [$Cu_4OCl_6(py)_4$] at low temperature is clearly desirable.

## Conclusion

The magnetic properties of [$Cu_4OCl_6(py)_4$] present a puzzle to which no fully satisfactory solution has yet been found. The unexpected observation of two low-energy (*ca.* 3 and 6 cm$^{-1}$) transitions in the inelastic neutron scattering spectrum of this compound (and also in that of the magnetically similar dimethyl sulfoxide adduct) has led us to propose a new interpretation that appears to reconcile the magnetic and INS data without invoking improbably large intercluster interactions. We suggest that distortion of the complex from tetrahedral symmetry, which is already manifested in the infrared spectrum at 100 K, results in an exchange Hamiltonian having approximately $C_{3v}$ symmetry at very low temperatures, with exchange parameters *ca.* −15 and +30 cm$^{-1}$. The effect of spin–orbit coupling is then to cause a zero-field splitting of the lowest level ($^3E$) into three approximately equally spaced sub-levels, the splittings of which can be identified with the two transitions seen in the INS spectrum.

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