Cuprophilicity? a rare example of a ligand-unsupported Cu^I–Cu^I interaction

Ulrich Siemeling,* Udo Vorfeld, Beate Neumann and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany

The reaction of 1,1′-bis(2-pyridyl)octamethylferrocene (L) with [Cu(NCMe)$_4$]BF$_4$ in CH$_2$Cl$_2$ affords [CuL][CuCl$_2$], the structure of which is determined by a single-crystal X-ray diffraction study; this reveals a remarkably short ligand-unsupported Cu^I–Cu^I contact of 281.0(2) pm.

Attractive interactions between formally closed-shell metal centres (s^2 of d^{10}) are well documented.[1] The body of evidence is especially large in the case of gold(I). Here, the term 'aurophilicity' has been coined to describe this special kind of metal–metal bonding interaction,[2] which can be as strong as 11 kcal mol^{-1} (1 cal = 4.184 J).[3] The question whether a similar metallophilicity[4] exists for the other two coinage metals, copper and silver, is still a matter of controversy. For example, the presence of such d^{10}–d^{10} bonding interactions has been disputed on theoretical grounds for the dinuclear complexes [M(MeC$_6$H$_4$NCHNC$_6$H$_4$Me)]$_2$ in spite of short metal–metal distances [247.7(2)/270.5(1) pm for M = Cu/Ag], which were therefore attributed to the ligand architecture.[5] A most instructive case is that of the trinuclear copper complex [Cu(MeC$_6$H$_4$N$_5$C$_6$H$_4$Me)]$_3$, the metal centres of which have an average distance of only 235 pm.[6] The existence of a bonding interaction between them has both been supported[7] and refuted[8] at various levels of theory.

Metallophilic effects are easily blurred by the effects exerted by a bridging ligand architecture, and hence examples of ligand-unsupported metal–metal interactions are of great importance in this discussion. They are, however, notoriously scarce for silver[9] and especially for copper.[10] The first example of a copper complex exhibiting such an interaction appears to be the trinuclear species [CuL′]$_3$ {HL′ = 2-[3(5)-pyrazolyl]pyridine}, which crystallises as a dimer showing two close metal–metal contacts between the two associated trinuclear units in the absence of any supportive bridging ligation [*d*(Cu–Cu) = 290.5(3) pm].[10]

We have obtained a species with an even shorter ligand-unsupported Cu^I–Cu^I contact from the reaction of 1,1′-bis(2-pyridyl)octamethylferrocene[11] (L) with [Cu(NCMe)$_4$]BF$_4$ in dichloromethane, which yielded [CuL][CuCl$_2$] **1**.† This species contains two copper(I) ions in an almost linear dicoordinate environment as shown by a single-crystal X-ray diffraction study (Figs. 1 and 2).‡ Whereas the [CuCl$_2$]$^-$ anion is very well known,[12] few structurally characterised examples of a copper(I) ion coordinated by just two N donors have been described to date.[13] The majority of the work published in this area was stimulated by the notion that complexes containing coordinatively unsaturated copper(I) ions and nitrogen heterocyclic ligands are of interest as possible models for deoxyhemocyanin.[14] An important feature of the structure of **1** is the short distance between the two copper centres of only 281.0(2) pm. The coordination axes of the anion and the cation, which are both slightly bent [N(1)–Cu(1)–N(2) 171.4(6), Cl(1)–Cu(2)–Cl(2) 176.9(3)°], are approximately perpendicular to each other [torsion angles: N(1)–Cu(1)–Cu(2)–Cl(1) 85.5, N(2)–Cu(1)–Cu(2)–Cl(2) 89.4°] (Fig. 3). There are no appreciable secondary interactions between the nitrogen-coordinated copper centre and the chlorine atoms of the anion, since both Cu–Cl distances [Cu(1)–Cl(1) 337, Cu(1)–Cl(2) 358 pm] are considerably larger than the sum of the van der Waals radii of Cu (140 pm) and Cl
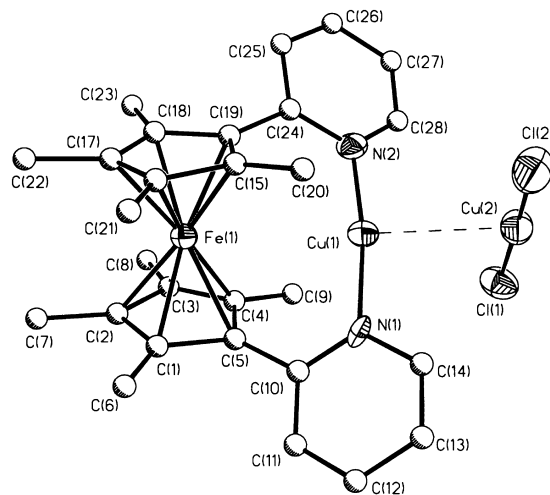

Fig. 1 Molecular structure of **1**. Selected bond lengths (pm) and angles (°): Cu(1)–N(1) 195(2), Cu(1)–N(2) 190(2), Cu(2)–Cl(1) 212.3(7), Cu(2)–Cl(2) 206.6(7); N(1)–Cu(1)–Cu(2) 94.9(4), N(2)–Cu(1)–Cu(2) 93.6(5), Cl(1)–Cu(2)–Cu(1) 84.9(2), Cl(2)–Cu(2)–Cu(1) 93.2.

(175 pm).[15] There is no indication for intermolecular interactions of the Cl-coordinated Cu centre, its shortest intermolecular contact (Cu–C 398 pm) being that to the methyl group attached to C(1) of a neighbouring [CuL]$^+$ unit.

It has been noted in the chemistry of gold(I) that metallophilic energy minima can be rather shallow.[16] The same is assumed to be true for copper(I), so that crystal packing forces[17] may very well overrule weak cuprophilic interactions. In comparison, this appears to be the case for [Cu(C$_5$H$_2$NMe$_3$-2,4,6)][CuCl$_2$],[13b,e] whose Cu^I–Cu^I distance of 361.1(2) pm is *ca.* 80 pm longer than that in **1**, although the coordination parameters of the respective Cu^I centres are quite similar for both complexes. Closer inspection reveals that the packing of the [Cu(C$_5$H$_2$NMe$_3$-2,4,6)]$^+$ units in the crystal, which involves stacking of
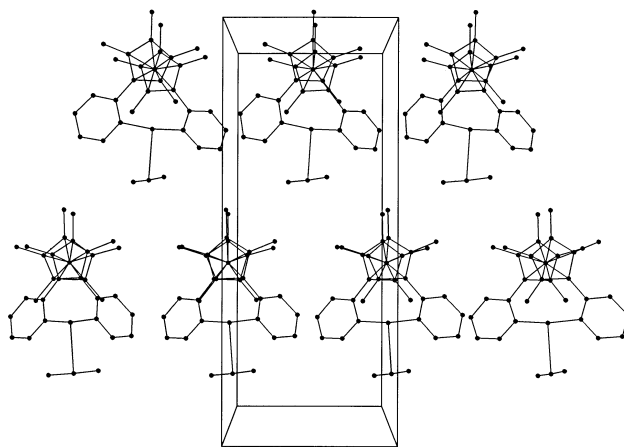

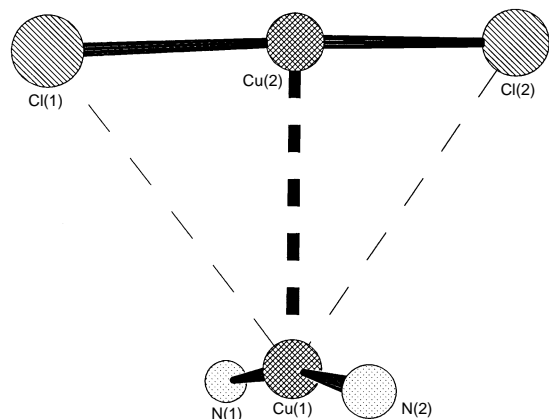**Fig. 2** Packing diagram of **1** (viewed down the *c* axis of the unit cell)

Fig. 3 View of the coordination spheres of the copper centres in **1**

neighbouring collidine ligands with a closest inter-ring distance of 348 pm,§ prohibits a closer approach of the copper centres.

In summary, we have synthesised a rare example of a complex which exhibits a remarkably short ligand-unsupported Cu^I–Cu^I contact, reflecting an interaction between the two formally closed-shell metal centres that may be due to a cuprophilic interaction between them.

Footnotes and References

* E-mail: usie@hrz.uni-bielefeld.de

† *Preparation*: a solution of L (362 mg, 0.80 mmol) in dichloromethane (5 cm³) was added at ambient temperature to a solution of [Cu(NCMe)$_4$]BF$_4$ (126 mg, 0.40 mmol) in CH$_2$Cl$_2$ (10 cm³) with vigorous stirring. After 12 h volatile components were removed *in vacuo* leaving a viscous, brown–red oil, which was dissolved in a minimal amount of CH$_2$Cl$_2$. Vapour-phase diffusion of *n*-pentane into this solution afforded **1** {66 mg, 43% with respect to [Cu(NCMe)$_4$]BF$_4$} as red crystals (decomp. *ca.* 160 °C), which are insoluble in hydrocarbons and diethyl ether, very soluble in dichloromethane and moderately soluble in CHCl$_3$. The solvent obviously participated in the reaction, since it was the only source of Cl present. The reaction proved to be irreproducible. *Selected spectroscopic data*: FABMS *m/z* 515 ([CuL]⁺, 100%), 453 ([HL]⁺, 67%). ¹H NMR (CDCl$_3$): δ 1.64, 1.86 (2 s, 24 H, Me), 7.25, 7.40, 7.74, 9.42 (4 br. s, 8 H, aromatic H). ¹³C{¹H} NMR (CDCl$_3$) δ 9.7, 12.0 (Me), 80.2, 82.6, 85.6 (cyclopentadienyl ring C), 122.5, 127.7, 137.7, 151.9 (pyridyl CH), 158.7 (q pyridyl C).

‡ *Crystal data*: C$_{28}$H$_{32}$Cl$_2$Cu$_2$FeN$_2$, M_r = 650.39; orthorhombic, space group *Pna*2$_1$, *a* = 21.238(4), *b* = 8.773(1), *c* = 14.257(1) Å, *U* = 2656.4(6) Å³, *Z* = 4, D_c = 1.626 g cm⁻³; *F*(000) = 1328, μ(Mo-Kα) = 2.347 mm⁻¹, λ = 0.71073 Å, *T* = 173(2) K, crystal size 0.30 × 0.10 × 0.10 mm. A total of 2423 reflections all of which were unique were collected with a Siemens P2(1) four-circle diffractometer using ω scans with 1.92 < θ < 25.04°. The structure was solved by direct methods and developed routinely. Full-matrix least-squares refinement with 184 parameters was based on *F*². Hydrogen atoms were considered in calculated positions. Carbon atoms were refined isotropically and all other atoms

anisotropically. The refinement converged at R_1 = 0.0688 and wR_2 = 0.1029 [for 1186 reflections with $I > 2\sigma(I)$] {$w = [\sigma^2(F_o^2) + (0.0319P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$}; final GOF = 1.039. The final difference map showed no peak > 0.6 and no hole < −0.5 e Å⁻³. Programs used were Siemens SHELXTL plus and SHELXL-93. CCDC 182/531.

§ Calculated from the crystallographic data given in ref. 13(*e*).

1 See, for example: (*a*) P. Pyykkö, *Chem. Rev.,* 1997, **97**, 597; (*b*) *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente,* ed. B. Krebs, VCH, Weinheim, 1992.

2 H. Schmidbaur, *Gold Bull.,* 1990, **23**, 11.

3 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.,* 1996, **118**, 2679.

4 P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.,* 1994, **218**, 133.

5 F. A. Cotton, X. Feng, M. Makusz and R. Poli, *J. Am. Chem. Soc.,* 1988, **110**, 7077.

6 J. Beck and J. Strähle, *Angew. Chem.,* 1985, **97**, 419; *Angew. Chem., Int. Ed. Engl.,* 1985, **24**, 409.

7 K. M. Merz, Jr. and R. Hoffmann, *Inorg. Chem.,* 1988, **27**, 2120.

8 C. Kölmel and R. Ahlrichs, *J. Phys. Chem.,* 1990, **94**, 5536.

9 For three examples, see: T. Yamaguchi and O. Lindqvist, *Acta Chem. Scand. Ser. A,* 1983, **37**, 685; G. W. Eastland, M. M. Mazid, D. R. Russell and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.,* 1980, 1682; P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.,* 1966, **20**, 502.

10 K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.,* 1997, **119**, 2942.

11 U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Chem. Ber.,* 1995, **128**, 481.

12 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 534–774.

13 See ref. 5 as well as (*a*) I. Sanyal, K. D. Karlin, R. W. Strange and N. J. Blackburn, *J. Am. Chem. Soc.,* 1993, **115**, 11 259; (*b*) A. Habiyakare, E. A. C. Lucken and G. Bernardinelli, *J. Chem. Soc., Dalton Trans.,* 1991, 2269; (*c*) G. O. Tan, K. O. Hodgson, B. Hedman, G. R. Clark, M. L. Garrity and T. N. Sorrell, *Acta Crystallogr., Sect. C,* 1991, **46**, 1773; (*d*) M. Munakata, S. Kitagawa, H. Shimono and H. Masuda, *Inorg. Chim. Acta,* 1989, **158**, 217; (*e*) P. C. Healy, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.,* 1989, **42**, 115; (*f*) L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.,* 1985, 117; (*g*) M. G. B. Drew, P. C. Yates, T.-C. Jadwiga, K. P. McKillop and S. M. Nelson, *J. Chem. Soc., Chem. Commun.,* 1985, 262; (*h*) T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.,* 1983, **105**, 6013; (*i*) M. J. Schilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem.,* 1982, **21**, 2637; (*j*) H. M. J. Hendriks, P. J. M. W. L. Birker, J. van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc.,* 1982, **104**, 3607; (*k*) T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.,* 1982, **104**, 2053; (*l*) P. J. W. M. L. Birker, H. M. J. Hendriks and J. Reedijk, *Inorg. Chim. Acta,* 1981, **55**, L17; (*m*) Y. Angus, R. Louis and R. Weiss, *J. Chem. Soc., Chem. Commun.,* 1980, 867; (*n*) J. E. O'Connor, G. A. Jansonius and E. R. Corey, *Chem. Commun.,* 1968, 445; (*o*) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.,* 1961, **14**, 480.

14 For reviews, see: Z. Tyeklár and K. D. Karlin, *Acc. Chem. Res.,* 1989, **22**, 241; T. N. Sorrell, *Tetrahedron,* 1989, **45**, 3.

15 A. Bondi, *J. Phys. Chem.,* 1964, **68**, 441.

16 P. Pyykkö, W. Schneider, A. Bauer, A. Bayler and H. Schmidbaur, *Chem. Commun.,* 1997, 111.

17 See A. Martin and A. G. Orpen, *J. Am. Chem. Soc.,* 1996, **118**, 1464 and references therein.