ω scans

Absorption correction:
empirical *via* ψ scan
(*SADABS*; Sheldrick,
1996)
$T_{min} = 0.012$, $T_{max} = 0.047$

6628 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 29.43°$
$h = -12 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 21$

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.141$
$S = 1.006$
9112 reflections
495 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 3.63$ e Å^{-3}
$\Delta\rho_{min} = -2.73$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Os1A—O1A	2.100 (9)	Os2B—O1B	2.112 (9)
Os1A—Os2A	2.7897 (7)	Os2B—Os3B	2.8104 (7)
Os1A—Os3A	2.8195 (7)	O1A—C1A	1.462 (17)
Os2A—O1A	2.109 (9)	O2A—C2A	1.418 (18)
Os2A—Os3A	2.8098 (7)	O1B—C1B	1.413 (16)
Os1B—O1B	2.108 (9)	O2B—C2B	1.41 (2)
Os1B—Os2B	2.8040 (7)	C1A—C2A	1.51 (2)
Os1B—Os3B	2.8282 (7)	C1B—C2B	1.50 (2)
Os2A—Os1A—Os3A	60.120 (18)	Os2B—Os1B—Os3B	59.866 (18)
Os1A—Os2A—Os3A	60.466 (18)	Os1B—Os2B—Os3B	60.495 (18)
Os2A—Os3A—Os1A	59.415 (18)	Os2B—Os3B—Os1B	59.640 (18)

The H atoms on the glycol fragment were placed in calculated idealized positions and allowed to ride on their attached C or O atoms. Of the two metal hydrides, one was located by a low angle ($2\theta < 30°$) difference map and allowed to refine with restraints on the Os—H bond lengths to be equal, while the other was placed in a calculated position using the *XHYDEX* program (Orpen, 1997) and refined with the Os—H distance fixed at 1.84 (1) Å. The largest residual peak in the final difference map was 3.63 e Å^{-3}, at a distance of 0.95 Å from Os1A.

Data collection: *SMART* (Bruker, 1997). Cell refinement: *SAINT* (Bruker, 1997). Data reduction: *SHELXTL* (Bruker, 1997). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1235). Services for accessing these data are described at the back of the journal.

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A monomeric and a dimeric copper(II) trigonelline adduct with chloride, and a dimeric copper(II) 1-methyl-2-pyrrole-carboxylate adduct with 3-methylpyridine

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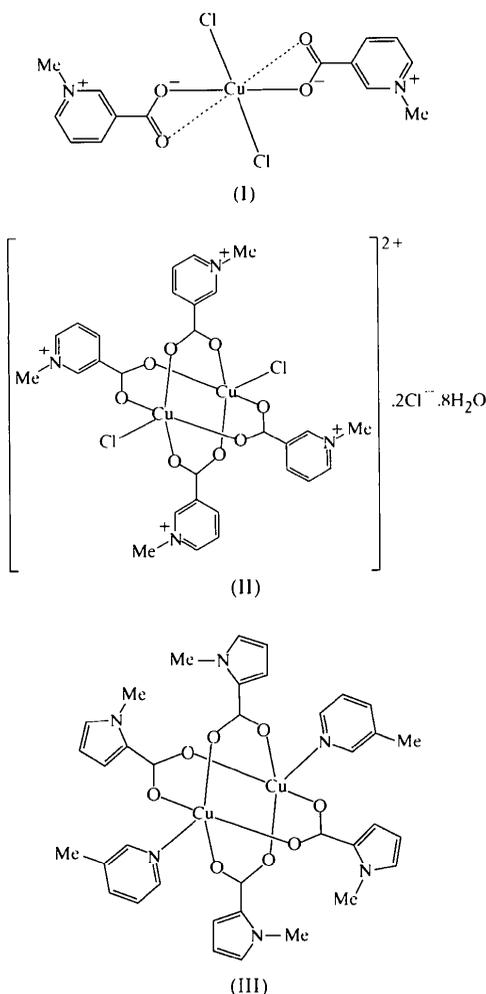
Abstract

In the crystal structure of *trans*-dichlorobis(trigonelline-*O,O'*)copper(II) (trigonelline is *N*-methylpyridinium-3-carboxylate), [CuCl₂(C₇H₇NO₂)₂], (I), the monomeric Cu^{II} complex has a distorted octahedral coordination. In the crystal structure of tetrakis(μ-trigonelline-*O:O'*)-bis[chlorocopper(II)] dichloride octahydrate, [Cu₂Cl₂-(C₇H₇NO₂)₄]Cl₂·8H₂O, (II), the dinuclear Cu^{II} complex has a slightly elongated cage structure, with a Cu···Cu distance of 2.770 (1) Å. In the crystal structure of tetrakis[μ-(1-methylpyrrole-2-carboxylato)-*O:O'*]-bis[(3-methylpyridine-*N*)copper(II)], [Cu₂(C₆H₆NO₂)₄-(C₆H₇N)₂], (III), the dinuclear Cu^{II} complex has a cage structure, with a Cu···Cu distance of 2.671 (1) Å. The magnetic $-2J$ value for (III) is 343 cm^{-1} ($H = -2JS_1.S_2$).

Comment

The title complexes, *trans*-dichlorobis(trigonelline)copper(II), (I), tetrakis(μ-trigonelline)bis[chlorocopper(II)] dichloride octahydrate, (II), and tetrakis[μ-(1-methyl-pyrrole-2-carboxylato)]bis[(3-methylpyridine)copper(II)], (III), all have a center of symmetry. The rotation angles (φ_{rot}) of the *N*-methylpyridyl ring relative to the COO$^-$ moiety in the trigonelline ligands are 7.0 (3)° in (I), and 14.2 (3) and 20.0 (3)° in (II). The corresponding φ_{rot} values in other reported dimeric copper(II) benzoates range from 5.3 (4) to 19.5 (8)° (Kawata *et al.*, 1992). The corresponding φ_{rot} angles of the *N*-methylpyrrole moieties of (III) are 1.7 (3) and 6.0 (3)°.

(I)

(II)

(III)

The antiferromagnetic interaction is greatly reduced when nitrogen is directly bonded to the COO$^-$ bridge; $-2J$ = 80 cm^{-1} for [Cu(Et$_2$NCOO)$_2$(NHEt$_2$)]$_2$ (Agostinelli *et al.*, 1988). In (III), an N atom is bonded to the α-carbon of the carboxylate ions. The $-2J$ and the g values of (III) were determined in the present study to be 343 cm^{-1} and 2.29, respectively. The corresponding 2-methylpyridine adduct, [Cu(pyr)$_2$(C$_6$H$_7$N)]$_2$ (pyr is 1-methylpyrrole-2-carboxylate), (IV), was also prepared [crystal data: M_r = 809.83, monoclinic, $P2_1/n$, a = 11.704 (3), b = 9.722 (2), c = 16.580 (1) Å, β = 92.88 (1)°, V = 1884.2 (6) Å^3, Z = 2, Cu$\cdots$Cu = 2.674 (2) Å; magnetic data: $-2J$ = 356cm^{-1}, g = 2.28]. The $-2J$ values of (III) and (IV) are slightly larger than that of [Cu(PhCOO)$_2$(py)]$_2$ (py is pyridine; $-2J$ = 328 cm^{-1}; Kawata *et al.*, 1992). Compound (II) was not suitable for magnetic measurement because of the

Fig. 1. The molecular structure of (I), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of arbitrary radii.

The Cu$\cdots$Cu distance of 2.770 (1) Å in (II) is *ca* 0.10 Å longer than in (III), and the average value of the *trans*-O—Cu—O angles of 164.7 (1)° in (II) is 2.6 (2)° smaller than in (III). These observations indicate a shift of the Cu atom from the O$_4$ pyramidal basal plane toward the axial Cl$^-$ ion. A similar deformation of the square-pyramidal coordination and elongation of the Cu$\cdots$Cu distance has been observed for the dimeric copper(II) benzoylformates (Harada *et al.*, 1997), in which the Cu$\cdots$Cu distance is elongated from 2.735 (1) to 2.843 (1) Å by replacement of the axial pyridine ligand with a Cl$^-$ ion. The total charge of the trigonelline bridge is neutral. Few structures of this type of dimeric copper carboxylate have been reported; examples include [Cu$_2$(Me$_3$NCH$_2$-COO)$_4$(ClO$_4$)$_2$](ClO$_4$)$_2$ (McEwen, 1973), [Cu$_2$(Me$_3$N-CH$_2$COO)$_4$Cl$_2$]Cl$_2$·2[Cu(Me$_3$NCH$_2$COO)$_2$Cl$_2$] (Chen & Mak, 1993) and [Cu$_2$(H$_3$NCH$_2$CH$_2$COO)$_4$(H$_2$O)$_2$]-(NO$_3$)$_4$·4H$_2$O (Kamwaya *et al.*, 1984). In (II), layers of binuclear Cu^{II} complex cations, and layers of Cl$^-$ anions and interstitial water molecules are stacked alternately, perpendicular to **b**.
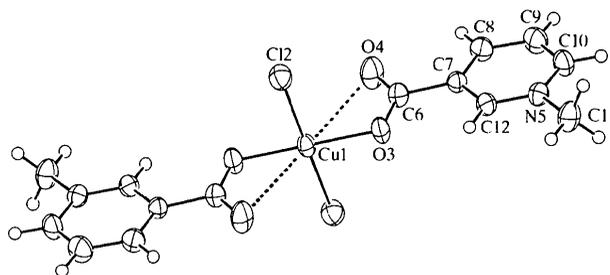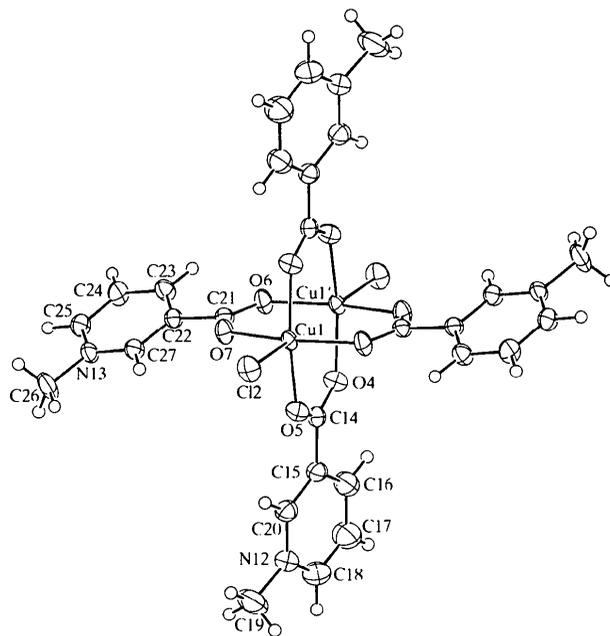

Fig. 2. The molecular structure of (II), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of arbitrary radii.

color change from green to blue under reduced pressure, suggesting a transformation of the dimer (II) to the monomer (I) after removal of the crystal water. The typical cage structure of a dimeric copper(II) benzoyl-DL-alanine adduct of water, [Cu{PhCONHCH(CH₃)-ᐟCOO}₂(H₂O)]₂, (V), was reported by Sandhu *et al.* (1989). Crystals of (V) have also been prepared and the lattice constants confirmed. The $-2J$ and g values of (V) were determined to be 348 cm⁻¹ and 2.26, respectively. The magnetic data for (III)–(V) indicate that there is a negligible influence on the antiferromagnetic interaction when the N atom is bonded to the α-carbon of the bridging carboxylate ions.
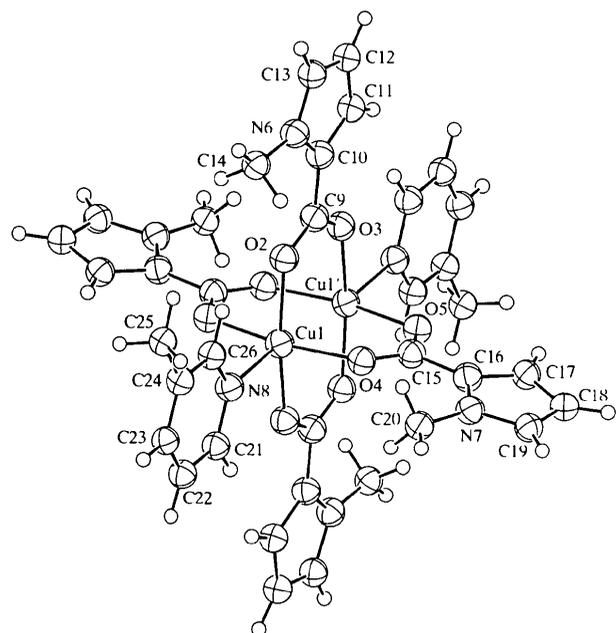

Fig. 3. The molecular structure of (III), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of arbitrary radii.

Experimental

For the preparation of (I), trigonelline hydrochloride (173 mg, 1.0 mmol) and Cu(CH₃COO)₂·H₂O (100 mg, 0.5 mmol) were suspended in water (25 ml), and the solution was stirred for 25 min at room temperature. When pyridine (40 mg, 0.5 mmol) was added to the solution, the color changed from light blue to blue, and crystals of (I) were obtained. For the preparation of (II), aqueous solutions of trigonelline hydrochloride and Cu(CH₃COO)₂·H₂O were mixed and stirred for 10 min, and then evaporated to dryness. The blue residue was dissolved in aqueous methanol (1:1), from which light-green plate-like crystals of (II) were obtained together with the light-blue powder of (I). For the preparation of (III), 1-methylpyrrole-2-carboxylic acid (pyrH; 83 mg, 0.66 mmol) and CuCO₃·Cu(OH)₂·H₂O (40 mg, 0.17 mmol) were suspended in aqueous methanol (1:1, 20 ml). The solution was

stirred for 40 min and then evaporated to dryness. The green residue was dissloved in acetonitrile and 3-methylpyridine (31 mg, 0.33 mmol) was added. From this solution, green crystals of (III) were obtained. The magnetic susceptibilities over the temperature range 80–300 K were determined by the Faraday method at Saga University. The procedure for determining $-2J$ values from cryomagnetic data, based on the Bleaney–Bowers equation, is the same as described by Harada *et al.* (1997).

Compound (I)

Crystal data

[CuCl₂(C₇H₇NO₂)₂]	Mo $K\alpha$ radiation
$M_r = 408.73$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 8.401 (1)$ Å	$\theta = 14$–15°
$b = 10.704 (1)$ Å	$\mu = 1.697$ mm⁻¹
$c = 9.325 (1)$ Å	$T = 295$ K
$\beta = 104.96 (1)°$	Prism
$V = 810.1 (2)$ Å³	$0.70 \times 0.20 \times 0.13$ mm
$Z = 2$	Blue
$D_x = 1.676$ Mg m⁻³	
D_m not measured	

Data collection

Rigaku AFC-5 diffractometer	1927 reflections with
	$|F_o| > 3\sigma(|F_o|)$
ω scans	$R_{int} = 0.041$
Absorption correction:	$\theta_{max} = 30°$
by integration (Coppens	$h = 0 \rightarrow 11$
et al., 1965)	$k = 0 \rightarrow 14$
$T_{min} = 0.539, T_{max} = 0.834$	$l = -12 \rightarrow 12$
2489 measured reflections	3 standard reflections
2348 independent reflections	every 100 reflections
	intensity decay: none

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.000225F^2]$
$R = 0.044$	$(\Delta/\sigma)_{max} = 0.03$
$wR = 0.045$	$\Delta\rho_{max} = 1.09$ e Å⁻³
$S = 1.23$	$\Delta\rho_{min} = -0.55$ e Å⁻³
1927 reflections	Extinction correction: none
106 parameters	Scattering factors from *Inter-*
H-atom parameters	*national Tables for X-ray*
constrained	*Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Cu1—Cl2	2.280 (1)	O3—C6	1.266 (3)
Cu1—O3	1.948 (2)	O4—C6	1.232 (3)
Cu1—O4	2.747 (1)		
Cl2—Cu1—O3	90.4 (1)	Cu1—O3—C6	109.3 (2)
Cl2—Cu1—O4	89.2 (2)	O3—C6—O4	125.1 (2)
O3—Cu1—O4	53.1 (1)		

Compound (II)

Crystal data

[Cu₂Cl₂(C₇H₇NO₂)₄]Cl₂·· 8H₂O	Mo $K\alpha$ radiation
$M_r = 961.58$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
	$\theta = 10$–15°

$a = 10.156$ (2) Å
$b = 13.883$ (2) Å
$c = 7.793$ (1) Å
$\alpha = 99.40$ (1)°
$\beta = 109.29$ (1)°
$\gamma = 75.57$ (1)°
$V = 1000.5$ (2) Å^3
$Z = 1$
$D_x = 1.596$ Mg m^{-3}
D_m not measured

$\mu = 1.401$ mm^{-1}
$T = 299$ K
Plate-like
$0.50 \times 0.25 \times 0.10$ mm
Blue

Data collection

Rigaku AFC-5 diffractom-
eter
θ–2θ scans
Absorption correction:
  by integration (Coppens
  et al., 1965)
  $T_{min} = 0.705$, $T_{max} = 0.872$
4848 measured reflections
4586 independent reflections

3714 reflections with
  $|F_o| > 3\sigma(|F_o|)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -10 \rightarrow 10$
3 standard reflections
  every 100 reflections
  intensity decay: 22.6%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.043$
$S = 1.48$
3714 reflections
244 parameters
H-atom parameters
  constrained

$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}
Extinction correction: none
Scattering factors from Inter-
  national Tables for X-ray
  Crystallography (Vol. IV)

Compound (III)

Crystal data

[Cu$_2$(C$_6$H$_6$NO$_2$)$_4$(C$_6$H$_7$N)$_2$]
$M_r = 809.83$
Monoclinic
$P2_1/a$
$a = 10.431$ (2) Å
$b = 17.795$ (3) Å
$c = 10.685$ (2) Å
$\beta = 114.40$ (1)°
$V = 1806.3$ (6) Å^3
$Z = 2$
$D_x = 1.489$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 10$–15°
$\mu = 1.237$ mm^{-1}
$T = 299$ K
Plate-like
$0.35 \times 0.35 \times 0.07$ mm
Green

Data collection

Rigaku AFC-5 diffractom-
  eter
θ–2θ scans
Absorption correction:
  by integration (Coppens
  et al., 1965)
  $T_{min} = 0.628$, $T_{max} = 0.902$
4366 measured reflections
4141 independent reflections

2525 reflections with
  $|F_o| > 3\sigma(|F_o|)$
$R_{int} = 0.061$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = -14 \rightarrow 14$
3 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.043$
$S = 1.26$
2525 reflections
235 parameters
H-atom parameters
  constrained

$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from Inter-
  national Tables for X-ray
  Crystallography (Vol. IV)

Table 2. Selected geometric parameters (Å, °) for (II)

Cu1—Cu1^i	2.770 (1)	Cu1—O7	1.978 (2)
Cu1—Cl2	2.413 (1)	O4—C14	1.255 (3)
Cu1—O4^i	1.994 (2)	O5—C14	1.255 (3)
Cu1—O5	1.985 (2)	O6—C21	1.253 (3)
Cu1—O6^i	1.989 (2)	O7—C21	1.256 (3)
Cl2—Cu1—O4^i	97.2 (1)	O5—Cu1—O7	87.9 (1)
Cl2—Cu1—O5	98.2 (1)	O6^i—Cu1—O7	164.7 (1)
Cl2—Cu1—O6^i	97.4 (1)	Cu1^i—O4—C14	126.7 (2)
Cl2—Cu1—O7	97.9 (1)	Cu1—O5—C14	122.4 (2)
O4^i—Cu1—O5	164.6 (1)	Cu1^i—O6—C21	125.3 (2)
O4^i—Cu1—O6^i	87.5 (1)	Cu1—O7—C21	122.8 (2)
O4^i—Cu1—O7	90.7 (1)	O4—C14—O5	126.2 (2)
O5—Cu1—O6^i	89.9 (1)	O6—C21—O7	126.8 (2)

Symmetry code: (i) $2 - x, 1 - y, 2 - z$.

Table 3. Hydrogen-bonding geometry (Å, °) for (II)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O8—H8A⋯Cl3	0.955	2.163	3.107 (4)	169
O8—H8B⋯O10^i	0.956	1.739	2.689 (5)	172
O8—H8C⋯O8^{ii}	0.959	1.848	2.746 (5)	155
O9—H9A⋯Cl3	0.957	2.209	3.128 (4)	161
O9—H9B⋯O10	0.971	1.802	2.728 (5)	158
O10—H10A⋯Cl2^{iii}	0.965	2.291	3.220 (3)	161
O10—H10B⋯N12^{iv}	0.966	2.366	3.203 (4)	145
O11—H11A⋯O9	0.960	1.787	2.669 (5)	151
O11—H11B⋯Cl3^v	0.961	2.234	3.102 (4)	150
O11—H11C⋯O11^{vi}	0.961	1.844	2.716 (6)	150

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, -z$; (iii) $x - 1, y, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, y, 1 + z$; (vi) $2 - x, -y, 2 - z$.

Table 4. Selected geometric parameters (Å, °) for (III)

Cu1—Cu1^i	2.671 (1)	Cu1—N8	2.206 (4)
Cu1—O2	1.975 (4)	O2—C9	1.265 (6)
Cu1—O3^i	1.962 (4)	O3—C9	1.267 (6)
Cu1—O4	1.973 (4)	O4—C15	1.261 (6)
Cu1—O5^i	1.975 (4)	O5—C15	1.262 (6)
O2—Cu1—O3^i	167.4 (2)	O5^i—Cu1—N8	98.2 (2)
O2—Cu1—O4	89.3 (2)	Cu1—O2—C9	119.8 (3)
O2—Cu1—O5^i	88.4 (2)	Cu1^i—O3—C9	128.2 (4)
O2—Cu1—N8	98.2 (2)	Cu1—O4—C15	125.9 (3)
O3^i—Cu1—O4	89.6 (2)	Cu1^i—O5—C15	121.7 (3)
O3^i—Cu1—O5^i	89.8 (2)	Cu1—N8—C21	119.8 (4)
O3^i—Cu1—N8	94.4 (2)	Cu1—N8—C26	122.9 (3)
O4—Cu1—O5^i	167.2 (2)	O2—C9—O3	124.5 (5)
O4—Cu1—N8	94.6 (2)	O4—C15—O5	124.8 (4)

Symmetry code: (i) $2 - x, -y, 2 - z$.

Intensity decay of the standard reflections was 22.6% for (II), which was corrected; it may be due to the partial loss of crystal water in air. The water H atoms of (II) were located from difference syntheses. The water O8 and O11 atoms lie near the center of symmetry and form a hydrogen bond with the corresponding symmetry-related molecule. One of two H atoms bonded to O8 or O11 has two possible positions with site-occupation factors of 50%. The positions of all other H atoms were calculated geometrically. A riding model was used

in their refinement [O/C—H 0.96 Å, U_{iso}(H) = 0.2 Å^2 for water H atoms and 0.1 Å^2 for other H atoms].

For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structures: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

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Tris(2-pyridylmethyl)triazacyclododecane complexes of Fe^{II} and Cu^{II}

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Abstract

The title complexes, [1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane-κ^3N] iron(II) tetrachloroferrate, [Fe(C$_{27}$H$_{36}$N$_6$)][FeCl$_4$], and [1,5,9-tris(2-pyridyl-

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methyl)-1,5,9-triazacyclododecane-κ^3N]copper(II) bis-(hexafluorophosphate) acetonitrile hemisolvate, [Cu-(C$_{27}$H$_{36}$N$_6$)](PF$_6$)$_2$·0.5CH$_3$CN, differ significantly in their conformations. The iron complex is near-octahedral, with Fe—N distances of 2.257 (5) (ring) and 2.226 (5) Å (pyridine), and fused chelate rings predominately in the boat form. The copper complex is tetragonally distorted, with four shorter and two longer Cu—N bonds [2.049 (6)–2.199 (7) and 2.280 (6)–2.473 (7) Å, respectively]; its chelate rings are disordered in boat, chair and skew forms.

Comment

Metal complexes of tris(2-pyridylmethyl)triazacyclononane ([9]-N3py$_3$) have been extensively investigated for their electrochemical, magnetic, spectroscopic and structural properties (Christiansen *et al.*, 1986; Wieghardt *et al.*, 1986). However, the corresponding cyclododecane complexes are less well known, partly because ligand synthesis has proved much more difficult. This problem has been overcome recently, and characterization and molecular mechanics studies of examples of these complexes have been reported by Zhang & Busch (1994).

We report here the structures of the iron and copper complexes of the ligand [12]-N3py$_3$ as the [FeCl$_4$]$^{2-}$, (1), and [PF$_6$]$^-$ salts, (2), respectively. Both complexes exist as discrete cations; the iron complex is symmetrical, with a crystallographic threefold axis, while the two independent copper cations have somewhat different conformations. In these complexes, the three fused six-membered rings formed by the ring N atoms can take up chair, boat or skew conformations. The metal geometry can vary between octahedral and trigonal prismatic, depending on the twist angle between the M—N(macrocycle) and M—N(py) directions.
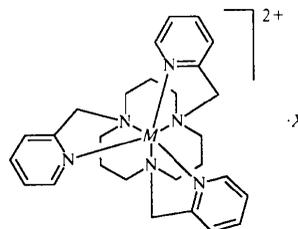
(1) M = Fe; X = [FeCl$_4$]$^{2-}$
(2) M = Cu; X = 2PF$_6^-$·0.5C$_2$H$_3$N

The most obvious difference between the nine- and 12-membered ring complexes is that the Fe^{II} ion changes from low to high spin when the ring size increases. The iron complex (Fig. 1) is disordered at C2. The major position [C2A, 0.69 (1) occupancy] corresponds to chair conformations for the chelate rings. For the minor position (C2B), the rings are in the boat form,