The First Difluoro-bridged Copper Chain, an Alternating Zig-zag, Stabilized by a Unique Intrachain Hydrogen Bond System. Crystal and Molecular Structure of *Catena*-poly[di-μ-fluoro-bis(3-methyl-4-ethyl-5-phenylpyrazole)copper(II)].

Fennegien S. Keij,[a] Rudolf A. G. de Graaff,[a] Jaap G. Haasnoot,[a] Ad J. Oosterling,[a] Erik Pedersen,[b] and Jan Reedijk[a]*

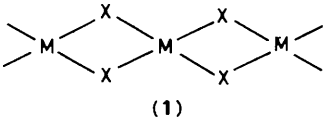
[a] *Gorlaeus Laboratories, Department of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

[b] *Department of Inorganic Chemistry, H. C. Ørsted Institute Universitetsparken 5, DK-2100 København, Denmark*

The synthesis, structure and magnetism of *catena*-poly[di-μ-fluoro-bis(3-methyl-4-ethyl-5-phenylpyrazole)copper(II)], $[CuF_2(C_{12}H_{14}N_2)_2]_\infty$ is described; a unique next-nearest neighbour hydrogen-bonding stabilization between N–H and the bridging fluoride ions is observed.

Co-ordination compounds of the type $M^{II}X_2(L)_2$ quite often have the linear-chain type structure (**1**), with L completing the distorted octahedral co-ordination, for M = Mn, Fe, Co, Ni, Cu; X = Cl, Br; and L, a variety of ligands.[1,2] However the number of *X*-ray structures known is rather small, apparently because polymeric structures are difficult to grow as single crystals. The synthesis of this type of compound, the characterization, and the determination of the structure is of great interest for a better understanding of the magnetic properties of chains, *e.g.* exchange-structure relationship and the presence of solitons.[1,3]

Difluoro-bridged chain compounds of the type $MF_2(L)_2$ (L = azole ligand) have never been sufficiently characterized structurally; only amorphous or microcrystalline products have been reported so far.[4] For Cu^{II}, a monofluoro bridged linear chain, though part of a polymeric network, has been



(**1**)

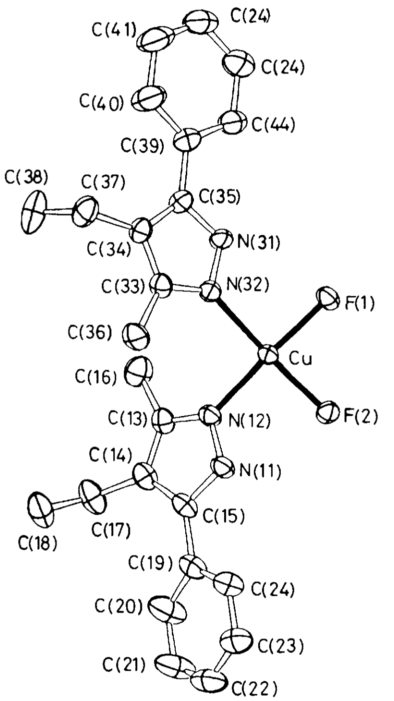


Figure 1. ORTEP drawing and atomic labelling system for the monomeric unit of $[CuF_2(L1)_2]_\infty$. Selected bond distances (Å) and angles (°) are Cu–N(12) 1.992(2), Cu–N(32) 1.996(2), Cu–F(1) 1.916(2), Cu–F(2) 1.915(1), F(1)–Cu–F(2) 88.66(6), N(12)–Cu–N(32) 95.86(9), F(1)–Cu–N(32) 88.49(9), F(2)–Cu–N(12) 88.51(8), C(16)–C(36) 3.629(5).

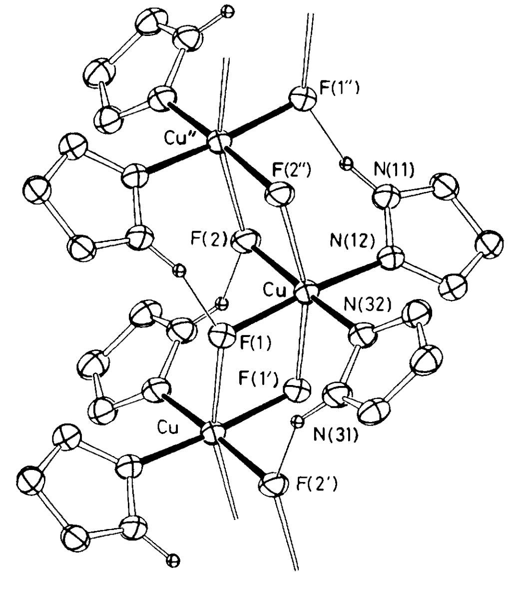


Figure 2. ORTEP drawing and atomic labelling system showing the extended structure of $[CuF_2(L1)_2]_\infty$. Selected bond distances (Å) and angles (°) are Cu–Cu′ 3.330(2), Cu–Cu″ 3.294(2), Cu–F(1)′ 2.448(2), Cu–F(2)″ 2.400(2), Cu′–Cu–Cu″ 117.79(2), Cu–F(1)–Cu′ 98.70(6), F(1)–Cu–F(1)′ 81.30(6), Cu–F(2)–Cu″ 98.89(6), F(2)–Cu–F(2)″ 81.11(6) N(11)–F(1)″ 2.693(3), N(11)–H(11)–F(1)″ 145.76(9), N(31)–F(2)′ 2.714(3), N(31)–H(31)–F(2)′ 142.32(9). Primed atoms are generated by symmetry operations: single prime = $1-x, -y, 1-z$; double prime = $1-x, -1-y, 1-z$.

recently reported for $FCu[AuF_4]$.[5] A diamagnetic difluoro-bridged zig-zag chain is reported for dioxouranium(VI) in *catena*-poly[di-μ-fluoro-(dimethyl sulphoxide)dioxouranium-(VI)].[6]

The formation of $MF_2(L)_2$ chain compounds has been made possible through controlled release of F^- from BF_4^- ions in the presence of azole ligands.[7] Later a few hydrated fluorides were also found to yield $MF_2(L)_2$ species.[8] However, so far structural characterization of such compounds has not been possible, despite numerous efforts to grow single crystals.

We now report an approach in which systematic variation in the ligand, in this case a substituted pyrazole, has yielded the first single crystal of a difluoro-bridged transition metal chain. The ligand 3-methyl-4-ethyl-5-phenylpyrazole (L1) was synthesized from hydrazine hydrate and 2-ethyl-1-phenyl-butane-1,3-dione.[9] $CuF_2(L1)_2$ was synthesized by adding a warm solution of L1 (4 mmol) in methanol (25 ml) to a warm suspension of $CuF_2{\cdot}2H_2O$ (1 mmol) in methanol (25 ml); after several minutes stirring the remaining insoluble $CuF_2{\cdot}2H_2O$ was filtered off. The resulting green solution was kept in a plastic vessel for 3 weeks after which pale green needle-like crystals formed.

The crystal structure was determined.† A projection of the monomeric unit is depicted in Figure 1, together with the atomic labelling. The structure consists of Cu^{II} ions co-ordinated by two pyrazole nitrogen atoms and two fluoride ions in a distorted square-planar arrangement; the axial ligands, two fluoride ions of nearby copper atoms (related to the central copper by an inversion centre), have significantly longer Cu–F bond lengths. Figure 2 shows the chain structure of the compound. The zig-zag chains, consisting of two different CuF_2Cu units, are positioned along the *b*-axis; copper–copper distances are 3.330(2) and 3.294(2) Å. The polymeric structure is stabilized further by hydrogen bonding of the pyrazole N–H to fluoride ions of nearby copper ions (ν_{N-H} 2800 cm^{-1}).

This structure is very different from the linear chain type structure (**1**) found for most transition metal halide bridged chains. The tendency of fluoride ions and the pyrazole N–H to form hydrogen bridges is strong. The pyrazole N–H cannot form hydrogen bridges with the fluoride ion which is nearest, since the angle formed would be too small. The presence of hydrogen bridges between neighbouring units in the chain imposes non-linearity on the chain structure, forcing the fluoride ions and the pyrazole ligands into a *cis*-configuration around the copper ion.

The co-ordination geometry around the copper ion results in a magnetic orbital consisting mainly of $d_{x^2-y^2}$. As these two magnetic orbitals are not in the same plane, overlap between the magnetic orbitals is minimal and the magnetic interaction in this compound is expected to be small. Indeed the magnetic susceptibility measurement shows no maximum down to 5 K.

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† *Crystal data* for $C_{24}H_{28}CuF_2N_4$, triclinic, $P\bar{1}$, $a = 13.888(6)$, $b = 5.671(3)$, $c = 15.181(6)$ Å, $\alpha = 91.95(4)$, $\beta = 111.56(3)$, $\gamma = 92.93(4)°$, $Z = 2$, $D_c = 1.42$ Mg m^{-3}, $F(000) = 471$. Intensities for 5432 independent reflections were measured on an Enraf-Nonius CAD-4 automatic diffractometer (Mo-K_α). The structure was solved using MULTAN and Fourier techniques and refined by least-squares methods. For one ethyl carbon, C(38), three different positions were found, owing to disorder in the structure. Hydrogen atom positions were calculated and the hydrogen atoms were kept at a fixed distance from their parent atom. The hydrogen atoms of the methyl groups and of the ethyl CH_3 were not located, owing to thermal motion. Final $R = 0.042$ ($R_w = 0.058$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Magnetic measurements at lower temperatures will give more information about the exchange in this compound.

Our results show that fluoro-bridged copper chain compounds can indeed be prepared, and studied structurally and magnetically. Compounds can be prepared with derivatives of 5-phenylpyrazole, on which preliminary measurements indicate that their structures are analogous to the structure of the compound presented here. This will be of importance in understanding the magnetic properties of fluoro-bridged transition metal chain compounds and a detailed comparison of structural and magnetic properties of halide bridged one-dimensional metal compounds will now become possible.

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