Dimeric Fluoro-bridged Copper(II) Co-ordination Compounds

By RICHARD W. M. TEN HOEDT and JAN REEDIJK*

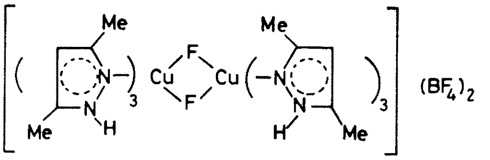
(*Department of Chemistry, Gorlaeus Laboratories, State University Leiden,*
P.O. Box 9502, 2300 *RA Leiden, The Netherlands*)

Summary The syntheses and characterisation of the first Cu^{II} dimers containing the CuF_2Cu group as a bridging unit are described.

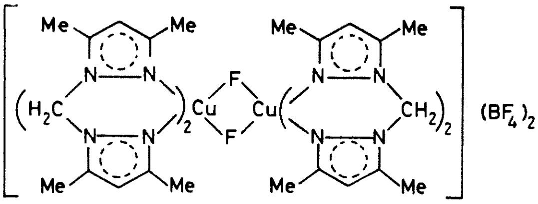
SINCE the first communication concerning the formation of fluoride-bridged polynuclear compounds (MF_2L_2; M = Co, Mn, Cd and L = 3,5-dimethylpyrazole) *via* ligand and solvent induced decomposition of the BF_4^- ion,[1] a few more reports have shown that the application of this method provides a simple synthesis for a variety of dimeric, tetrameric, and polymeric fluoride-bridged metal compounds.[2-6] However, so far, no copper compounds of these types have been obtained. In view of the reported linear relationship between the superexchange coupling parameter J and the bridging angle in hydroxo-bridged copper(II) dimers,[7] a study of the corresponding fluoro-bridged compounds would be of great interest.

In this communication we report the first two examples of such fluoro-bridged copper(II) dimers. The first compound, (**1**), was obtained by reaction of $Cu(H_2O)_6(BF_4)_2$ with 3,5-dimethylpyrazole (dmpz) using ethanol as a solvent, and correctly analysed as $Cu_2F_2(dmpz)_6(BF_4)_2$. The second compound, (**2**), was prepared by reaction of (**1**) in ethanol with the ligand bis(3,5-dimethylpyrazolyl)methane (bdpm) and correctly analysed as $Cu_2F_2(bdpm)_4(BF_4)_2$. Both (**1**) and (**2**) are stable, blue compounds (m.p. >230 °C).

Evidence for the structures of (**1**) and (**2**) was deduced from e.s.r. and far-i.r. spectra. The e.s.r. spectra (obtained both at X-band and at Q-band frequencies) are characteristic of triplet-state compounds. At room temperature and at 77 K both $\Delta m = 1$ and $\Delta m = 2$ transitions are observed. In frozen solution (CH_2Cl_2, dimethyl sulphoxide) the $\Delta m = 2$ line is split into 7 lines ($A = 75$ G), as expected for hyperfine splitting due to coupling with 2 Cu ($I = 3/2$) nuclei. Spectra recorded at different temperatures show no significant changes in intensities of the resonance lines for both compounds. This indicates that both (**1**) and (**2**) have a very small separation between the singlet and the triplet level, as is further supported by low-temperature magnetic susceptibility measurements. No maxima were observed in the susceptibility χ *vs.* temperature curves down to 2 K. This indicates that the exchange coupling, $|J|$, is $<0{\cdot}4$ cm^{-1}.



(**1**)



(**2**)

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According to Hendrickson *et al.*[8] additional e.s.r.-lines may be expected for Cu-dimers with very small J-values. Indeed, both (**1**) and (**2**) show the presence of a few extra lines which cannot be assigned to intra-triplet transitions. Detailed assignments of the e.s.r. spectra are therefore quite complicated and need further measurements at varying frequencies. At present, only approximate parameters can be given: compound (**1**) ($D = 0{\cdot}10$ cm^{-1}, $E \leqslant 0{\cdot}01$ cm^{-1}, $g_{\parallel} = 2{\cdot}09$, $g_{\perp} = 2{\cdot}26$), compound (**2**) ($D = 0{\cdot}06$ cm^{-1}, $E \leqslant 0{\cdot}01$ cm^{-1}, $g_{\parallel} = 2{\cdot}23$, $g_{\perp} = 2{\cdot}08$). These parameters suggest that the co-ordination geometry of (**1**) is based on a d_{z^2} ground state (*i.e.* most likely trigonal bipyramidal) and that of (**2**) on a $d_{x^2-y^2}$ ground state (*i.e.* distorted octahedral).[9]

Ligand-field spectra of both compounds show a maximum at 14,000 cm^{-1}, although (**2**) has a low-energy shoulder at about 10,000 cm^{-1}. These data are in agreement with the structures proposed above.

The small value for $|J|$ in both compounds may seem quite surprising considering the expected short Cu $\cdots$ Cu distance in F-bridged dimers. However, the unpaired electron in compound (**1**) is probably localized in the orbital pointing towards a single F^- ion. This apparently results in weak exchange *via* bridging F^- anions, since this is not an effective exchange pathway for the unpaired electron.[10] A similar small value for the magnetic exchange, J, was found in the crystallographically established corresponding Co^{II} dimer.[3] The small value of $|J|$ in (**2**) must be due to counterbalancing effects of antiferromagnetic and ferromagnetic terms, just as found for hydroxo-bridged dimers having a Cu–O–Cu angle of *ca.* 97·5°. Another explanation could be a ground-state orbital outside the CuF_2Cu plane.[10]

Additional support for the CuF_2Cu units comes from the far-i.r. spectra. Compound (**1**) has a spectrum similar to that of $Co_2F_2(dmpz)_6(BF_4)_2$, whereas (**2**) shows absorptions similar to those of other members of the series $M_2F_2(bdpm)_4(BF_4)_2$ for which dimeric structures have also been proposed.[4] The strong absorption bands at 443 [(**1**)] and 458 [(**2**)] cm^{-1} are tentatively assigned to Cu–F stretchings.

For a full understanding of the magnetic behaviour, as a function of the bridge geometry, single crystal X-ray studies for these and related compounds are needed.

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