# Tetrakis(imidazole)copper(II) Fluorides. The Crystal and Molecular Structure of Diaquatetrakis(imidazole)copper(II) Difluoride †

**Wim Vreugdenhil, Paul J. M. W. L. Birker, Richard W. M. ten Hoedt, Gerrit C. Verschoor, and Jan Reedijk** *
*Department of Chemistry, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Two new fluoride-containing co-ordination compounds $[Cu(Him)_4(H_2O)_2]F_2$ and $[Cu(Him)_4][BF_4]F$ (Him = imidazole) are described. From i.r. spectra, ligand-field spectra, and e.s.r. spectra it is concluded that the fluoride ions in both compounds are not co-ordinated to the metal ion. The crystal structure determination of $[Cu(Him)_4(H_2O)_2]F_2$ confirmed these conclusions. The compound crystallizes in space group $C2/c$, with cell dimensions $a = 12.708(3)$, $b = 10.299(2)$, $c = 13.915(3)$ Å, $\beta = 106.63(2)°$, and $Z = 4$. The structure was solved using direct phasing and difference-Fourier techniques and refined by full-matrix least-squares methods. The final discrepancy factor, $R = 0.027$, was based on 1 468 reflections. The copper ions are co-ordinated by four imidazoles and two water molecules. The $F^-$ ions are not co-ordinated to copper. They are strongly hydrogen bonded in a distorted tetrahedron of two imidazole H atoms and two H atoms of water molecules.

Decomposition of transition-metal tetrafluoroborate compounds is a promising method for the preparation of fluoride-containing co-ordination compounds. Linear, dimeric, and tetrameric structures have been reported.[1-8] In all these compounds the fluoride ions form bridges between metal ions. As an extension of the investigations on $(Cu{-}F_y)_x$ compounds ($y = 1$ or 2; $x = 2$) we applied a ligand-exchange reaction, starting from $[Cu_2F_2(Hdmpz)_6][BF_4]_2$ (Hdmpz = 3,5-dimethylpyrazole). Spectroscopic and magnetic characterization indicate that $[Cu_2F_2(Hdmpz)_6][BF_4]_2$ is a fluoro-bridged copper dimer. Some results of this investigation have already been published, dealing only with derivatives of pyrazoles as exchanging ligands.[4,5] Exchange reactions with other pyrazoles appear to maintain the $Cu_2F_2$ core. In the present paper we describe exchange reactions of $[Cu_2F_2(Hdmpz)_6][BF_4]_2$ with imidazole (Him), leading to mononuclear copper–imidazole compounds, with fluoride counter ions, and the *X*-ray analysis of one of the formed products.

## Experimental

*Synthesis of* $[Cu(Him)_4(H_2O)_2]F_2$ *and* $[Cu(Him)_4][BF_4]F$.—The complex $[Cu_2F_2(Hdmpz)_6][BF_4]_2$ (0.5 mmol) and (Him) (5 mmol) were refluxed for 30 min in acetonitrile (20 cm³) containing 1% of $H_2O$ {for $[Cu(Him)_4(H_2O)_2]F_2$}, or in ethanol (10 cm³) {for $[Cu(Him)_4][BF_4]F$}. In both cases a dark blue precipitate was formed which was filtered off, washed with diethyl ether, and dried *in vacuo*. Alternatively, we also succeeded in synthesizing $[Cu(Him)_4(H_2O)_2]F_2$ from a suspension of $CuF_2$ (5 mmol) and Him (30 mmol) in ethanol (10 cm³); $[Cu(Him)_4][BF_4]F$ could also be prepared from a suspension of $CuF_2$ (1 mmol), $Cu(BF_4)_2$ (1 mmol), and Him (8 mmol) in ethanol (15 cm³). Crystals suitable for *X*-ray analysis were obtained from a saturated solution (at 20 °C) of $[Cu(Him)_4(H_2O)_2]F_2$ in ethanol after cooling to −20 °C.

*Analysis and Spectroscopic Measurements.*—Copper was determined by standard ethylenediaminetetra-acetic acid titrations; C, H, N, and F analyses were carried out by the ' Mikroanalytisches Laboratorium ' of Dr. E. Pascher, Bonn. Infrared spectra (4 000—180 cm$^{-1}$) were recorded on a model 580 Perkin-Elmer i.r. spectrometer, using Nujol mulls, KBr pellets and polyethylene pellets (in the region 600—180 cm$^{-1}$). U.v.-visible spectra (35 000—4 000 cm$^{-1}$) were obtained on a Beckman DK-2A spectrophotometer by using the diffuse-reflectance technique, with MgO as a reference. E.s.r. spectra were recorded on a Varian E-3 (9.5 GHz) spectrometer using powdered samples and frozen ethanol solutions. Conductivities were determined as $10^{-3}$ mol dm$^{-3}$ solutions in methanol. Analytical and spectroscopic data are listed in Table 1.

X-*Ray Structure Determination.*—Crystal data were collected on an Enraf-Nonius CAD-4 single-crystal diffractometer.

*Crystal data.* $C_{12}H_{20}CuF_2N_8O_2$, $M = 409.86$, $a = 12.708(3)$, $b = 10.229(2)$, $c = 13.915(3)$ Å, $\beta = 106.63(2)°$, space group $C2/c$, $U = 1\,733.2$ Å³, $D_m = 1.57(2)$, $Z = 4$, $D_c = 1.570$ g cm$^{-3}$, $F(000) = 845$, Mo-$K_\alpha$ radiation (graphite monochromator), $\lambda(\text{Mo-}K_\alpha) = 0.709\,30$ Å, $\mu(\text{Mo-}K_\alpha) = 13.0$ cm$^{-1}$, $T = 20$ °C, crystal dimensions 0.45 × 0.27 × 0.17 mm.

*Data collection, solution, and refinement.* Cell parameters were determined by least-squares fit to the setting angles of 25 centred reflections with $10 < \theta < 14°$. Intensity data were collected in the range $2 \leqslant \theta \leqslant 28°$. Reflections were scanned using the $\omega/\theta$ mode in a maximum scan time of 90 s. Three check reflections indicated a variation in standard intensity of ±6%. A total of 2 089 unique data were collected of which 1 468 were used in the refinement. Final residual indices were $R = \{\Sigma(||F_c| - |F_o||)/\Sigma|F_o|\} = 0.027$ and $R' = \{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.033$. The structure was solved using direct methods (MULTAN 78) and difference-Fourier techniques. In the least-squares refinement weights $(\sigma_F)^{-2}$ were used. All hydrogen atoms were located from difference-Fourier maps. All atoms were refined anisotropically, with the exception of the hydrogen atoms, which were refined isotropically. Atomic scattering factors were taken from International Tables.[9] The final difference-Fourier maps did not show significant features. Final atomic parameters are given in Table 2.

## Results and Discussion

*Description of Structure.*—In the fluoro-containing co-ordination compounds so far reported,[1-8] the $F^-$ ions are invariably co-ordinated to a metal ion. In the present compound the fluoride ions are not co-ordinated to the copper ion

---

† *Supplementary data available* (No. SUP 23815, 11 pp.): structure factors, thermal parameters, H-atom co-ordinates, bond lengths and angles of imidazole ligands. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

**Table 1.** Spectroscopic and analytical data for $[Cu(Him)_4(H_2O)_2]F_2$, $[Cu(Him)_4][BF_4]F$, and $[Cu(Him)_4][BF_4]_2$

| | Analysis [a] (%) | | | | | $10^{-3}\lambda_{max.}/cm^{-1}$ | | E.s.r. | | $\Lambda$ [b]/ohm$^{-1}$ cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Cu | C | H | N | F | Solid | Solution [b] | Solid | Solution [c] | |
| $[Cu(Him)_4(H_2O)_2]F_2$ | 16.20<br>(15.50) | 34.30<br>(35.15) | 4.75<br>(4.93) | 26.65<br>(27.35) | | 18.0 | 15.6 | $g = 2.10$ | $g_\perp = 2.04$<br>$A_\perp = 15$<br>$g_\parallel = 2.25$<br>$A_\parallel = 183$ | 96 |
| $[Cu(Him)_4][BF_4]F$ | 14.10<br>(14.40) | 32.10<br>(32.65) | 3.70<br>(3.65) | 25.15<br>(25.30) | 21.5<br>(21.5) | 17.8 | 16.2 | $g = 2.05$ | $g_\perp = 2.04$<br>$A_\perp = 15$<br>$g_\parallel = 2.25$<br>$A_\parallel = 181$ | 137 |
| $[Cu(Him)_4][BF_4]_2$ [d] | | | | | | 18.6 | 16.3 | $g_\perp = 2.06$<br>$g_\parallel = 2.24$<br>$A_\parallel = 195$ | $g_\perp = 2.04$<br>$A_\perp = 15$<br>$g_\parallel = 2.25$<br>$A_\parallel = 178$ | 197 |

[a] Calculated values are given in parentheses. [b] Obtained as a solution in methanol. [c] Frozen solution in ethanol; $A$ values are in G ($=10^{-4}$T).
[d] Compound prepared for comparison of spectral properties (see J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 1451).

**Table 2.** Final fractional atomic co-ordinates ($\times 10^4$) of non-hydrogen atoms, with estimated standard deviations in parentheses

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| Cu | 2 500 | 2 500 | 0 |
| N(11) | 3 485(1) | 967(2) | 398(1) |
| C(12) | 3 327(2) | −202(2) | 7(2) |
| N(13) | 4 101(2) | −1 033(2) | 488(2) |
| C(14) | 4 803(2) | −360(2) | 1 238(2) |
| C(15) | 4 425(2) | 870(2) | 1 178(2) |
| N(21) | 2 352(1) | 2 562(2) | 1 419(1) |
| C(22) | 2 985(2) | 3 170(2) | 2 199(2) |
| N(23) | 2 691(2) | 2 932(2) | 3 027(1) |
| C(24) | 1 812(2) | 2 105(2) | 2 762(2) |
| C(25) | 1 607(2) | 1 879(2) | 1 771(1) |
| O | 5 814(2) | 4 093(2) | 4 344(1) |
| F | 3 965(1) | 3 486(1) | 4 859(1) |

but are instead strongly hydrogen bonded to two imidazole N–H groups and two water molecules. The co-ordination around copper is elongated tetragonal with four imidazoles as equatorial ligands and the water molecules as axial ligands (see Table 3). Figure 1 shows the cation $[Cu(Him)_4(H_2O)_2]^{2+}$ with the atom-labelling system. In Figure 2 a stereodiagram of the unit cell is shown. Figure 3 illustrates the hydrogen bonding around the fluoride ion.

The relevant interatomic distances and angles around $Cu^{II}$ are presented in Table 3 and in the supplementary publication. The bond lengths and angles around the hydrogen-bonded fluoride ions are collected separately in Table 4. The copper–nitrogen distances fall in the range usually observed for Cu–N(azole) ligands.[5,8,10–12] The copper–oxygen distances of 2.638 Å are in the range observed for semi-co-ordination [13,14] and is a clear consequence of the $^2E_g$ ground state of $Cu^{II}$ resulting in a Jahn–Teller stabilization by splitting in $^2A_{1g}$ and $^2B_{1g}$ (see also below for spectral behaviour). The present copper–oxygen distances are nevertheless significantly larger than the value of 2.456 Å in $[Cu(dmtp)_4(H_2O)_2][PF_6]_2$ (dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine), with a very similar co-ordination geometry,[15] and also longer than in $[Cu(C_{14}H_{24}N_4)(H_2O)_2][NO_3]_2$ ($C_{14}H_{24}N_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene), where 2.556 Å was found.[16] The strong hydrogen-bonding interaction in the present compound seems to weaken the axial interaction of the water molecules with the copper ion.

The most unusual aspect of the structure is the fact that the fluoride ions do not co-ordinate to the metal ion, as would be expected for an electronegative ion, but instead are hydrogen bonded to the water molecules. Figure 3 illustrates the hydrogen-bonding network through which the cations are linked *via* the fluoride anions. Each fluoride ion is in a distorted tetrahedron, strongly hydrogen bonded by two water molecules and two imidazole rings (F–N distances are *ca.* 2.65 Å and F–O *ca.* 2.70 Å, see Table 4). In this way infinite chains, consisting of $\rangle O\text{–}Cu\text{–}O\langle{}^{F}_{F}\rangle O\text{–}Cu\text{–}O\langle$ units, are formed. The O···F and N···F contacts are comparable to those found in other hydrated fluorides and related compounds.[17]

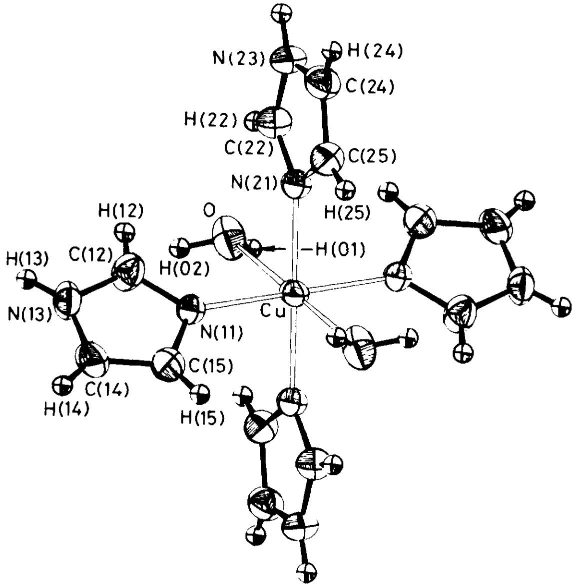

**Figure 1.** ORTEP drawing (50% probability ellipsoids) of the cation $[Cu(Him)_4(H_2O)_2]^{2+}$

*Spectroscopic Data.*—The unique non-metal-binding behaviour of the fluoride ions was already expected from the spectroscopic measurements. The absence of Cu–F bands in the far-i.r. region suggested that no fluoride ions were co-ordinated. The ligand-field maximum of *ca.* 18 000 cm$^{-1}$ resembled the ligand-field maximum of $[Cu(Him)_4][BF_4]_2$, again indicating a $CuN_4$ chromophore with weak axial

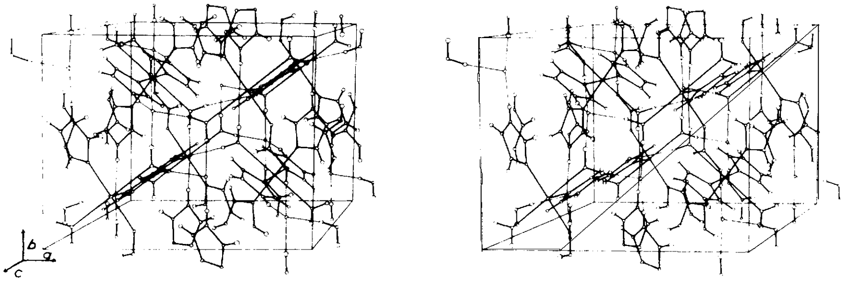

**Figure 2.** ORTEP stereodrawing of the unit cell, showing the hydrogen-bonding network (thin lines)

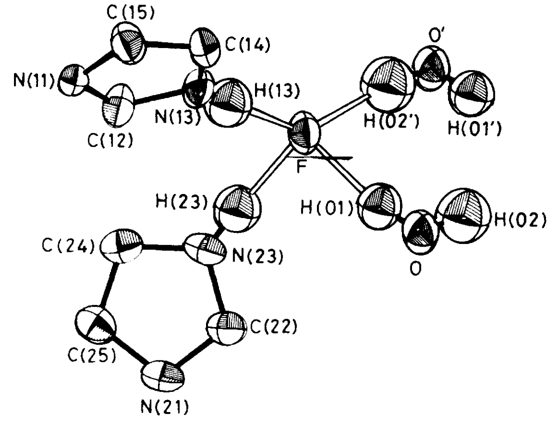

**Figure 3.** Hydrogen-bonding scheme for the fluoride ions in $[Cu(Him)_4(H_2O)_2]F_2$. Symmetry operation for ring 1: $x$, $-y$, $z + \frac{1}{2}$; for O′, H(O1′), and H(O2′): $-x + 1$, $-y + 1$, $-z + 1$; and for all other atoms: $x$, $y$, $z$

**Table 3.** Bond lengths (Å) and angles (°) around copper in $[Cu(Him)_4(H_2O)_2]F_2$ with estimated standard deviations in parentheses

| | |
|---|---|
| Cu–N(11) | 1.984(2) |
| Cu–N(21) | 2.033(2) |
| Cu–O′ | 2.638(2) |
| N(11)–Cu–N(21) | 88.84(6) |
| N(11)–Cu–O′ | 90.37(7) |
| N(21)–Cu–O′ | 86.39(7) |

A prime indicates the symmetry operation $-x + 1, y, -z + \frac{1}{2}$.

**Table 4.** Bond lengths (Å) and angles (°) around the fluoride ions in $[Cu(Him)_4(H_2O)_2]F_2$ with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| F′–H(13″) | 1.83(3) | F′–N(13″) | 2.647(2) |
| F′–H(23′) | 1.81(3) | F′–N(23′) | 2.661(2) |
| F′–H(01′) | 1.89(3) | F′–O′ | 2.717(2) |
| F′–H(02‴) | 1.81(3) | F′–O‴ | 2.695(2) |
| H(13″)–F′–H(23′) | 95(1) | H(23′)–F′–H(01′) | 97(1) |
| H(13″)–F′–H(01′) | 108(1) | H(23′)–F′–H(02‴) | 123(1) |
| H(13″)–F′–H(02‴) | 136(1) | H(01′)–F′–H(02‴) | 89(1) |

A prime indicates the symmetry operation: $x$, $y$, $z$; two primes: $-\frac{1}{2} + x, \frac{1}{2} + y, z$; three primes: $-x + 1, -y + 1, -z + 1$.

ligands.[14,16] In the case of a $CuN_4F_2$ co-ordination a ligand-field maximum at lower energy is expected.[14,15]

Frozen ethanol solutions of $[Cu(Him)_4][BF_4]_2$, $[Cu(Him)_4][BF_4]F$, and $[Cu(Him)_4(H_2O)_2]F_2$ all gave similar e.s.r. spectra: $g_\perp = 2.04$, $A_\perp = 15$ G, $g_\parallel = 2.25$, $A_\parallel = 180$ G. There was hardly any influence of the anion on the e.s.r. spectra. This indicates that in the solutions of $[Cu(Him)_4][BF_4]F$ and $[Cu(Him)_4(H_2O)_2]F_2$ and of $[Cu(Him)_4][BF_4]_2$ the same species must exist. From the nitrogen superhyperfine splitting (9 lines) in the spectra it is concluded that the solutions contain $[Cu(Him)_4]^{2+}$ chromophores.

The ligand-field spectra of ethanol solutions all showed a maximum at *ca.* 16 000 cm$^{-1}$ (see Table 1). This indicates [14,18] that the axial interaction is slightly larger than in the solid state, probably due to different hydrogen bonding.

The equivalent conductivities of methanol solutions of these three compounds decreased with the increasing number of fluoride ions. This effect can be ascribed to the difference in ionic mobilities of the anions or to partial association between the cations and the anions. The strong N–H · · · F hydrogen bonding in the solid state was in fact predicted from the i.r. spectra, since eight peaks are observed in the region 4 000—2 000 cm$^{-1}$, varying from 3 400 to 2 600 cm$^{-1}$. The bands in this spectral region are in fact similar to those in the i.r. spectra of $[Ni(Him)_6][O_2CH]_2$ and of $[Ni(Him)_6][tcp]_2$ (tcp = 2,4,6-trichlorophenolate).[19,20] The low N–H stretching vibrations in all these compounds are undoubtedly due to strong hydrogen bonding between the anions and the N–H group.

## Conclusions

As far as we know the two compounds $[Cu(Him)_4(H_2O)_2]F_2$ and $[Cu(Him)_4][BF_4]F$ are the first examples of copper co-ordination compounds containing fluoride counter ions which are not co-ordinated to the metal ion. Even in the series $[MF_2(NH_3)_6]$ (M = Co, Ni, Zn, Cu, or Cd), described by Patil and Secco,[21] the composition of which might suggest the existence of $[M(NH_3)_6]^{2+}$ groups, a strong ν(M–F) frequency has been assigned in the far-i.r. region. No uncommon N–H stretching vibrations due to strong N–H · · · F hydrogen bonding are mentioned by those authors. It is evident that the strong hydrogen bonding is necessary to stabilize the present compounds. In the compound $[Cu(Him)_4][BF_4]F$ the fluoride ion will most likely be hydrogen bonded by four imidazole hydrogen atoms. It appears possible to isolate similar compounds with other imidazole ligands, for example 2-methylimidazole and 2-isopropylimidazole. The synthesis starting from $CuF_2$ and $Cu(BF_4)_2$ is the easiest one in all cases. Details of such work will be reported at a later date.

## Acknowledgements

The present investigations have been carried out with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

## References

1 J. C. Jansen, H. van Koningsveld, and J. Reedijk, *Nature (London)*, 1977, **269**, 318.
2 J. Reedijk, J. C. Jansen, H. van Koningsveld, and G. C. van Kralingen, *Inorg. Chem.*, 1978, **17**, 1990.
3 J. C. Verbiest, J. A. C. van Ooijen, and J. Reedijk, *J. Inorg. Nucl. Chem.*, 1980, 1971.
4 R. W. M. ten Hoedt and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1980, 844.
5 R. W. M. ten Hoedt, J. Reedijk, and G. C. Verschoor, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 400.
6 R. W. M. ten Hoedt and J. Reedijk, *Inorg. Chim. Acta*, 1981, **51**, 23.
7 J. Reedijk, *Comments Inorg. Chem.*, 1982, **1**, 379.
8 F. J. Rietmeijer, R. A. G. de Graaff, and J. Reedijk, *Inorg. Chem.*, in the press.
9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
10 D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1975, 263 and refs. therein.
11 R. Y. Wong, K. J. Palmer, and Y. Tomimatsu, *Acta Crystallogr., Sect. B*, 1976, **32**, 567.
12 H. A. Hendricksson, *Acta Crystallogr., Sect. B*, 1977, **33**, 1947.
13 B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1970, **5**, 1.
14 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.
15 T. L. F. Favre, J. G. Haasnoot, G. C. Verschoor, and J. Reedijk, unpublished work.
16 A. Pajunen, *Acta Crystallogr., Sect. B*, 1982, **38**, 928.
17 J. Emsley, D. J. Jones, R. S. Osborn, and R. E. Overill, *J. Chem. Soc., Dalton Trans.*, 1982, 809 and refs. therein.
18 J. Reedijk, *Transition Met. Chem.*, 1980, **6**, 195 and refs. therein.
19 J. C. Jansen and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 245.
20 R. C. van Landschoot, J. A. M. van Hest, and J. Reedijk, *Inorg. Chim. Acta*, 1980, **46**, 41.
21 K. C. Patil and E. A. Secco, *Can. J. Chem.*, 1972, **50**, 567.

*Received* 11*th May* 1983; *Paper* 3/750