DALTON
COMMUNICATION

Preparation, magnetic properties and crystal structure of bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II)

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The crystal structure of $[CuL_2]\cdot 2.5H_2O\cdot 0.5thf$ [L = 3-(4-pyridyl)pentane-2,4-dionate; thf = tetrahydrofuran] has been solved; a small intermolecular antiferromagnetic interaction between Cu sites implies that L would be useful in synthesising heterobimetallic and polymeric species with interesting magnetic properties.

The use of acetylacetonate (pentane-2,4-dionate) as a ligand in co-ordination chemistry is extremely widespread. Particular uses are in corrosion inhibitor models,[1] catalysis[2] and photochemistry.[3] Derivatives of this ligand have also been studied as components in molecular magnets.[4] One recently made derivative, 3-(4-pyridyl)pentane-2,4-dionate,[5] L, has relatively unknown co-ordination chemistry. Nevertheless it is of considerable interest due to its potential for being the basis of a wide range of new heterobimetallic complexes with tuneable properties. Of specific interest to our group are the bulk magnetic properties of any resulting materials.

In this communication we report the synthesis and full characterisation of $[CuL_2]\cdot 2.5H_2O\cdot 0.5thf$ (thf = tetrahydrofuran). We also present a review of the ability of the dione to mediate electronic exchange interactions, specifically to produce molecular magnetic materials. As yet only a few viable compounds have been found for this purpose. Research is dominated by complexes of oxalate,[6a] oxamide[6b] and cyanide.[6c] With only two exceptions[6c,7] the field of molecular magnetism has produced compounds with low critical temperatures, and even these are unstable under normal atmospheric conditions. Hence there is a need to discover new candidates which can commute magnetic interactions.

The compound HL was prepared by adaption of the method described by Sanders and co-workers.[5] Satisfactory ^1H NMR spectra were obtained in $CDCl_3$.

For the copper complex excess HL (0.5 g, 2.8 mmol) was added to a solution of $CuNO_3\cdot 2.5H_2O$ (0.15 g, 0.64 mmol) in MeOH–H_2O (1:1, v/v, 10 cm^3). Whilst stirring at ambient temperature $NaHCO_3$ (0.235 g, 2.8 mmol) was very slowly added. The resulting olive green precipitate was isolated and washed with H_2O and diethyl ether. Purification was by recrystallisation from thf giving green hexagonal plates suitable for X-ray diffraction (yield 82%). Microanalysis of the dried crystals was satisfactory (Found: C, 50.2; H, 5.6; Cu, 13.2; N, 5.9. $C_{20}H_{20}CuN_2O_4\cdot 2.5H_2O$ requires C, 49.9; H, 6.0; Cu, 13.2; N, 5.9%). Fast atom bombardment mass spectrometry gave the molecular ion at *m/z* 416 and both IR and UV/VIS spectroscopies gave characteristic bands. The crystal structural analysis of $[CuL_2]\cdot 2.5H_2O\cdot 0.5thf$‡ found the copper in a slightly distorted square-planar environment (Fig. 1) with the two dionates co-ordinating to the copper in the usual manner of β-diketones. This represents the first crystallographically characterised complex containing L. In the structure the C–C bond lengths are 1.49(2) for C(1)–C(2) and 1.50(1) Å for C(4)–C(5) as compared to the C–C bonds in the pyridyl fragment which range from 1.36 to 1.39 Å, this reflects their respective bond order. Since the C(3)–C(6) bond length is 1.49(1) Å it can be identified as a single bond and therefore delocalisation of the electronic system in L does not include this bond. This may suggest the absence of an electronic pathway between the copper centre and the nitrogen atoms. Furthermore, the pyridyl ring is aligned approximately perpendicular to the rest of the $[CuL_2]$ molecule which means that the p orbitals on C(3) and C(6) are unlikely to overlap. This lack of orbital pathway was confirmed by electron spin echo envelope modulation (ESEEM) spectroscopy in a thf–MeOH (1:1, v/v) glass at 8.4 K. One weakly coupled resonance was found at 13 MHz indicating no interaction between the unpaired electron density and the ^{14}N nuclear spin ($I = 1$, natural abundance 99.985%). The single resonance being due to an unpaired electron interaction with proton nuclei ($I = \frac{1}{2}$), probably those of the CH_3 unit.

Fig. 2 represents the intermolecular relationship within the crystal packing scheme and shows that any given molecule packs with two identical molecules above and below the CuO_4 plane, with the nitrogen atom of the second and third molecule pointing towards the copper atom of the first molecule. The distance between the copper centre of one molecule and the nitrogen atom of another molecule is 2.567(9) Å, which can only be considered a weak interaction not a formal bond. Therefore the co-ordination environment about the metal is distorted octahedral, as predicted from the Jahn–Teller theorem. Overall the system architecture is of a three-dimensional superstructure.

Since there is a possible Cu to Cu pathway, SQUID magnetometry can provide a more sensitive method than crystallography or ESEEM spectroscopy of investigating electronic exchange across L, by measuring any interaction communicated between the metal sites. The experiment was achieved with a Quantum Design MPMS-5 magnetometer in the range 300–2 K on 25 mg of finely powdered sample. The results from 2–40 K are shown in Fig. 3 in the form of a χT *versus* T graph

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‡ Crystal data: $C_{21}H_{20}CuN_2O_{6.5}$, $M = 467.94$, green hexagonal plates, crystal dimensions 0.20 × 0.20 × 0.10 mm, rhombahedral (hexagonal phase), space group $R\bar{3}c(h)$ (no. 167), $a = 23.10(1)$, $c = 22.760(4)$ Å, $U = 10\,519(8)$ Å^3, $D_c = 1.329$ g cm^{-3}, $Z = 18$, $F(000) = 4338$. Diffraction data were measured on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å), μ(Cu-Kα) = 16.18 cm^{-1}, $T = 22 \pm 1$ °C. The ω–2θ scan technique gave 3362 reflections of which 1898 were independent. Transmission factors 0.79 to 1.36. Absorption correction was by empirical methods and the program DIFABS.[8] The structure was solved by Patterson methods and refined by full-matrix least-squares calculations.[9] The final discrepancy factors were $R = 0.069$ and $R' = 0.078$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/439.

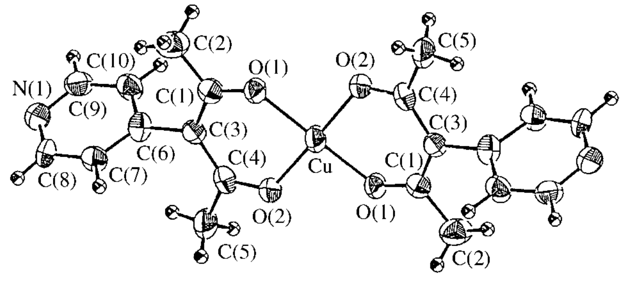

Fig. 1 An ORTEP[10] view of [CuL_2] showing 50% thermal ellipsoids and the atom numbering scheme

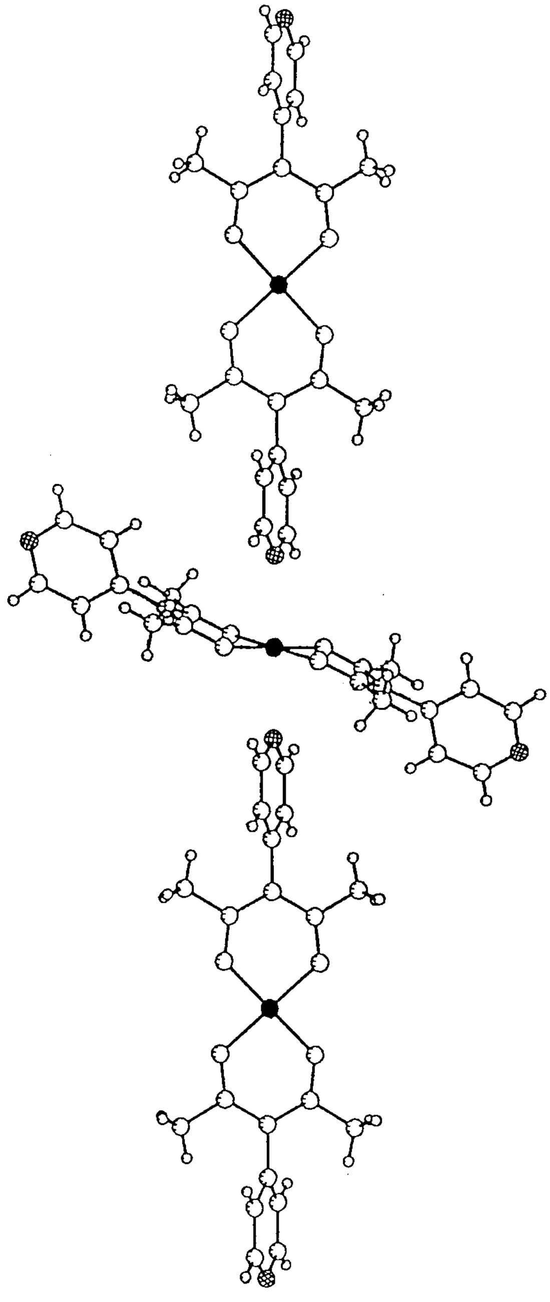

Fig. 2 Intermolecular relationship in [CuL_2]

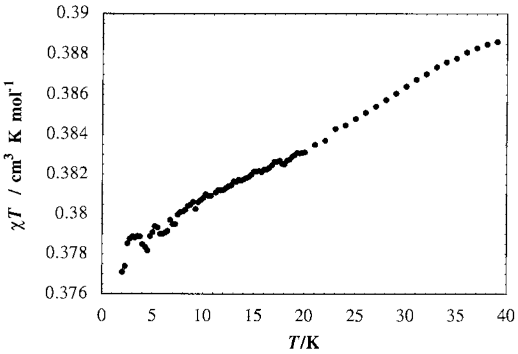

Fig. 3 Graph of χT *versus* T for [CuL_2] in the temperature range 2–40 K

where χ = molar susceptibility ($cm^3\ mol^{-1}$). The values of χT at 300 and 2 K are 0.46 and 0.37 $cm^3\ mol^{-1}$ respectively, indicating a small reduction in χT with decreasing temperature. Since there is an absence of spin–orbit coupling in this complex the reduction can only be due to an antiferromagnetic interaction between the metal centres. The curve is typical of weakly coupled centres, certainly with only nearest neighbour or short range interactions. A Curie–Weiss fit to the $1/\chi$ *versus* T curve in the high temperature (<50 K) regime gave a small, negative Curie constant of −4.4.

In conclusion L has proven to commute a weak interaction between metals co-ordinated to its oxygen and nitrogen donors. A full paper will explore the co-ordination chemistry of this compound for a wide range of transition and f-block metals and the magnetic behaviour of both homo- and hetero-metallic materials.

Acknowledgements

We would like to thank J. K. M. Sanders of Cambridge University Chemistry Department for correspondence regarding the preparation of HL and the EPSRC for financial support.

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Received 8*th January* 1997; *Communication* 7/00198C