Pergamon

Polyhedron Vol. 14, No. 17–18, pp. 2389–2396, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 \$9.50+0.00

0277–5387(95)00074–7

SYNTHESIS AND CHARACTERIZATION OF COPPER(I) HALIDE IMINE COMPLEXES

HELGARD G. RAUBENHEIMER,* STEPHANIE CRONJE,
GERT J. KRUGER and PIERRE J. OLIVIER

Department of Chemistry and Biochemistry, Rand Afrikaans University,
Auckland Park 2006, South Africa

(*Received* 13 *December* 1994; *accepted* 18 *January* 1995)

Abstract—The complexes $[\mathrm{Cu_2(\mu\text{-}X)_2\{\overline{N{=}CHYCR^1{=}C}R^2\}_4}]$ ($X = Cl$ or I; $Y = S$ or NCH_3; $R^1 = H$, $R^2 = CH_3$; $R^1 = R^2 = CH_3$ or $R^1R^2 = C_4H_4$) were prepared by quenching a mixture of CuCl or CuI and thiazolyllithium or imidazolyllithium with CF_3SO_3H, indicating the availability of chloride or iodide in the cuprate aggregate for further reaction and the basicity of the coordinated carbon atom. CuCl and 1-methylimidazol-2-yllithium do not form a cuprate aggregate at −80°C. After alkylation the 1,2-dimethylimidazole formed coordinates to CuCl.

Copper(I) halide complexes with nitrogen ligands have been used as catalysts {in the atom transfer cyclization of α-chloroglycine derivatives and α-chloroglycolic acid derivatives with $[Cu_2(\mu\text{-}Cl)_2(2,2'\text{-bipyridine})_4]$[1]}, as models for the catalysis of the reduction of O_2 and H_2O with the copper(I)-containing protein tyrosinase {$[Cu(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})_2Cl]$ and $[Cu(2,2'\text{-bipyridine})_2Cl]$ catalyse the reduction of O_2, H_2O and alcohols[2]} and as models for the reversible bonding of CO to the copper-containing respiratory protein haemocyanin {binuclear $[Cu_2(\mu\text{-}Cl)_2(2,2'\text{-bipyridine})_4]$ reacts reversibly with CO[3]}.

In the solid form, copper(I) halide complexes with nitrogen ligands (diamine,[4–6] diimine,[7] pyrazole[8,9] and pyridine[10–16]) exist as three-coordinate monomers, halogen-bridged dimers or products of ligand disproportionation, leading to the formation of a pseudotetrahedral $[N_4Cu^I]^+$ cation and linear dihalocopper(I) anion.[4,17] The nature of the adduct formed between the ligand and the copper(I) halide is sensitively poised between steric and electronic effects, lattice forces and solvation effects.[4,5,13,16]

A considerable number of copper(I) halide complexes with phosphorus, arsenic or nitrogen ligands of the general formulae $(MXL_2)_2$ and MXL_2 have been synthesized and characterized.[16] These results suggest that the dimer is a common structural form in this system, with the coordination number of the copper being four.

In our quest to prepare copper(I) carbene complexes we have isolated and characterized for the first time copper(I) halide thiazole and imidazole complexes from the reaction of CuX ($X = Cl$ or I), thiazolyllithium or 1-methylbenzimidazol-2-yllithium and CF_3SO_3H, and from the reaction of CuCl, 1-methylimidazol-2-yllithium and $CF_3SO_3CH_3$.

EXPERIMENTAL

Reactions were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. Copper(I) chloride was prepared from $CuCl_2$,[18] copper(I) iodide was purchased from Riedel-De Haën and n-butyllithium from Merck. Benzothiazole (stored over 4 Å molecular sieves) and 1-methylimidazole were purchased from Fluka. The other thiazoles, 4-methylthiazoles and 4,5-dimethylthiazole as well as CF_3SO_3H (trifluoromethanesulphonic acid) and $CF_3SO_3CH_3$ (methyltrifluoromethanesulphonate) were purchased from Aldrich and used without fur-

---

* Author to whom correspondence should be addressed.

ther purification. Benzimidazole (BDH) was used to prepare 1-methylbenzimidazole.[19]

NMR spectra were recorded on a VXR 200 instrument and mass spectra (electron impact) on a Finnigan Mat 8200 instrument. Melting points were determined on a Büchi 535 melting point apparatus. Elemental analyses were carried out by the Division for Energy Technology, CSIR, Pretoria, South Africa. Physical and analytical data are given in Table 1.

Preparation of $[Cu_2(\mu\text{-}Cl)_2(\text{thiazole})_4]$ (I–III), $[Cu_2(\mu\text{-}I)_2(\text{thiazole})_4]$ (IV *and* V) *and* $[Cu_2(\mu\text{-}Cl)_2(\text{imidazole})_4]$ (VI *and* VII)

$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSCH{=}C}(CH_3)\}_4]$ (**I**). 4-Methylthiazol-2-yllithium[20] was prepared from 4-methylthiazole (0.80 cm^3, 8.8 mmol) and 1.6 mol dm^{-3} n-butyllithium in hexane (5.4 cm^3, 8.6 mmol) in THF (20 cm^3) at −80°C and stirred for 15 min before a suspension of CuCl (0.43 g, 4.3 mmol) in THF (10 cm^3) was added. The mixture was stirred for 1 h, prior to the addition of CF_3SO_3H (0.40 cm^3, 4.6 mmol) at −20°C. Stirring was continued at this temperature for 30 min, before warming to room temperature. After filtration through anhydrous $MgSO_4$ (18 g), concentration *in vacuo* to *ca* 15 cm^3 and addition of pentane (5 cm^3), white crystals of **I** suitable for X-ray structure determination were formed at −20°C. Yield: 0.62 g (49%).

$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSC(CH_3){=}C}(CH_3)\}_4]$ (**II**). Complex **II** was prepared similarly from 4,5-dimethylthiazole (0.60 cm^3, 5.7 mmol), 1.6 mol dm^{-3} n-butyllithium in hexane (3.5 cm^3, 5.6 mmol), CuCl (0.27 g, 2.7 mmol) and CF_3SO_3H (0.30 cm^3, 3.4 mmol). The acidification with CF_3SO_3H at −80°C yielded white crystals after work-up. Yield: 0.39 g (44%).

$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSC_6}H_4\text{-}o\}_4]$ (**III**). The analogous reaction using benzothiazole (0.60 cm^3, 5.5 mmol), 1.6 mol dm^{-3} n-butyllithium in hexane (3.5 cm^3, 5.6 mmol), CuCl (0.28 g, 2.8 mmol) and CF_3SO_3H (0.25 cm^3, 2.8 mmol) afforded white crystals of **III**. Yield: 0.40 g (39%).

$[Cu_2(\mu\text{-}I)_2\{\overline{N{=}CHSCH{=}C}(CH_3)\}_4]$ (**IV**). Complex **IV** was prepared similarly from 4-methylthiazole (0.60 cm^3, 6.6 mmol), 1.6 mol dm^{-3} n-butyllithium in hexane (3.9 cm^3, 6.2 mmol), CuI (0.59 g, 3.1 mmol) and CF_3SO_3H (0.30 cm^3, 3.4 mmol). The concentrate yielded white crystals. Yield: 1.15 g (48%).

$[Cu_2(\mu\text{-}I)_2\{\overline{N{=}CHSC(CH_3){=}C}(CH_3)\}_4]$ (**V**). The analogous reaction using 4,5-dimethylthiazole (0.60 cm^3, 5.7 mmol), 1.6 mol dm^{-3} n-butyllithium

Table 1. Physical and analytical data

		Melting point (°C)	Analyses (%) Found (Calc.) C	H	N
I	$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSCH{=}C}(CH_3)\}_4]$	53 (decomp.)	32.3 (32.4)	3.4 (3.4)	9.5 (9.4)
II	$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSC(CH_3){=}C}(CH_3)\}_4]$	73 (decomp.)	37.2 (36.9)	4.2 (4.3)	8.4 (8.6)
III	$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHSC_6}H_4\text{-}o\}_4]$	134 (decomp.)	45.6 (45.5)	2.5 (2.7)	7.9 (7.6)
IV	$[Cu_2(\mu\text{-}I)_2\{\overline{N{=}CHSCH{=}C}(CH_3)\}_4]$	134 (decomp.)	24.9 (24.7)	2.2 (2.6)	7.1 (7.2)
V	$[Cu_2(\mu\text{-}I)_2\{\overline{N{=}CHSC(CH_3){=}C}(CH_3)\}_4]$	109 (decomp.)	28.9 (28.8)	3.3 (3.4)	6.6 (6.7)
VI	$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}CHN(CH_3)C_6}H_4\text{-}o\}_4]$	83 (decomp.)	55.2 (55.2)	4.9 (5.2)	14.4 (14.3)
VII	$[Cu_2(\mu\text{-}Cl)_2\{\overline{N{=}C(CH_3)N(CH_3)CH{=}CH}\}_4]$	89 (decomp.)	41.0 (41.3)	5.4 (5.5)	19.6 (19.2)

in hexane (3.4 cm^3, 5.4 mmol), CuI (0.52 g, 2.7 mmol) and CF_3SO_3H (0.24 cm^3, 2.7 mmol) afforded white crystals of **V**. Yield: 0.47 g (42%).

$[Cu_2(\mu\text{-}Cl)_2\{N{=}CHN(CH_3)C_6H_4{-}o\}_4]$ (**VI**). Complex **VI** was prepared in the same way as **II** from 1-methylbenzimidazole (0.76 g, 5.8 mmol), 1.6 mol dm^{-3} n-butyllithium in hexane (3.6 cm^3, 5.8 mmol), CuCl (0.28g, 2.8 mmol) and CF_3SO_3H (0.30 cm^3, 3.4 mmol). The concentrate yielded an unstable white precipitate at −20°C. Yield: 0.31 g (28%).

$[Cu_2(\mu\text{ - }Cl)_2\{N{=}C(CH_3)N(CH_3)CH{=}CH\}_4]$ (**VII**). Compound **VII** was prepared from 1-methylimidazole (0.80 cm^3, 10.1 mmol), 1.6 mol dm^{-3} n-butyllithium (6.0 cm^3, 9.6 mmol), CuCl (0.47 g, 4.7 mmol) and $CF_3SO_3CH_3$ (0.53 cm^3, 4.7 mmol). The reaction mixture was alkylated with $CF_3SO_3CH_3$ at −80°C and stirred at −50°C (1 h), −20°C (1 h) and 0°C (1 h) before warming to room temperature. The concentrate yielded light yellow, air- and moisture-sensitive crystals. Yield: 0.58 g (42%).

X-ray crystallography

The crystal and molecular structure of **I** was determined by single-crystal X-ray diffraction. Data were collected from a small, regular single crystal and the conditions as well as crystal data are detailed in Table 2. Lorentz polarization and empirical psi scan absorption corrections were applied. The solution of the structure was carried out using the heavy-atom method after having located the position of copper from a Patterson map. Difference electron density maps revealed all the non-hydrogen atoms. During least-squares refinement all atoms except hydrogens were refined anisotropically (hydrogen atoms were placed in calculated positions but not refined).* The computer program SHELX-76[21] was used for the determination and refinement of the structure and SCHAKAL[22] for the preparation of illustrations.

Attempts to determine the structure of **VII** were unsuccessful due to problems with disorder. Diffraction data were collected for a monoclinic unit cell of dimensions $a = 7.334(9)$, $b = 7.652(2)$, $c = 11.303(1)$ Å, $\beta = 90.40(0)°$ with space group $P2_1/m$, $Z = 4$ and $V = 639.4(2)$ Å.

RESULTS AND DISCUSSION

Synthetic aspects

The successive treatment of CuCl or CuI with thiazolyllithium or 1-methylbenzimidazol-2-yllithium and CF_3SO_3H in THF at −80°C yielded white crystals of complexes **I**–**VI** after filtration and concentration of the mixture (Scheme 1). Complex **VII** was prepared by alkylation of the reaction mixture obtained from the reaction of CuCl and 1-methylimidazol-2-yllithium with $CF_3SO_3CH_3$ at −80°C (Scheme 2). Moisture- and air-sensitive, light yellow crystals were isolated. A spot test with 2,9-dimethyl-1,10-phenanthroline confirmed that these crystals contained copper(I) compounds.[23] Complex **III** is only slightly soluble in THF, while the other complexes are soluble in acetone, methylene chloride and THF.

We established that these compounds can also be prepared by stirring CuX with the neutral ligands. Nevertheless, our method is of interest since:

(i) it shows that quenching of the cuprates with CF_3SO_3H leads to carbon protonation in the preparation of **I**–**VI**;
(ii) the Cl^- is retained in these compounds in spite of Li^+ being present;
(iii) the cuprate of 1-methylimidazole only forms at *ca* −40°C.

We recently reported the synthesis and characterization of copper(I) carbene compounds prepared by generally alkylating cuprate reaction mixtures at −80°C with $CF_3SO_3CH_3$.[24] To produce a carbene complex from 1-methylimidazol-2-yllithium and CuCl, the cuprate has to be alkylated at −20°C.

NMR spectroscopy

The ^{1}H NMR and ^{13}C NMR spectra (Table 3) of compounds **I**–**VI** produced by the acidification of the cuprate reaction mixture and **VII** produced by the alkylation of the 1-methylimidazol-2-yllithium and CuCl mixture at −80°C indicated that they were copper(I) coordination compounds and not the targeted copper carbene compounds.

The SCHN protons at *ca* δ 9.00 in the ^{1}H NMR spectra of **I**–**VI** and the signal at δ 2.45 for the $CH_3NC(C\mathit{H}_3)NCu$ group in **VII** confirmed that no carbene complex had formed. All the signals in the ^{1}H NMR spectra are shifted less than 0.5 ppm downfield from the peaks of the free ligands, suggesting that the ligands are coordinated to copper.[8] Allylic couplings (< 1 Hz) are observed between the SCCH and $NCCH_3$ protons in **I**, **II**, **IV** and **V**.

---

* Tables of atomic coordinates, structure factors, thermal parameters and a complete list of bond lengths and angles were deposited with the Editor and at the Cambridge Crystallographic Data Centre.

Table 2. Crystal data for **I**

Formula	$C_8H_{10}ClCuN_2S_2$
Formula weight	297.32
Space group	$P2_1/c$
Systematic absences	$h0l: l = 2n$; $0k0: k = 2n$; $00l: l = 2n$
a (Å)	8.524(1)
b (Å)	7.415(1)
c (Å)	19.358(4)
β (°)	98.42(1)
V (Å^{-3})	1210.3(4)
Z	4
D_{calc} (g cm^3)	1.631
Crystal size (mm)	$0.60 \times 0.50 \times 0.45$
μ(Mo-K_α) (cm^{-1})	24
Data collection instrument	CAD-4
Radiation (monochromated incident beam)	Mo-K_α ($\lambda = 0.71073$ Å)
Orientation reflections number and range 2θ	25; $2\theta < 18°$
Temperature (°C)	25
Scan method	ω–2θ
Data collection range (2θ,°)	3–30
Total number of unique data	3704
Data with $F_o^2 > 3\sigma(F_o^2)$	2683
Number of parameters refined	157
Transmission factors max., min. (%)	100.0, 69.8
R^a	0.064
$R_w{}^b$	0.052
Largest shift/e.s.d. final cycle	0.347
Largest peak (e Å^{-3})	0.77; 0.418 Å from copper

[a] $R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$.
[b] $R_w = [\Sigma(|F_o|-|F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|f|)$.

These protons appear as broad singlets, multiplets or doublets.

The ^{13}C NMR spectra show the same trends as the ^1H NMR spectra. The signals appear at 0–5 ppm lower than those in the free ligands, except for those of the SCNCu signals, which are shifted upfield by 0–2 ppm. The ^{13}C NMR spectrum of **III** could not be determined due to the insolubility of the compound.

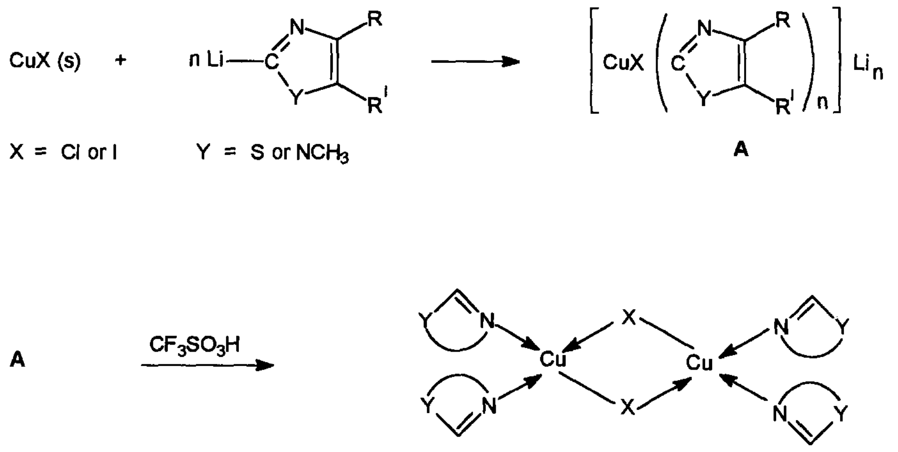
Mass spectra and elemental analysis

The mass spectra of **I**–**VII** did not show molecular ions. The fragments of the thiazole or imidazole ligands as well as a Cu_4Cl_4 unit and fragments thereof in **I**–**III** and **VII** or a Cu_3I_3 unit and subsequent fragments formed in **IV** and **V** were observed.

Elemental analysis indicated a 1 : 1 copper : halide and a 2 : 1 ligand : copper ratio. Known copper(I) nitrogen-coordination compounds have the general formulae $L_2CuX_2CuL_2$, L_3CuX, L_2CuX, $LCuX$, $LCuX_2CuL$, $[LCuX]_4$, $[CuL_2]^+[CuX_2]^-$, $[(LCuX)_2]_\infty$ and $[LCuX]_\infty$.[17] The good solubility of our products excluded polymeric structures. Variables like ligand structure, the stoichiometry of reagents, temperature of crystallization and the solvent used for the reaction influence the structure of the products.[13] Complexes of the types $L_2CuX_2CuL_2$, L_2CuX or $[CuL_2]^+[CuX_2]^-$ (X = Cl or I and L = ligand) were possible for **I**–**VII**. The crystal structure determination of **I** confirmed the first structural type.

Mechanistic considerations

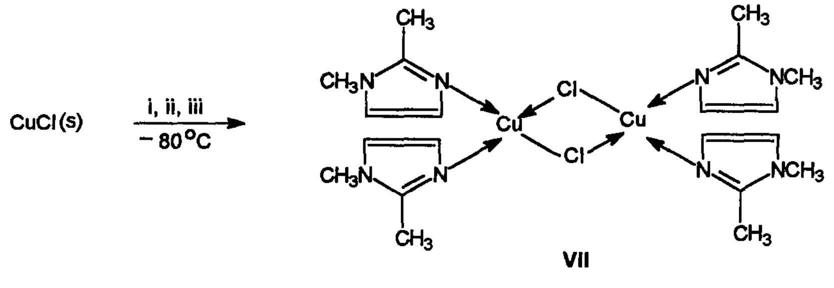
The reaction of 4-methylthiazole with CuCl (2 : 1 ratio) at room temperature in THF and acetone also yielded **I** in 80% yield. This reaction did not occur at −80°C in THF, but only proceeded upon warming to room temperature. The formation of **I** according to the reaction in Scheme 1 can be explained as the protonolysis of a cuprate aggregate, followed by coordination of the protonolysis products to CuCl. The reaction of the cuprate aggregate with one or two molar equivalents of CF_3SO_3H produced the same products, albeit in varying yields. Insoluble, unidentifiable byproducts were ob-



I – VI

	X	Y	R	R'
I	Cl	S	CH_3	H
II	Cl	S	CH_3	CH_3
III	Cl	S	CH=CHCH=CH	
IV	I	S	CH_3	H
V	I	S	CH_3	CH_3
VI	Cl	NCH_3	CH=CHCH=CH	

Scheme 1.



i n-BuLi, ii $HC{=}NCH{=}CHNCH_3$, iii $CF_3SO_3CH_3$

Scheme 2.

served in the reaction with two molar equivalents of CF_3SO_3H.

The exact composition of the cuprate aggregate A is not known. The structures of cuprates like $[Li(12\text{-crown-}4)_2Cu(CH_3)_2]$, $[Li(12\text{-crown-}4)_2Cu(C_6H_5)_2]$,[25] $[Li_2Cu_2\{C_6H_4CH_2N(CH_3)_2\text{-}2\}_4]$,[26] $[\{Li[O(CH_2CH_3)_2]\}Cu(C_6H_5)_2]_2$[27] and $[Li_2Cu_2(C_6H_5)_4\{S(CH_3)_2\}_3]$,[28] prepared from halide-free organocopper and organolithium reagents, have been reported, but those of the more reactive cuprates[29] prepared from two molar equivalents of organolithium compound and copper(I) halide have not yet been determined. The retention of the CuX unit during the formation of carbenes from CuX, $LiC{=}NCR^1{=}CR^2Y$ and $CF_3SO_3CH_3$ (X = Cl or I; Y = S or NCH_3; $R^1 = CH_3$, $R^2 = H$; $R^1 = R^2 = CH_3$; $R^1R^2 = C_4H_4$ or $R^1 = R^2 = H$)[24] supports the already mounting evidence[30] that the halide ion forms part of the cuprate aggregate. The protonolysis of the thiazolyl or imidazolyl ligands of the cuprate aggregate can also be encouraged by the inclusion of $CF_3SO_3^-$ groups through inter-

Table 3. NMR data

		Chemical shift[a] (integration multiplicity, assignment)
I	$[Cu_2(\mu\text{-}Cl)_2\{N{=}CHSCH{=}C(CH_3)\}_4]$[b]	9.18 (4H, br s, NCHS); 7.37 (4H, br s, SCH); 2.50 [12H, d, *J*(HH) = 0.9 Hz, CH_3] 156.2 (s, NC); 153.8 (s, SCN); 115.4 (m, SC); 17.1 (s, CH_3)
II	$[Cu_2(\mu\text{-}Cl)_2\{N{=}CHSC(CH_3){=}C(CH_3)\}_4]$[c]	8.89 (4H, br s, NCHS); 2.50 (12H, br s, $NCCH_3$); 2.40 (12H, br s, $SCCH_3$) 153.5 (s, NC); 148.8 (m, SCN); 128.2 (m, SC); 15.8 (s, $NCCH_3$); 11.8 (s, $SCCH_3$)
III	$[Cu_2(\mu\text{-}Cl)_2\{N{=}CHSC_6H_4\text{-}o\}_4]$[c]	9.23 (4H, br s, SCHN); 8.22 (4H, m, CHCS); 8.00 (4H, m, NCCH); 7.55 [8H, m, $NCCH(CH)_2CHCS$]
IV	$[Cu_2(\mu\text{-}I)_2\{N{=}CHSCH{=}C(CH_3)\}_4]$[b]	8.96 [4H, d, *J*(HH) = 2 Hz, NCHS]; 7.21 (4H, m, SCH); 2.47 [12H, d, *J*(HH) = 0.9 Hz, CH_3] 154.1 (s, SCN); 153.9 (s, NC); 114.4 (s, SC); 16.9 (s, CH_3)
V	$[Cu_2(\mu\text{-}I)_2\{N{=}CHSC(CH_3){=}C(CH_3)\}_4]$[b]	9.11 (4H, br s, NCHS); 2.48 (12H, m, $NCCH_3$); 2.41 (12H, m, $SCCH_3$) 152.7 (s, NC); 148.2 (s, SCN); 128.2 (s, SC); 14.9 (s, $NCCH_3$); 11.3 (s, $SCCH_3$)
VI	$[Cu_2(\mu\text{-}Cl)_2\{N{=}CHN(CH_3)C_6H_4\text{-}o\}_4]$[b]	8.44 (4H, br s, NCHN); 7.77 [4H, dm,[d] *J*(HH) = 7.5 Hz, CH_3NCCH]; 7.63 [4H, dm, *J*(HH) = 7.5 Hz, CuNCCH]; 7.34 [8H, m, $NCH(CH)_2CHN$]; 3.09 (12H, s, NCH_3) 146.1 (s, NCHN); 142.7 [s, $CuNC(CH)_4CNCH_3$]; 134.8 [s, $CH_3NC(CH)_4CNCu$]; 124.4 [s, $CuNCCHCH(CH)_3CNCH_3$]; 123.6 [s, $CH_3NCCHCH(CH)_2CNCu$]; 119.7 (s, CuNCCH); 111.4 (s, CH_3NCCH); 31.7 (NCH_3).
VII	$[Cu_2(\mu\text{-}Cl)_2\{N{=}C(CH_3)N(CH_3)CH{=}CH\}_4]$[c]	6.90 [4H, d, *J*(HH) = 1.6 Hz, CuNCH]; 6.85 [4H, d, *J*(HH) = 1.4 Hz, CH_3NCH]; 3.67 (12H, s, NCH_3); 2.45 (12H, s, $NCCH_3N$) 146.4 (s, NCN); 127.3 (s, CuNCHCHN); 121.9 (s, CH_3NCHCH); 33.7 (s, NCH_3); 13.6 (s, $NCCH_3N$)

[a] In ppm, relative to solvent, ^1H NMR 200 MHz, ^{13}C NMR 50 Hz.
[b] $(CD_3)_2CO$ solution.
[c] CD_2Cl_2 solution.
[d] dm, doublet of multiplets.

aggregate exchange to form $[R_{2-n}CuLi(O_3SCF_3)_n]_m$.[30,31] The inclusion of strongly electron accepting $CF_3SO_3^-$ groups reduces the electron density in the Cu_n—C region and thus the kinetic stability of the Cu_n—C bond.[31]

The reaction of $LiC{=}NCH{=}CHN(CH_3)$ with CuCl at −80°C and the subsequent alkylation of the reaction mixture with $CF_3SO_3CH_3$ at −80°C yielded compound **VII** (Scheme 2). The isolation of $\{CuCl[CN(CH_3)CH{=}CHN(CH_3)]\}$[24] when the reaction mixture is warmed to −40°C before alkylation suggests that the cuprate aggregate only forms at −40°C in the case of 1-methylimidazolyllithium and that compound **VII** is formed as a result of the coordination of neutral $(CH_3)C{=}NCH{=}CHN(CH_3)$ [obtained via the direct alkylation of $LiC{=}NCH{=}CHN(CH_3)$] to CuCl. The alkylation of the reaction mixture of $LiC{=}NC_6H_4N(CH_3)\text{-}o$ and CuCl at −80°C yields only the copper carbene complex $[CuCl\{CN(CH_3)C_6H_4N(CH_3)\text{-}o\}]$,[24] indicating that in the case of 1-methylbenzimidazol-2-yllithium the cuprate aggregate has already formed at this low temperature.

Molecular structure of I

The molecular structure of complex **I** is shown in Fig. 1 and selected bond lengths and angles are

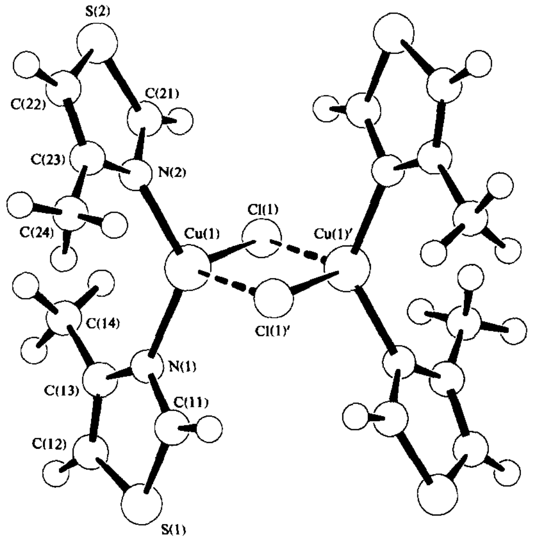


Fig. 1. The molecular structure of **I**.

listed in Table 4. Several similar structures with pyrazole,[8,9] 2-methylpyridine,[10] 2-benzylpyridine,[15] quinoline[14] and 1,4-diazo-1,3-diene[7] have been reported. The asymmetric $(\text{4-methylthiazole})_2\mathrm{CuCl}$ unit of **I** forms a centrosymmetric dimer about a crystallographic inversion centre. Each copper atom in **I** is surrounded by two nitrogen-coordinated thiazole rings [Cu(1)—N(1) 2.019(3) Å and Cu(1)—N(2) 1.997(3) Å] and two chlorides [at 2.395(1) and 2.542(1) Å]. The chlorides bridge the copper atoms (Cu · · · Cu 2.926 Å and Cl · · · Cl 3.980 Å). The bond lengths and distances observed agree with those found for $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\text{2-benzylpyridine})_4]$[15] [Cu—N 2.013(5) and 2.014(4), Cu—Cl 2.498(2) and 2.443(2) and Cu · · · Cu 3.008(1) Å], $\{\mathrm{Cu_2}(\mu\text{-Cl})_2[N,N\text{-bis(1-pyrazolylmethyl)aminoethane}]_2\}$[8] [Cu—N 2.011(2) and 2.047(2), CuCl 2.3874(8) and 2.4094(8), Cu · · · Cu 2.9511(7) and Cl · · · Cl 3.782(1) Å] and $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\text{quinoline})_4]$[14] [Cu—N 2.00(2), 2.08(2), 2.02(2) and 2.05(2), Cu—Cl 2.675(6), 2.357(7), 2.381(7) and 2.443(6), Cu · · · Cu 3.121(5) and Cl · · · Cl 3.806(8) Å].

The unsymmetrical bridging position of the chlorides (difference of 0.147 Å between the two Cu—Cl distances) is similar to the situation found for $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\text{1,4-diaza-1,3-diene})_4]$ (difference of 0.15 Å between the Cu—Cl distances), which dissociates in solution to form a three-coordinate species $[\mathrm{CuCl}(\text{1,4-diaza-1,3-diene})_2]$.[7]

The bond distances and angles within the 4-methylthiazole ligand rings do not differ significantly from the geometry of the ligands found previously in $[\mathrm{Cu^{II}}(\text{4-methylthiazole})_3\mathrm{Cl_2}]$.[32] These ligand rings and the chlorides are arranged in a pseudo-tetrahedral fashion around each copper atom [N(1)—Cu(1)—N(2) 129.4(2)°, Cl(1)—Cu(1)—Cl(1)′ 107.4(1)°, N(1)—Cu(1)—Cl(1) 101.7(1)°, N(2)—Cu(1)—Cl(1) 114.3(1)°, N(1)—Cu(1)—Cl(1)′ 101.7(1)° and N(2)—Cu(1)—Cl(1)′ 100.0(1)°], similar to those for $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\text{2-benzylpyridine})_4]$[15] [N(1)—Cu(1)—N(2) 135.0(2)°, Cl(1)—Cu(1)—Cl(1)′ 105.03(6)°, N(1)—Cu(1)—Cl(1) 103.1(1)°, N(2)—Cu(1)—Cl(1) 103.2(1)°, N(1)—Cu(1)—Cl(1)′ 104.0(1)° and N(2)—Cu(1)—Cl(1)′ 103.5(1)°] and $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\text{quinoline})_4]$[14] [N(1)—Cu(1)—N(2) 131.2(7) and 122.3(7)°, Cl(1)—Cu(1)—Cl(1)′ 97.5(2) and 104.9(2)°, N(1)—Cu(1)—Cl(1) 103.5(5) and 116.0(4)°, N(2)—Cu(1)—Cl(1) 104.2(5) and 106.6(5)°, N(1)—Cu(1)—Cl(1)′ 105.3(6) and 99.8(5)° and N(2)—Cu(1)—Cl(1)′ 110.0(5) and 105.0(4)°].

The pseudo-tetrahedral arrangement around each four-coordinate copper atom forces the two 4-methylthiazole ligands into a non-co-planar arrangement. The 75.7(2)° dihedral angle between the planes of the two rings is significantly larger than the angle observed for $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\mathrm{pzH})_4]$ (pzH = pyrazole, $\mathrm{C_3H_4N_2}$) (18.1°).[9] This is also reflected in the N(1)—Cu(1)—N(2) angle

Table 4. Bond distances (Å) and angles (°) for **I**

Cu(1)—Cl(1)	2.395(1)	Cu(1) · · · Cl(1)′	2.542(1)
Cu(1) · · · Cu(1)	2.926(1)	Cl(1) · · · Cl(1)′	3.980(1)
Cu(1)—N(1)	2.019(3)	Cu(1)—N(2)	1.997(3)
N(1)—C(11)	1.300(6)	N(2)—C(21)	1.321(6)
N(1)—C(13)	1.372(6)	N(2)—C(23)	1.372(6)
N(1)—Cu(1)—N(2)	129.4(2)	Cl(1)—Cu(1)—Cl(1)′	107.4(1)
N(1)—Cu(1)—Cl(1)	101.7(1)	N(2)—Cu(1)—Cl(1)	114.3(1)
N(1)—Cu(1)—Cl(1)′	101.7(1)	N(2)—Cu(1)—Cl(1)′	100.0(1)
C(11)—N(1)—C(13)	110.8(4)	C(21)—N(2)—C(23)	110.8(4)
Cu(1)—Cl(1)—Cu(1)′	72.6(4)		

{129.4(2)° for **I** and 146.8(9)° for $[Cu_2(\mu\text{-}Cl)_2(pzH)_4]^9$}. The dihedral angles for the quinoline rings in $[Cu_2(\mu\text{-}Cl)_2(\text{quinoline})_4]^{14}$ are 77.2, 77.2, 76.9 and 62.4°, with the deviations of the copper atom from the ligand planes 0.220, 0.130, 0.236 and 0.045 Å. For **I** the deviations of the copper atom from the ligand planes are 0.342 and 0.051 Å.

REFERENCES

1. J. H. Udding, H. Hiemstra and W. N. Speckamp, *J. Chem. Soc., Perkin II* 1992, 1529.
2. M. Munakata, S. Nishibayashi and H. Sakamoto, *J. Chem. Soc., Chem. Commun.* 1980, 219.
3. S. Kitagawa and M. Munakata, *Inorg. Chem.* 1981, **20**, 2261.
4. M. F. Garbauskas, D. A. Haitko and J. S. Kasper, *J. Cryst. Spectrosc. Res.* 1986, **16**, 729.
5. L. M. Engelhardt, R. I. Papasergio and A. H. White, *Aust. J. Chem.* 1984, **37**, 2207.
6. D. A. Haitko, *J. Coord. Chem.* 1984, **13**, 119.
7. H. Tom Dieck and L. Stamp, *Acta Cryst.* 1983, **C39**, 841.
8. Y. C. M. Pennings, W. L. Driessen and J. Reedijk, *Polyhedron* 1988, **7**, 2583.
9. M. A. Angaroni, G. A. Ardizzoia, T. Beringhelli, G. D'Alfonso, G. La Monica, N. Masciocchi and M. Moret, *J. Organomet. Chem.* 1989, **363**, 409.
10. W. Hiller, *Acta Cryst.* 1986, **C42**, 149.
11. W. Hiller, *Z. Naturfor.* 1984, **39b**, 861.
12. N. P. Rath, E. M. Holt and K. Tanimura, *J. Chem. Soc., Dalton Trans.* 1986, 2303; J. C. Dyason, L. M. Engelhardt, P. C. Healy and A. H. White, *Aust. J. Chem.* 1984, **37**, 2201; J. C. Dyason, P. C. Healy, C. Pakawatchai, V. A. Patrick and A. H. White, *Inorg. Chem.* 1985, **24**, 1957.
13. N. P. Rath, J. L. Maxwell and E. M. Holt, *J. Chem. Soc., Dalton Trans.* 1986, 2449.
14. J. C. Dyason, L. M. Engelhardt, P. C. Healy, C. Pakawatchai and A. H. White, *Inorg. Chem.* 1985, **24**, 1950.
15. P. C. Healy, J. D. Kildea, B. W. Skelton, A. F. Waters and A. H. White, *Acta Cryst.* 1991, **C47**, 1721.
16. P. C. Healy, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.* 1983, 1917.
17. L. M. Engelhardt, P. C. Healy, J. D. Kildea and A. H. White, *Aust. J. Chem.* 1989, **42**, 185.
18. A. Haas, J. Helmbrecht and U. Niemann, in *Handbuch der Präparativen Anorganischen Chemie* (Edited by G. Brauer), Vol. 2, p. 972. Ferdinand Enke, Stuttgart (1978).
19. L. J. Mathias and D. Burkett, *Tetrahedron Lett.* 1979, 4709.
20. H. Gilman and J. A. Beel, *J. Am. Chem. Soc.* 1949, **71**, 2328.
21. G. M. Sheldrick, SHELX76, in *Computing in Crystallography* (Edited by H. Schenk, P. Olthof-Hazekamp, H. Van Koningsveld and G. C. Bassi). Delft University Press, Delft, The Netherlands (1978).
22. E. Keller, SHALKAL88, Program for the Graphic Representation of Molecular and Crystallographic Models. Albert-Ludwigs-University, Freiburg (1988).
23. F. Feigl and V. Anger, *Spot Tests in Inorganic Analysis*, p. 203. Elsevier, Amsterdam (1972).
24. H. G. Raubenheimer, S. Cronje, P. H. van Rooyen, P. J. Olivier and J. G. Toerien, *Angew. Chem., Int. Edn Engl.* 1994, **33**, 672; H. G. Raubenheimer, S. Cronje and P. J. Olivier, *J. Chem. Soc., Dalton Trans.* 1995, 313.
25. H. Hope, M. M. Olmstead, P. P. Power, J. Sandell and X. Xu, *J. Am. Chem. Soc.* 1985, **107**, 4337.
26. G. van Koten and J. T. B. H. Jastrzebski, *J. Am. Chem. Soc.* 1985, **107**, 697.
27. N. P. Lorenzen and E. Weiss, *Angew. Chem., Int. Edn Engl.* 1990, **29**, 300.
28. M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.* 1990, **112**, 8009.
29. G. van Koten and J. G. Noltes, *J. Organomet. Chem.* 1979, **174**, 367; G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.* 1972, 940; B. H. Lipshutz, J. A. Kozlowski and C. M. Breneman, *J. Am. Chem. Soc.* 1985, **107**, 3197.
30. B. H. Lipshutz, S. H. Dimock and B. James, *J. Am. Chem. Soc.* 1993, **115**, 9283.
31. G. van Koten, J. T. B. H. Jastrzebski and J. G. Noltes, *J. Org. Chem.* 1977, **42**, 2047.
32. W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.* 1988, **27**, 1819.