Crystal Structure and Magnetic Properties of a Binuclear Triketonate Complex of Five-co-ordinate Copper(II) : Bis[heptanetrionato(2−)]bispyridinedicopper(II)

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The crystal and molecular structures of the title compound have been determined by single-crystal X-ray diffraction photography. The structure was solved by Patterson and Fourier methods and refined anisotropically by the method of least squares to R 11·1% for 1743 visually estimated observed reflections. The black crystals are triclinic, space group $P\bar{1}$, and the reduced unit cell, of dimensions $a = 9{\cdot}60$, $b = 9{\cdot}94$, $c = 8{\cdot}61$ (±0·03) Å, $\alpha = 123{\cdot}7$, $\beta = 91{\cdot}6$, $\gamma = 108{\cdot}2$ (±0·3)°, contains one centrosymmetric binuclear molecule. The triketonate ligands are terdentate, with the central O atoms linking the Cu atoms to give a planar Cu_2O_2 ring with angles Cu–O–Cu 103 and O–Cu–O 77°. Each copper atom is bonded to four coplanar O atoms and a pyridine N atom in a square-pyramidal arrangement, with Cu–O 1·93 (mean) and Cu–N 2·32 Å, the two pyridine ligands being on opposite sides of the molecule. The effective magnetic moment per Cu falls from 0·75 at 335 to 0·0 B.M. at 87 K; the magnetic data are consistent with intramolecular exchange giving a singlet–triplet separation $2|J|$ 690 cm^{-1}, with g 2·09.

By the combination of magnetic with crystallographic investigations, progress has been made in recent years in elucidating the relationship between superexchange and molecular structure in polynuclear complexes, especially in those containing a Cu_2O_2 ring.[1-5] Valuable information about the mechanism of exchange can also be obtained by examining how the strength of the interaction varies as the metal ions are varied,[6,7] which can most easily be done by the use of so-called ' binucleating ligands,' *e.g.* 1,3,5-triketones.[8-12] A good example is the recent determination of the crystal structures and magnetic properties of the compounds $[M_2\{(Ph{\cdot}CO{:}CH{\cdot})_2CO\}_2(py)_4]$ (M = Co or Ni).[11,12] Several copper complexes of the type $[Cu_2\{(R{\cdot}CO{:}CH{\cdot})_2CO\}_2]$ have also been studied magnetically, but in these cases the interpretation was impeded by the lack of detailed structural information, and by field dependence of the susceptibility in some and the apparent presence of paramagnetic impurities in others.[9,10] Although the latter compounds are insoluble in most solvents, they can be recrystallised from pyridine;[8] crystals of $[Cu_2\{(MeCO{:}CH{\cdot})_2CO\}_2(py)_2]$ do not suffer from the disadvantages mentioned, and we now report the crystal structure of this compound, and its mean magnetic susceptibility between 85 and 335 K.

EXPERIMENTAL

Heptane-2,4,6-trione (H_2hpt) and $[Cu_2(hpt)_2]$ were prepared by methods given in the literature.[8,13] The green complex was dissolved in hot pyridine to give a dark brown solution, which, when set aside overnight, deposited black, well-formed crystals of $[Cu_2(hpt)_2(py)_2]$ (Found: C, 50·9; H, 4·75. Calc. for $C_{24}H_{26}Cu_2N_2O_6$: C, 51·0; H, 4·64%). The mass spectrum (after removal of pyridine under vacuum at room temperature) showed a strong peak at m/e 406, assigned to $[Cu_2(hpt)_2{}^+]$, as well as peaks attributable to $[Cu_2(hpt)]^+$, $[Cu(hpt)_2]^+$, $[Cu(hpt)]^+$, and ions formed from these by loss of Me, MeCOCH, and MeCOCHCO.

Magnetic Measurements.—The crystals were ground and the powder packed into a silica tube in a glove box in an atmosphere saturated with pyridine vapour. The susceptibility was measured by the Gouy method, with thermostatic temperature control and a liquid-nitrogen heat sink. The field was calibrated with $CuSO_4,5H_2O$, for which we assumed $\chi = (22\,200 \pm 300)/(T + 1)$ mm^3 kg^{-1} (*cf.* ref. 14). Measurements at magnetic field strengths of *ca.* 330 and 520 A mm^{-1} showed that the susceptibility was independent of field strength. A gradual decrease in the susceptibility after a few hours at temperatures >50 °C was noted, possibly due to thermal decomposition.

The measured susceptibility has only a small positive value at room temperature, and becomes negative at low temperatures, and in such circumstances it is important to obtain an accurate estimate of the underlying diamagnetism and temperature-independent paramagnetism (TIP). The diamagnetic susceptibility calculated from Pascal constants[15] is −3·0 mm^3 per mole of dimer, while for the TIP a value of 0·75 mm^3 per mole of Cu is commonly assumed,[15,16] which would give a total temperature-independent susceptibility for the dimer of *ca.* −1·5 mm^3 mol^{-1}. In fact, however, the uncorrected molar susceptibility falls below this value at *ca.* 160 K, and can reasonably be extrapolated to a value of *ca.* −2·2 mm^3 mol^{-1} at $T = 0$. If the calculated diamagnetism is correct, this would indicate a TIP of only *ca.* 0·4 mm^3 per mole of Cu, which is surprisingly low, though not impossible. (It would correspond to an orbital-

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reduction factor of *ca.* 0·6.) Figgis and Harris observed that the TIP contribution is ' inexplicably absent ' in the case of $\mathrm{Cu(acac)_2}$.[16]

In the light of these observations the data shown in Table 5 have been corrected for the presence of an assumed temperature-independent susceptibility of $-2{\cdot}2$ mm^3 mol^{-1}.

Crystallographic Examination

Unit-cell dimensions were determined from zero- and first-level Weissenberg and precession photographs of three different crystals.

Crystal Data.—$\mathrm{C_{24}H_{26}Cu_2N_2O_6}$, $M = 565{\cdot}6$, Triclinic, $a = 8{\cdot}61 \pm 0{\cdot}02$, $b = 8{\cdot}83 \pm 0{\cdot}02$, $c = 10{\cdot}29 \pm 0{\cdot}03$ Å, $\alpha = 59{\cdot}7$, $\beta = 74{\cdot}1$, $\gamma = 69{\cdot}5$ (all $\pm 0{\cdot}3°$), $U = 627{\cdot}9 \pm 5{\cdot}6$ Å^3, $D_m = 1{\cdot}52 \pm 0{\cdot}02$, $Z = 1$, $D_c = 1{\cdot}50$, $F(000) = 290$. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; $\mu(\text{Cu-}K_\alpha) = 25{\cdot}8$ cm^{-1}. Space group $P\bar{1}$ assumed, and confirmed by successful refinement.

All co-ordinates, *etc.*, are referred to this unit cell. The Delaunay reduced cell has dimensions $a = 9{\cdot}60$, $b = 9{\cdot}94$, $c = 8{\cdot}61$ Å, $\alpha = 123{\cdot}7$, $\beta = 91{\cdot}6$, $\gamma = 108{\cdot}2°$, and is obtained by means of the transformation matrix $(01\bar{1}/1\bar{1}0/\bar{1}00)$.

The crystals used for data collection were sealed in glass capillary tubes (of internal diameter *ca.* 0·2 mm) to prevent decomposition, and timed-exposure multiple-film Weissenberg photographs were obtained by use of one crystal for the levels 0—5*kl* and another for *h*0—5*l*. Diffraction intensities were estimated visually. Corrections were made for the Lorentz and polarisation effects, and relative scaling of the twelve levels was accomplished by the logarithmic least-squares method.[17] No corrections for absorption were applied. Merging the levels gave 1743 unique reflections, *R* for this process being 0·074.

Structure Determination and Refinement.—The copper atoms were located from a three-dimensional sharpened Patterson map, and two cycles of phase calculation and Fourier synthesis then revealed the remaining atoms (other than H) with *R* 0·39. Atomic parameters were refined by the method of least squares (block-diagonal approximation), first assuming individual isotropic temperature factors, then with anisotropic temperature factors for all atoms, convergence being reached at *R* 0·111. The quantity minimised was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$ and $w = [1 + (F_o/F^*)^2]^{-1}$, with $F^* = 5$ chosen to give the least variation in $w\Delta^2$ with $|F_o|$. A final difference-Fourier synthesis showed no significant peaks. No attempt was made to locate hydrogen atoms.

Atomic scattering factors were taken from ref. 18, without correction for anomalous dispersion. All calculations were carried out on the Hull University I.C.L. 1905E computer, using programs of ref. 19.

RESULTS AND DISCUSSION

Structure.—Observed and calculated structure factors and atomic vibrational parameters are listed in Supplementary Publication No. SUP 21111 (6 pp.).* Table 1 gives the atomic fractional co-ordinates, with their standard deviations. The atomic vibrational parameters showed no unexpected features. Figure 1 and Table 2 show the bond lengths and angles in the molecule, and Table 3 gives the equations of weighted mean planes passing through certain groups of atoms, the distances of various atoms from these planes, and the angles between the planes. Table 4 gives some distances between non-bonded atoms.

TABLE 1

Atomic fractional co-ordinates [a, b]

Atom	*x*	*y*	*z*
Cu	−0·0943(2)	−0·0074(2)	0·1512(2)
O(1)	−0·2505(15)	0·1783(14)	0·1925(12)
O(2)	−0·0315(14)	0·1634(11)	−0·0587(10)
O(3)	0·1814(14)	0·2004(14)	−0·3262(11)
C(1)	−0·3906(25)	0·4710(22)	0·1685(21)
C(2)	−0·2610(20)	0·3508(17)	0·1063(16)
C(3)	−0·1640(24)	0·4302(19)	−0·0324(19)
C(4)	−0·0538(20)	0·3415(16)	−0·1124(15)
C(5)	0·0382(24)	0·4335(19)	−0·2532(19)
C(6)	0·1476(21)	0·3642(21)	−0·3455(17)
C(7)	0·2412(28)	0·4861(26)	−0·4892(22)
N	0·1344(15)	−0·0071(14)	0·2281(13)
C(8)	0·2944(23)	−0·0723(23)	0·1773(19)
C(9)	0·4330(22)	−0·0690(27)	0·2228(21)
C(10)	0·4133(24)	−0·0012(27)	0·3240(21)
C(11)	0·2476(25)	0·0645(22)	0·3772(18)
C(12)	0·1161(22)	0·0610(21)	0·3214(17)

[a] In this and subsequent Tables, estimated standard deviations are given in parentheses. [b] Origin at $\bar{1}$.

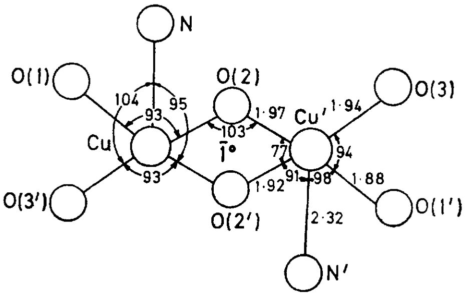

FIGURE 1 Dimensions of the $\mathrm{Cu_2O_6N_2}$ system. Distances (Å) have σ 0·02 Å and angles (°) have σ 1°

The unit cell contains a single, centrosymmetric, binuclear molecule, with the two copper atoms bridged by two approximately planar heptanetrionate ligands. Figure 2 shows a view of the molecule from a point on the positive *b* axis, together with the atomic numbering. The structure is similar to that of the analogous compounds $\mathrm{[M_2(Ph{\cdot}CO{:}CH{\cdot}CO{\cdot}CH{:}CO{\cdot}Ph)_2(py)_4,4(py)]}$ (M = Co [11] or Ni [12]), except that each Cu atom has only a single pyridine ligand, with a relatively long Cu–N bond, a difference similar to that between $\mathrm{[Co(acac)_2(py)_2]}$ [20] and $\mathrm{[Cu(acac)_2(quinoline)]}$.[21]

The co-ordination geometry is square pyramidal, the

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

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four oxygen atoms attached to each Cu atom being coplanar, with the Cu atom displaced 0·24 Å from this plane towards the N atom, as in the acac complex. Although the Cu–O bond lengths cover a rather wide range (1·88—1·97 Å), their mean (1·93) and the Cu–N distance (2·32 Å) are also similar to those in $Cu(acac)_2(quinoline)$.[21]

TABLE 2

Ligand bond lengths (Å) and angles (°) *

(*a*) Heptanetrione group			
C(1)–C(2)	1·50(4)	C(6)–C(7)	1·53(3)
C(2)–C(3)	1·41(2)	C(5)–C(6)	1·36(3)
C(3)–C(4)	1·38(3)	C(4)–C(5)	1·42(2)
O(1)–C(2)	1·30(3)	O(3)–C(6)	1·29(4)
O(2)–C(4)	1·34(3)		
Cu–O(1)–C(2)	124(1)	Cu′–O(3)–C(6)	125(1)
Cu–O(2)–C(4)	126(1)	Cu′–O(2)–C(4)	130(1)
O(1)–C(2)–C(1)	114(2)	O(3)–C(6)–C(7)	114(2)
O(1)–C(2)–C(3)	127(2)	O(3)–C(6)–C(5)	126(2)
O(2)–C(4)–C(3)	120(2)	O(2)–C(4)–C(5)	118(2)
C(1)–C(2)–C(3)	119(2)	C(5)–C(6)–C(7)	120(3)
C(2)–C(3)–C(4)	126(3)	C(4)–C(5)–C(6)	128(3)
C(3)–C(4)–C(5)	122(3)		
(*b*) Pyridine molecule			
N–C(8)	1·36(3)	N–C(12)	1·32(3)
C(8)–C(9)	1·41(4)	C(11)–C(12)	1·42(4)
C(9)–C(10)	1·39(5)	C(10)–C(11)	1·41(3)
Cu–N–C(8)	122(2)	Cu–N–C(12)	121(1)
N–C(8)–C(9)	122(3)	N–C(12)–C(11)	126(2)
C(8)–C(9)–C(10)	122(2)	C(10)–C(11)–C(12)	118(3)
C(8)–N–C(12)	116(2)	C(9)–C(10)–C(11)	116(2)

* Dimensions of the $Cu_2O_6N_2$ system are given in Figure 1.

TABLE 3

Planes of best (least-squares) fit to selected groups of atoms

(*a*) Atoms defining planes, and their distances (Å) [a]

Plane	Group	Atoms
(*A*)	$(CO{\cdot}CH{\cdot}CO{\cdot}CH{\cdot}CO)_2$	O(1) 0·0, C(2) −0·07, C(3) 0·01, C(4) 0·01, O(2) −0·07, C(5) 0·08, C(6) 0·06, O(3) −0·12
(*B*)	O_4	O(1) 0·01, O(2) −0·01, O(2′) 0·01, O(3′) −0·01
(*C*)	Cu_2N_2	Cu, N, Cu′, N′
(*D*)	Pyridine	N 0·01, C(8) 0·01, C(9) −0·01, C(10) 0·0, C(11) 0·01, C(12) −0·02

(*b*) Equations of planes [b] in the form $lX + mY + nZ = p$

Plane	10^3l	10^3m	10^3n	10^3p
(*A*)	807	394	441	0
(*B*)	806	434	403	0
(*C*)	−329	844	−423	0
(*D*)	95	−633	769	−699

(*c*) Distances (Å) of other atoms from planes

(*A*): Cu 0·28, C(1) −0·22, C(7) 0·22
(*B*): Cu 0·24, C(1) −0·12, C(2) 0·01, C(3) 0·15, C(4) 0·14, C(5′) −0·27, C(6′) −0·24, C(7′) −0·48
(*D*): Cu −0·01

(*d*) Interplanar angles (°)

(*A*)–(*B*) 3·1, (*B*)–(*C*) 94·0, (*B*)–(*D*) 83·6, (*C*)–(*D*) 27·1

[a] Atoms defining the planes were given weights proportional to their atomic numbers. [b] Orthogonal co-ordinates X, Y, Z are related to the fractional co-ordinates of Table 1 as follows: $X = ax \sin\gamma - cz \sin\alpha \cos\beta^*$, $Y = by + ax \cos\gamma + cz \cos\alpha$, $Z = cz \sin\alpha^* \sin\beta$. l, m, n are the direction cosines of the plane normal, and p is in Å.

The angles within the Cu_2O_2 ring are quite close to the corresponding angles in the cobalt and nickel compounds[11,12] (M–O–M 102·7, 101·5, and 103°; O–M–O 77·3, 78·5, and 77°, for M = Co, Ni, and Cu), but the decrease in metal–oxygen bond lengths in the series Co, Ni, Cu is reflected in a progressive reduction in the distances M ··· M′ (3·27, 3·17, and 3·05) and O(2) ··· O(2′) (2·62, 2·59, and 2·41 Å) and in the 'external' angles O(1)–M–O(3′) (106·6, 102·3, and 94°). The Cu_2O_2 ring dimensions also closely resemble those in the $Cu(acac)(OCH_2Ph)$ dimer (the Cu–O–Cu angles in the latter are unequal because one oxygen atom is involved in further co-ordination, but their mean is 103°).[22]

TABLE 4

Selected distances (Å) between non-bonded atoms [a]

(*a*) Within molecule [b]			
Cu ··· Cu′	3·051(3)		
O(1) ··· O(2)	2·78	O(2) ··· O(3)	2·79
O(1) ··· O(3′)	2·80	O(2) ··· O(2′)	2·41
O(1) ··· C(12)	3·38	O(2) ··· C(8′)	3·32
(*b*) Between molecules [c]			
C(3) ··· $C(3')^{I}$	3·77	C(9) ··· $C(6')^{IV}$	3·74
C(7) ··· $C(5')^{II}$	3·70		
C(7) ··· $C(6')^{II}$	3·69	C(9) ··· $O(3')^{IV}$	3·39
C(12) ··· $C(11')^{III}$	3·78	C(10) ··· $O(3')^{IV}$	3·31
C(12) ··· $C(12')^{III}$	3·49	C(10) ··· $O(1')^{IV}$	3·41

[a] All distances O ·· O $\leqslant$3·0, O ··· C $\leqslant$3·5, and C ··· C $\leqslant$3·8 Å are given, except within the ligands. [b] Primed and corresponding unprimed atoms are related by inversion in the origin. [c] Roman numerical superscripts denote the following equivalent positions relative to x, y, z:

I $x, y + 1, z$
II $x, y + 1, z - 1$
III $x, y, z + 1$
IV $x + 1, y, z$

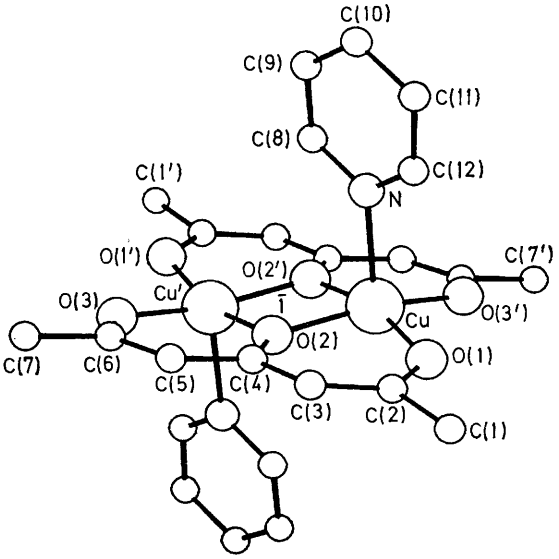

FIGURE 2 View of the molecule from a point on the positive *b* axis

The bond lengths and angles in the triketonate groups are similar to those in the analogous cobalt and nickel complexes, but there are greater deviations from planarity, presumably as a result of the displacements of the two Cu atoms from the planes of their co-ordinated oxygen atoms. This twisting effect on the ligands is shown in Figure 3.

[22] J. E. Andrew and A. B. Blake, *J.C.S. Dalton*, 1973, 1102.

Figure 4 illustrates the molecular packing. There are no unusually short intermolecular distances, the closest contacts being those of C(10) with O(3′) of the molecule related by an *a* translation, and of C(12) with C(12′) of the molecule related by a *c* translation.

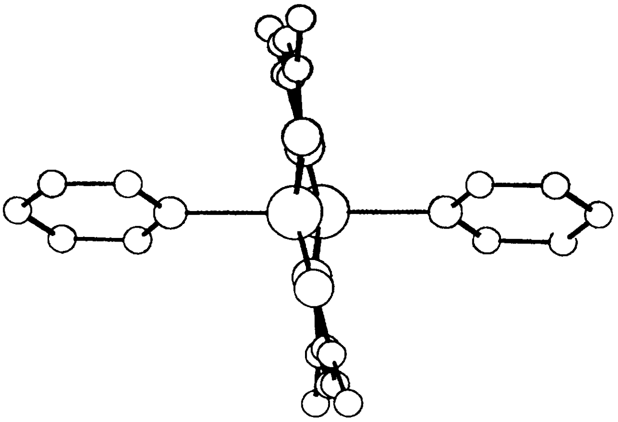

FIGURE 3 View of the molecule from a point in the O_6 plane, showing the distortion of the heptanetrionate ligands

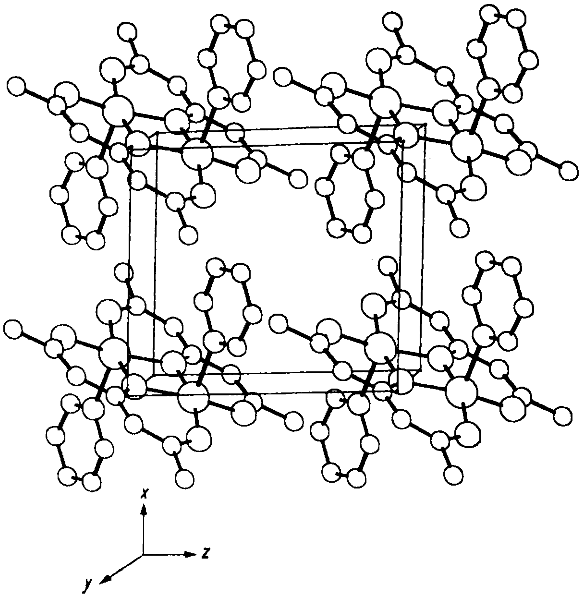

FIGURE 4 Unit cell viewed from the point with co-ordinates 5*a*, 60*b*, 5*c*. Molecules centred in the $y = 0$ plane are shown

Magnetism.—The molar susceptibility (not including TIP) of a pair of Cu^{2+} ions with their spins coupled by a Heisenberg exchange operator $-2J\ \boldsymbol{S}_1\cdot\boldsymbol{S}_2$ is given by equation (1). By fitting this to the experimental data

$$\chi_M = 2Ng^2\mu_B{}^2[\boldsymbol{k}T(e^{-2J/\boldsymbol{k}T} + 3)]^{-1} \qquad (1)$$

by the method of least squares we find g 2·09 and J −345 cm^{-1}, with the discrepancy index $[\Sigma(\chi_o - \chi_c)^2/\Sigma\chi_o{}^2]^{\frac{1}{2}} =$ 0·024. The calculated curve and experimental points are shown in Figure 5. (The fit is within experimental error over a range of *ca.* ±10 cm^{-1} in J, for fixed g.) We are not able to determine g directly because the sample did not give a detectable e.s.r. signal, but the value is not unreasonable. In unsolvated $[Cu_2(hpt)_2]$, whose detailed structure is not known, a value of −395 cm^{-1} has been estimated for J (assuming g 2·0, and allowing for *ca.* 1% of a paramagnetic impurity).[9]

Although many factors undoubtedly influence the value of J in compounds containing the Cu_2O_2 system, the Cu–O–Cu angle is currently regarded as being one of the most important, partly because theoretical arguments predict ferromagnetic coupling at 90° and antiferromagnetic coupling at 180°, presumably with a continuous variation in between.[23] A considerable body of experimental evidence has recently been accumulated bearing this out, and, indeed, for hydroxo-bridged complexes an almost linear inverse relationship appears to exist, with the change from positive to negative J occurring at an angle in the region of 98°.[1-3] Although we cannot expect such direct correlation of J with bridge angle in a series of complexes with different bridging ligands, we can compare the value of −345 cm^{-1} in $[Cu_2(hpt)_2(py)_2]$ (Cu–O–Cu 103°) with −298 in $[Cu_2(MeCO{\cdot}CH{:}CMe{\cdot}NH{\cdot}C_6H_4O)_2]$ (97 and 101°),[24] −312 in $[Cu_2(acac)_2(OCH_2Ph)_2]$ (101 and 106°),[22,25] *ca.* −280 in $[Cu_2(C_8H_{10}N_2O)_2]$ (104°),[5] −255 in $[Cu_2(Me_4en)_2(OH)_2]Br_2$ (104°),[26] −325 in $[Cu_2(pyO)_2Cl_4]$ (108°),[27] and +7·5 cm^{-1} in $[Cu_2(pyO)_4(NO_3)_4]$ (103°).[28] Apart from the apparent anomaly in the last case (which is readily explained [29] by the fact that this is an 'axial–

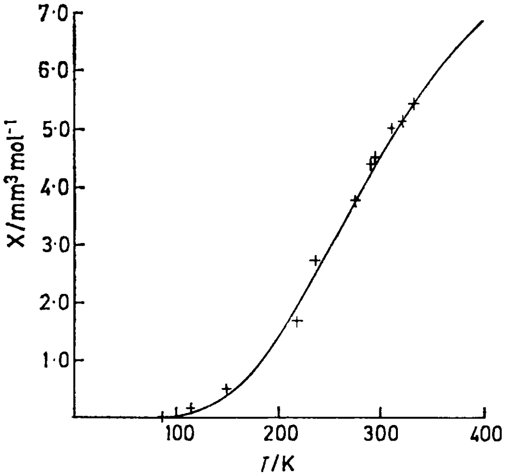

FIGURE 5 Magnetic susceptibility of $[Cu_2(hpt)_2(py)_2]$. Crosses show observed values, corrected on the assumption that the first-order paramagnetism falls to zero at 87 K. The curve is that calculated for g 2·09, J −345 cm^{-1}

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basal ' interaction in which each bridging oxygen atom is in contact with a spin-containing Cu orbital on one side only), these values show only a relatively modest spread. The rather scanty evidence available thus suggests that the angular dependence of J is less marked for angles between 100 and 109° than for those between 95 and 100°.

TABLE 5

Molar magnetic susceptibility,[a] and effective magnetic moment per Cu, after correction for TIP and diamagnetism

T/K	χ/mm^3 mol^{-1}	μ_{eff} [b]
334·8	5·42	0·76
324·2	5·08	0·72
315·3	4·96	0·71
298·1	4·45	0·65
294·9	4·36	0·64
276·8	3·72	0·57
240·2	2·70	0·45
216·4	1·65	0·34
150·2	0·42	0·14
115·8	0·15	0·07
87·0	0·0	0·0

[a] The values of χ in cm^3 mol^{-1} (c.g.s.) can be obtained by dividing the values shown by $4\pi \times 10^3$. [b] $\mu_{\mathrm{eff}} = 797{\cdot}6\,(0{\cdot}5\,\chi_M T)^{\frac{1}{2}}$.

It is interesting to compare the exchange interaction in $[\mathrm{Cu_2(hpt)_2(py)_2}]$ with that in the structurally similar $[\mathrm{Ni_2\{(Ph{\cdot}CO{:}CH{\cdot})_2CO\}_2(py)_4,4(py)}]$.*,[12] By regarding the latter as a system of two $S = 1$ ions interacting through an exchange term $-2J\,\boldsymbol{S}_1{\cdot}\boldsymbol{S}_2$, and fitting the magnetic data of Lintvedt *et al.* to the corresponding susceptibility equation,[12] we estimate g 2·06 and J −19 cm^{-1}.† The smallness of this value compared with that in the copper complex of similar structure is at first sight surprising, though it is in line with other experimental results showing that antiferromagnetic exchange in binuclear nickel(II) complexes rarely leads to $|J|$ values greater than *ca.* 20 cm^{-1},[30] whereas values ten or twenty times greater are common in copper(II) complexes. One reason for this difference is probably the presence of a competing ferromagnetic interaction in the nickel case, which we can roughly estimate as follows.

The exchange parameter for a pair of Ni^{2+} ions can be written in the form (2), with $S_{\mathrm{Ni}} = 1$, where θ and ε are

$$J_{\mathrm{Ni}} = [J(\theta\theta) + 2J(\theta\varepsilon) + J(\varepsilon\varepsilon)]_{\mathrm{Ni}}/4S_{\mathrm{Ni}}^2 \qquad (2)$$

the metal d_{z^2} and $d_{x^2-y^2}$ orbitals, respectively, and the exchange integrals $J(\phi_1\phi_2)$ are the diagonal matrix elements of the orbital part of the exchange operator.[7] The major negative (antiferromagnetic) interaction will be $J(\varepsilon\varepsilon)$, while $J(\theta\varepsilon)$ is expected to be positive. We shall make the assumption that $J(\theta\theta)$, the exchange interaction between the d_{z^2} orbitals (taking z perpendicular to the molecular plane), is negligible, which is a reasonable approximation in view of the small overlap of the latter with the triketone ligand orbitals. In the case of two Cu^{2+} ions in square-pyramidal co-ordination, the only interaction present is $J(\varepsilon\varepsilon)$, and the exchange parameter is given by equation (3), with $S_{\mathrm{Cu}} = \frac{1}{2}$. The exchange

$$J_{\mathrm{Cu}} = [J(\varepsilon\varepsilon)]_{\mathrm{Cu}}/4S_{\mathrm{Cu}}^2 \qquad (3)$$

integrals $J(\varepsilon\varepsilon)$ for nickel and copper will probably not be equal, since they depend on the ionisation potentials of the metal atoms, but we can get a rough estimate of their ratio by analogy with the case of cobalt and nickel. A value of *ca.* 1·3 for $[J(\varepsilon\varepsilon)]_{\mathrm{Ni}}/[J(\varepsilon\varepsilon)]_{\mathrm{Co}}$ is suggested by a comparison of the Néel temperatures of NiO and CoO,[7] while Nesbet has estimated theoretically a value of *ca.* 1·6 for this quantity.[31] Since a roughly similar increase is to be expected from Ni to Cu as from Co to Ni, we assume $[J(\varepsilon\varepsilon)]_{\mathrm{Cu}}/[J(\varepsilon\varepsilon)]_{\mathrm{Ni}}$ *ca.* 1·5 ± 0·2. From this, and the values of J_{Ni} and J_{Cu} found in the triketone complexes, we find by use of equations (2) and (3), $[J(\varepsilon\varepsilon)]_{\mathrm{Cu}}$ −345, $[J(\varepsilon\varepsilon)]_{\mathrm{Ni}}$ −230 ± 30, and $[J(\theta\varepsilon)]_{\mathrm{Ni}}$ +77 ± 15 cm^{-1}. It is seen that the overall $J_{\mathrm{Cu}} : J_{\mathrm{Ni}}$ ratio of *ca.* 18 : 1 consists of a normalisation factor of 4 due to the respective values of S^2, a factor of *ca.* 1·5 due to the intrinsically greater strength of e_g–e_g superexchange in the copper case, and a factor of *ca.* 3 due to ferromagnetic exchange effectively cancelling out two thirds of the antiferromagnetic interaction in $[\mathrm{Ni_2\{(Ph{\cdot}CO{:}CH{\cdot})_2CO\}_2(py)_4}]$. Obviously, this is an oversimplification; it will be inaccurate to the extent that $[J(\theta\theta)]_{\mathrm{Ni}}$ is different from zero, and of course it tells us nothing about the ligand orbitals contributing to the exchange integrals.

In the only other pair of structurally similar copper and nickel binuclear complexes whose magnetic properties have been compared, the compounds $[\mathrm{M_2(tren)_2(C_2O_4)}][\mathrm{BPh_4}]_2$ (M = Ni or Cu),[32] the copper complex shows no detectable exchange interaction, whereas the nickel complex has J *ca.* −17 cm^{-1}. In these compounds the ligand field is likely to be strongest perpendicular to the plane of the bridging oxalate ligand, so that the unpaired spin of the Cu^{2+} ion will be localised mainly in a d_{z^2} type orbital, and hence $J_{\mathrm{Cu}} = [J(\theta\theta)]_{\mathrm{Cu}}$, while J_{Ni} is still given by equation (2). It appears from the absence of exchange that $J(\theta\theta)$ is approximately zero in the copper complex (and presumably also in the nickel), which is in agreement with our foregoing assumption, though the reason may well be more subtle than a simple matter of σ overlap, as has been pointed out.[32] An unfortunate consequence is that in such cases the copper compound provides no information from which to estimate the relative magnitudes of the other terms in equation (2).

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* In making this comparison we need to be satisfied that the value of J will not be seriously affected by the presence of two axial ligands rather than one, and of different terminal groups in the triketones. Inspection of the data of Lintvedt *et al.*[12] for the compounds $[\mathrm{Ni_2\{(R{\cdot}CO{:}CH{\cdot})_2CO\}_2L_4}]$ and of Murtha and Lintvedt[10] and Baker *et al.*[9] for $[\mathrm{Cu_2\{(R{\cdot}CO{:}CH{\cdot})_2CO\}_2}]$ indicates that these differences will probably not affect J by >10—15%, which is sufficient for our purpose.

† Our result differs somewhat from that obtained by Lintvedt *et al.*,[12] namely, g 2·0 and J 18° (equivalent to −12·5 cm^{-1}).

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