Magnetic Exchange Interactions in Tetranuclear Copper(II) Complexes. Effect of Ligand Electronegativity

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Magnetic susceptibility measurements are reported for a series of tetranuclear copper(II) complexes [$Cu_4OX_6L_4$] (X = Br or Cl; L = Cl, Br, C_5H_5N, C_5H_5NO, tetramethylurea, or dimethyl sulphoxide). These data and literature data on other tetranuclear complexes describe a range of magnetic behaviour, varying from strong intramolecular antiferromagnetic interaction, through weak antiferromagnetic interaction, to apparent ferromagnetism. Intermolecular interactions are found to be negligible. The results are used to evaluate current theoretical models for such systems, and are consistent with the existence of a significant symmetric component in the pairwise exchange Hamiltonian.

UNUSUAL magnetic properties have been observed[1-7] in five different complexes having the general formula [$Cu_4OX_6L_4$], where X is a bridging halogen (Cl or Br) and L an axially bonded unidentate ligand, as shown in the structure[7-10] in Figure 1. Unfortunately, intercomparison between these and other, related, complexes has been restricted by the limited magnetic data available, and the results have been interpreted in somewhat different ways,[1,2,4-6] but the similarity of the other properties[3,11,12] and the results of three single-crystal *X*-ray structural determinations[7-10] suggest that all the complexes [$Cu_4OX_6L_4$] have the same structural skeleton, with four copper atoms at the corners of a tetrahedron around the central oxygen atom. The five complexes studied so far appear to fall, phenomenologically, into two distinct classes (I and II) based on their magnetic properties: the magnetic moments either decrease monotonically with decreasing temperature, or pass through a maximum and then decrease at low temperatures. The former type of behaviour indicates strong intramolecular antiferromagnetism, the latter has been attributed to a ferromagnetic interaction in addition to the antiferromagnetism[1] and to the presence of orbital effects in addition to exchange interactions,[2] but no quantitative explanation was given in either case for the two different complexes reported. Lines *et al.*[5] investigated these two complexes plus a third, and quantitatively interpreted the maximum in the curve of magnetic moment *vs.* temperature in terms of an orbitally degenerate ground state for the copper atoms, undergoing antiferromagnetic exchange interactions; a different, singlet, ground state was proposed for the complex[4] for which the moment decreases monotonically, so that the simple Heisenberg exchange Hamiltonian gives an accurate representation of the magnetic properties in that case.[1,2,4,6]

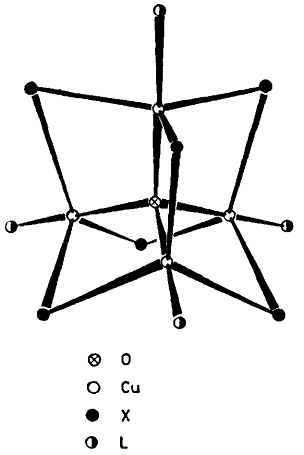

FIGURE 1 Molecular structure of the tetranuclear copper(II) cluster complex [$Cu_4OX_6L_4$]

In this paper we compare the magnetic properties of the wider range of Cu_4OX_6-type complexes presently available.[3,9-11] These produce five classes of behaviour, or in our view representatives of a continuous range of behaviour from class I through II and beyond (Table 1). An apparent discrepancy in the non-observance of a maximum (for [Cu_4OCl_6]$\cdot C_5H_5N$)[8] in the μ *vs.* *T* data in a compound type for which a maximum had previously been reported ([Cu_4OBr_6]$\cdot C_5H_5N$)[6] (in agreement with our previous unpublished data) was re-examined: a slight maximum was again observed for both cases.

EXPERIMENTAL

The syntheses of the complexes and the measurement of magnetic moments (80—400 K) were carried out as previously described.[3,11-13] Measurements were made at different magnetic field strengths and no field-strength dependence was found for any complex within experimental error. Measurements below 77 K were made using Gouy, Faraday, and Foner[14] balances, and a SQUID magnetometer[15,16] was used to remeasure data over the entire temperature range for [$Cu_4OCl_6(tmu)_4$] (tmu = tetramethylurea).

RESULTS AND DISCUSSION

The effective magnetic moments per gram atom copper(II) are given in Table 2 and are corrected for diamagnetism of the constituent atoms using Pascal's constants, but not for temperature-independent paramagnetism. The $\mu_{eff.}$ *vs.* temperature data in Table 2 are plotted in Figure 2 with the curves representing the best fit to the models described below.

There appears to be no correlation of the magnetic properties with the size of L, which is important in

TABLE 1

Classes of magnetic behaviour for Cu_4OX_6 complexes

Complex	Class	Ref.
$[NMe_4]_4[Cu_4OCl_{10}]$	I	*, 4
$[NMe_4]_4[Cu_4OCl_6Br_4]$	I	*
$[Cu_4OCl_6(C_5H_5N)_4]$	II	6
$[Cu_4OBr_6(C_5H_5N)_4]$	II	*, 5
$[Cu_4OCl_6(OPPh_3)_4]$	II	5
$[Cu_4OBr_6(OPPh_3)_4]$	II	5
$[Cu_4OCl_6(pyo)_4]$	III	*
$[Cu_4OCl_6(tmu)_4]$	III	*
$[Cu_4OCl_6(dmso)_4]$	III	*
$[Cu_4OBr_6(dmso)_4]$	III	*
$[Cu_4OCl_6(3\text{-quin})_4]$	III	7

* This work. 3-quin = Quinuclidin-3-one.

determining how far the Cu_4OX_6 units are apart in the lattice; moreover, the crystal structures available so far all place these units relatively far apart.[7-10] Thus magnetic interactions between neighbouring tetranuclear units should be relatively small. Although significant intermolecular interactions can occur between discrete molecules if there is significant electron delocalization on the ligands,[15] these should be quite small compared to the relatively large intramolecula interactions observed here.

The classes I—III can be construed in the simple Heisenberg model to represent decreasing strengths of antiferromagnetic interactions (μ decreasing monotonically), going through to ferromagnetic interactions (μ increasing to a maximum near 4 K), although it is clear from Figure 2 that such representations are at best crude. As there is no systematic effect of ligand size, nor any reason for steric interaction with the ligands (L), the ligand effect must be electronic.

The $CuOX_3L$ co-ordination sphere of copper(II) in the tetranuclear cluster has trigonal-bipyramidal C_{3v} point symmetry with O and L in axial positions. Under C_{3v} symmetry, the electronic 3*d* orbital degeneracy splits to form three levels, $e(xz,yz)$, $e(x^2-y^2,xy)$, and $a(z^2)$

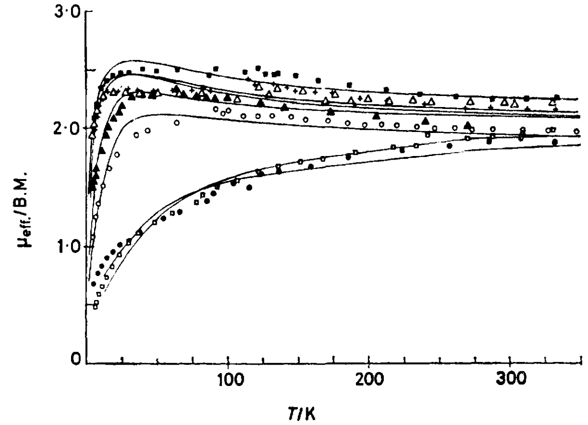

FIGURE 2 Effective magnetic moments plotted as a function of temperature for analogous $[Cu_4OX_6L_4]$ complexes. The smooth curves are the best fit to the orbitally degenerate model of Lines *et al.*[5] with the parameters listed in Table 3. X,L = Cl,Cl (□); Cl,Br (●); Br, C_5H_5N (○); Br, dmso (dimethyl sulphoxide) (■); Cl, dmso (△); Cl, pyo (pyridine *N*-oxide) (+); Cl, tmu (▲)

TABLE 2

Magnetic moments

(*a*) $[NMe_4]_4[Cu_4OCl_{10}]$

T/K	334	331	309	288	288	270	242	234
μ/B.M.	1.91	1.98	1.96	1.93	1.93	1.92	1.94	1.85
T/K	218	191	191	168	152	136	123	121
μ/B.M.	1.84	1.81	1.79	1.75	1.72	1.68	1.65	1.63
T/K	108	107	93	83	61.4	48.7	37.2	30.1
μ/B.M.	1.51	1.58	1.50	1.43	1.28	1.21	1.12	1.02
T/K	23.6	18.6	14.7	11.6	9.3	7.2	6.5	
μ/B.M.	0.93	0.83	0.74	0.66	0.59	0.52	0.50	

(*b*) $[NMe_4][Cu_4OCl_6Br_4]$

T/K	332	308	286	258	224	186	160	159
μ/B.M.	1.88	1.90	1.89	1.84	1.81	1.75	1.66	1.70
T/K	137	126	123	116	108	103	91	88
μ/B.M.	1.64	1.63	1.59	1.49	1.55	1.53	1.45	1.44
T/K	85.9	66.9	55.2	38.0	30.6	24.7	19.5	15.5
μ/B.M.	1.38	1.29	1.23	1.11	1.05	1.01	0.95	0.89
T/K	11.5	8.8	5.8					
μ/B.M.	0.83	0.77	0.68					

(*c*) $[Cu_4OBr_6(C_5H_5N)_4]$

T/K	353	327	309	288	273	261	247	234
μ/B.M.	1.97	1.98	1.99	1.99	1.99	2.00	2.00	2.01
T/K	220	209	197	185	171	155	132	122
μ/B.M.	2.02	2.03	2.03	2.04	2.06	2.07	2.09	2.10
T/K	122	112	101	92	64.5	43.8	36.1	22.3
μ/B.M.	2.10	2.10	2.15	2.16	2.04	1.98	1.93	1.66
T/K	16.7	12.1	8.8	6.8	4.7	4.2		
μ/B.M.	1.66	1.51	1.36	1.24	1.09	1.07		

(*d*) $[Cu_4OCl_6(pyo)_4]$

T/K	332	312	286	269	267	239	213	194
μ/B.M.	2.16	2.16	2.17	2.18	2.17	2.21	2.23	2.26
T/K	193	175	162	148	142	133	123	119
μ/B.M.	2.25	2.29	2.31	2.32	2.35	2.38	2.36	2.36
T/K	115	88.1	83	75.3	61.4	48.1	36.7	28.4
μ/B.M	2.42	2.32	2.33	2.33	2.32	2.32	2.32	2.32
T/K	21.9	17.0	12.7	9.4	7.2	5.6		
μ/B.M.	2.31	2.31	2.27	2.20	2.11	2.00		

(*e*) $[Cu_4OCl_6(tmu)_4]$

T/K	271	241	206	174	141	124	108	101
μ/B.M.	2.02	2.05	2.09	2.14	2.18	2.21	2.25	2.26
T/K	92	86	79	71	66	48	40	33.2
μ/B.M.	2.25	2.25	2.29	2.29	2.34	2.32	2.31	2.27
T/K	30.1	26.4	24.1	22.5	19.9	16.9	14.6	11.6
μ/B.M.	2.27	2.19	2.14	2.14	2.08	2.01	1.94	1.82
T/K	8.2	7.1	6.0	5.2	4.3			
μ/B.M.	1.66	1.61	1.55	1.53	1.47			

(*f*) $[Cu_4OCl_6(dmso)_4]$

T/K	333	331	304	297	274	272	245	232
μ/B.M.	2.22	2.22	2.20	2.22	2.20	2.25	2.22	2.25
T/K	215	200	188	177	170	154	136	130
μ/B.M.	2.23	2.25	2.23	2.29	2.23	2.32	2.36	2.30
T/K	123	82	66	51.3	38.4	28.4	20.1	12.9
μ/B.M.	2.36	2.30	2.30	2.30	2.30	2.31	2.31	2.28
T/K	8.2	6.2	4.2					
μ/B.M.	2.18	2.07	1.95					

(*g*) $[Cu_4OBr_6(dmso)_4]$

T/K	333	311	288	262	236	212	186	164
μ/B.M.	2.25	2.25	2.24	2.26	2.29	2.33	2.36	2.40
T/K	148	136	133	127	122	113	92	87
μ/B.M.	2.44	2.46	2.45	2.45	2.50	2.47	2.50	2.45
T/K	64.5	50.2	40.2	30.4	24.6	19.1	15.8	13.9
μ/B.M.	2.50	2.48	2.50	2.47	2.47	2.44	2.40	2.40
T/K	10.6	7.3	5.7					
μ/B.M.	2.34	2.20	2.09					

1 B.M. ≈ 9.27×10^{-24} A m².

listed in order of increasing energy for cases of strong crystal fields, and which have angular momentum contributions of $|\pm 1\rangle$, $|\pm 2\rangle$, and $|0\rangle$, respectively. The two doubly degenerate e terms have the same representations and will allow some mixing of levels, therefore the assigned angular momentum quantum numbers are only representative. The symmetry of the orbitals under the C_{3v} representation is illustrated in Figure 3. The relative energies of the levels is very dependent on the orientation and strength of the crystal field. In a strong crystal field, which may be approximated by the CuX_5^{3-} model,[17] the a_1 level is highest in energy followed by $e(x^2 - y^2,xy)$. If the crystal field is weakened along the three-fold axis (*e.g.* replacing an axial X^- with a neutral ligand), the a_1 orbital decreases in energy and drops below the $e(x^2 - y^2,xy)$ orbital which to first order is unaffected by the change in crystal field. In the case of a strong crystal field the electron hole resides in the a_1 level giving the orbitally non-degenerate A_1 ground state and in weak crystal fields the $e(x^2 - y^2,xy)$ orbital is highest, resulting in the orbitally degnerate E ground state.

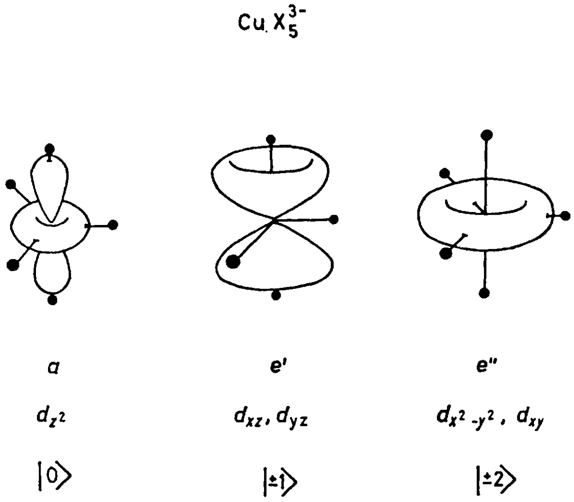

FIGURE 3 Symmetry of the 3*d* electron orbitals under crystal fields of C_{3v} symmetry

The tetranuclear clusters which have copper(II) in a strong crystal field (*e.g.* $Cu_4OX_{10}^{4-}$) may be analyzed with the orbitally non-degenerate Heisenberg $S = \frac{1}{2}$ tetramer equation. The susceptibility per gram atom copper(II) ion is given by the following equation.

$$H = \frac{Ng^2\mu_B^2}{2kT} \cdot \frac{5 + 3\exp(-2J/kT)}{5 + 9\exp(-2J/kT) + 2\exp(-3J/kT)}$$

The cases of intermediate and weak crystal field must take into account the effects of orbital degeneracy and the model proposed by Lines *et al.*[5] was used in the analysis. The parameter values for the best fit to the appropriate models are given in Table 3 (where the symbols have their usual meaning).

It is clear that the results can be successfully parameterized, within experimental error, using the orbitally degenerate model, and that the results span most of the range of curves that can be generated from this model, although the parameter values are not unique. It is also clear that the simple isotropic Heisenberg Hamiltonian is unable to reproduce the experimental results nearly as well, except for the strong crystal-field analogues, its main shortcoming being an inability to produce the observed maximum in the magnetic moment curves, without the addition of a large intercluster exchange term. Indeed there is an apparent correlation between ligand electronegativity in going from class I to class III. It is possible that there may also be correlations between J and structural parameters such as CuOCu, CuClCu, and CuBrCu angles and the ligand environment about the metal, as has been observed for other polynuclear complexes.[1,2,18-25] However, there are insufficient structural data to establish this, and the few structural data available so far do not vary sufficiently to suggest such a correlation. More crystal-structure data are needed to examine this possible effect more closely and separate it from the effect of the ligand. In any case, the electronegativity of the ligand substituent appears to be far more important than any structural effects.

TABLE 3

Values of the parameters for the best fit to the orbitally degenerate model of Lines *et al.*[5] for $[Cu_4OX_6L_4]$

X, L	J_+/cm^{-1}	D/cm^{-1}	γ
Br, C_5H_5N	−24.5	77.0	0.734
Cl, tmu	−15.5	61.9	0.661
Cl, pyo	−5.0	61.8	0.620
Cl, dmso	8.56	61.4	0.651
Br, dmso	8.66	70.4	0.594
	g	J/K	
Cl, Br	2.31	−43.0	
Cl, Cl	2.37	−38.0	

Situations where orbital effects are important in magnetic exchange in copper complexes are extremely rare, a fact which makes these systems especially important, and which also requires that the model continue to be tested very closely before this unusual situation is accepted, when such a very large number of copper complexes in which the interactions are explained by the simple Heisenberg Hamiltonian are known.[1,2,23]

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