Synthesis, Structure, and Magnetic Properties of a Novel Difluoro-bridged Copper(II) Dimer with Unusually Strong Antiferromagnetic Coupling

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The crystal structure of $Cu_2F_2(mppzH)_4(BF_4)_2$ contains dimeric co-square-planar cations $[(mppzH)_2Cu_2F_2(mppzH)_2]^{2+}$ (mppzH = 3-methyl-5-phenylpyrazole), and exhibits an unusually strong antiferromagnetic interaction.

During recent years it has become clear that the magnetic exchange in dimeric units MX_2M (where X = small bridging ligand) first of all depends on the orientation of the magnetic orbitals of the metal with respect to the bridging unit[1] and secondly on the bridging geometry, such as the M–X–M angle.[1,2] Examples of small bridging ligands are OH^-, Cl^-, Br^-, N_3^-, and MeO^-, and for each of these a variety of compounds has been prepared and studied by spectroscopic and

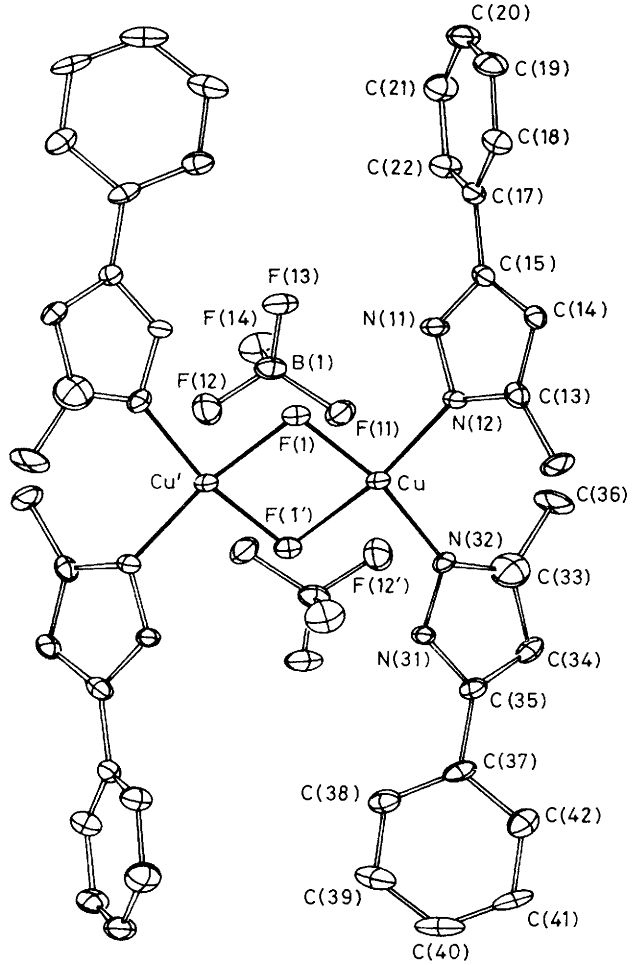

Figure 1. ORTEP drawing (20% probability ellipsoids) and atomic labelling system for $[Cu(mppzH)_2F]_2(BF_4)_2$. Important distances (Å) around copper are: Cu–F(1) 1.918(3); Cu–F(1′) 1.927(3); Cu–N(12) 1.952(4); Cu–N(32) 1.926(5); Cu–F(11) 2.537(4); Cu–F(12′) 2.692(4); B–F distances vary from 1.356 to 1.399 Å; distances in the phenyl and pyrazole rings are normal. Important bond angles are Cu′–F(1)–Cu 98.9(1); F(1)–Cu–F(1′) 81.1(1); N(12)–Cu–N(32) 102.0(2); F(11)–Cu–F(12′) 165.4(1)°.

magnetic techniques. For a more quantitative understanding of the magnetic exchange, using *e.g.* extended Hückel or angular overlap calculations, relatively simple systems, such as those having only one unpaired electron on each metal ion and having a limited number of electrons on the bridging ligand,[3] are required. Copper(II) is therefore the most studied metal ion. Although the simplest bridging ligand would be H^-, all known dimers are essentially diamagnetic. Other simple bridging ligands are F^-, O^{2-}, and OH^-.

Co-ordination compounds with O^{2-} and OH^- as a bridging ligand occur quite generally. Those with F^- as a bridging ligand, on the other hand, are very rare but have recently become available through controlled decomposition reactions of transition metal tetrafluoroborates in the presence of certain ligands.[4] Copper fluorides obtained so far, however, invariably are very weakly antiferromagnetic. We have now found that with the ligand 3-methyl-5-phenylpyrazole (mppzH) a species analysed as $Cu(mppzH)_2BF_5$ can be isolated, that shows a strong magnetic exchange coupling. The structure appears to be dimeric with CuF_2Cu units.

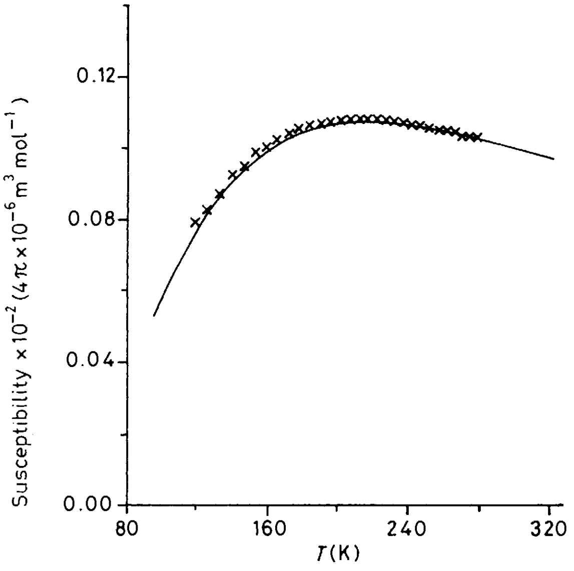

Figure 2. Magnetic susceptibility data for $[Cu(mppzH)_2F]_2(BF_4)_2$ in the range 120—300 K and the theoretical curve calculated according to the Bleaney–Bowers equation (ref. 9). The best fit was obtained with the following parameters g = 2.14(2) and $-J$ = 118.5(15); paramagnetic impurity less than 1%.

$Cu_2F_2(mppzH)_4(BF_4)_2$ [di-μ-fluoro-tetrakis(3-methyl-5-phenylpyrazole)dicopper(II) bis(tetrafluoroborate)], was prepared by reaction of hydrated copper(II) tetrafluoroborate (1 mmol) in 2 ml of triethyl orthoformate and ethanol (6 ml) with 2 mmol of mppzH in 8 ml of ethanol. When left for several days at 40 °C, blue crystals separated from the solution. These were isolated by filtration, washed with diethyl ether and dried at room temperature. The product was characterized by elemental analyses (Cu, C, H, N, B, and F) and spectroscopic techniques (i.r., u.v.-visible, and e.s.r.),† as well as by magnetic susceptibility measurements. To understand the unusual magnetic properties the crystal structure was determined,‡§ using a local set of programs developed by Kinneging and de Graaff.[6] Hydrogen atom positions were calculated. The hydrogens of the Me groups were not located at all, due to thermal movements.

A projection of the structure is depicted in Figure 1, together with the atomic labelling system used and some geometric information. Each copper(II) ion is co-ordinated by two F ions (bridging) and two mppzH ligands. The dimeric system seems to be further stabilized by hydrogen

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† I.r. bands originating from the ligand are (main bands only): 3370, 3345, 1572, 1495, 1480, 1414, 1300, 1275, 1207, 958, 809, 764, 692, and 469 cm^{-1}. In addition bands are observed at 1055 and 515 cm^{-1} (BF_4^- ions) and at 420 cm^{-1} (Cu–F stretching) and 340 cm^{-1} (metal–ligand vibration). Ligand field maximum occurs at 14 800 cm^{-1}. E.s.r. powder spectra show weak signals ascribed to an S = 1 system with a significant zero-field splitting (ref. 5).

‡ *Crystal data:* $C_{40}H_{40}Cu_2F_2N_8(BF_4)_2$, monoclinic, $P2_1/c$, a = 9.912(2), b = 9.993(2), c = 21.330(6) Å, β = 92.69(2)°, Z = 2 (calculated on the basis of 2 Cu per formula unit), D_m = 1.51 Mg m^{-3}, D_c = 1.527 Mg m^{-3}. Intensities of 1639 independent reflections [$I > 2\sigma(I)$] were obtained (Mo-K_α) from a crystal of 0.2 × 0.2 × 0.4 mm, R = 0.0521.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication no. SUP 23768 (9 pp.) from the British Library Lending Division. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.

bonding of the N–H groups to the fluoride ions. The BF_4^- ions co-ordinate weakly to the copper ions [Cu–F 2.531(5) and 2.693(2) Å]. This co-ordination may be designated as 'semi-co-ordination'[7] and may be compared with the co-ordination of BF_4 to copper in Cu(ethylenediamine)$_2$(BF_4)$_2$ [8] with Cu–F 2.56 Å. In fact the bridging of the BF_4 anion through the long Cu · · · F bonds is unique and has not been observed before for copper dimers. The observed Cu–F and Cu–N distances given in the caption to Figure 1 are considered normal for copper(II). The Cu–Cu distance of 2.922(2) Å is of the same order of magnitude as found for the well-known dihydroxo-bridged Cu dimers. The BF_4^- anions are attached to the cations *via* trifurcated hydrogen bonds with the N(11) and N(31) hydrogen atoms (F–N contacts between 2.72 and 3.14 Å; F · · · H contacts vary from 2.10 to 2.76 Å, whereas F · · ·N–H values are 89 to 163°). The pyrazole rings make angles of 35 and 53° with the CuN_2F_2 planes [Cu is 0.049(2) Å above this plane]. The angles between the phenyl and the pyrazole rings are 26 and 30°.

The symmetric bridging unit CuF_2Cu has not been observed before. The co-ordination squares of both copper ions are co-planar. Therefore, the magnetic orbitals can be considered to be co-square as well ($d_{x^2-y^2}$). The magnetic susceptibility of the compound (120—300 K) is shown in Figure 2, together with a least-squares fit to the Bleaney–Bowers equation for $S = 1$ dimers.[9] At temperatures below 80 K the compound appeared to be diamagnetic. The J value of the present compound ($-118\ \text{cm}^{-1}$) is much more negative than the value calculated for Cu(OH)$_2$Cu dimers with a Cu–O–Cu angle of 98.9° from the linear relationship of Hatfield and Hodgson[2] (calculated value $-65\ \text{cm}^{-1}$). This agrees with the predictions of Kahn[1] and Hoffman.[10] The larger electronegativity of fluorine compared with oxygen will result in more electron density in the bridge (and thus stronger antiferromagnetism[10]), whereas it will also decrease the value of the angle for which $J = 0$ (accidental degeneracy[10]).

The structure of this compound and its magnetic behaviour have opened the route for a new class of (anti)ferromagnetic dimers in which the size of the exchange coupling is determined by the bridge geometry and by the terminal ligands. The availability of a group of such compounds will allow detailed theoretical studies on the CuF_2Cu unit.

The authors are indebted to Dr. R. A. G. de Graaff and Mr. S. Gorter for their assistance in the *X*-ray analysis, and to Mr. B. J. M. van der Griendt for the magnetic susceptibility measurements. The present investigation was supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

Received, 12th August 1983; Com. 1103

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