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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1057). Services for accessing these data are described at the back of the journal.

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

NATHANIEL W. ALCOCK,[a] DELONG ZHANG[b]† AND DARYLE H. BUSCH[a]

[a]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England, and* [b]*Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA. E-mail: msrbb@csv.warwick.ac.uk*

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Abstract

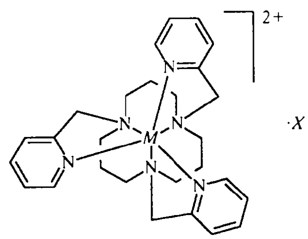
The title complexes, [1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane-κ^3N]iron(II) tetrachloroferrate, $[Fe(C_{27}H_{36}N_6)][FeCl_4]$, and [1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane-κ^3N]copper(III) bis(hexafluorophosphate) acetonitrile hemisolvate, $[Cu(C_{27}H_{36}N_6)](PF_6)_2 \cdot 0.5CH_3CN$, 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.

† Current address: Praxair Inc., 175 East Park Drive, PO Box 44, Tonawanda, NY 14151-0044, USA.

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=$2PF_6^- \cdot 0.5C_2H_3N$

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 [C2*A*, 0.69 (1) occupancy] corresponds to chair conformations for the chelate rings. For the minor position (C2*B*), the rings are in the boat form,

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which is presumably slightly less stable. The twist angle is 41.8°, considerably closer to octahedral (60°) than trigonal prismatic (0°) coordination. The Fe—N(ring) distance is slightly shorter than the Fe—N(py) distance [2.226 (7) and 2.257 (5) Å, respectively]. They are both 0.25 Å longer than the corresponding distances in the low-spin [9]-N3 complex (Christiansen *et al.*, 1986). Significantly, the ideal best-fit *M*—N distance estimated by molecular mechanics is 0.15 Å longer again (Zhang & Busch, 1994). It is clear that the rigid 12-membered macrocyclic ring enforces *M*—N distances substantially longer than with the [9]-N3 ring, thus stabilizing the larger high-spin Fe^{II} ion. It also favours larger M^{II} ions over M^{III}, producing a shift of +0.45 V in the Fe^{III}/Fe^{II} potential (Zhang & Busch, 1994).

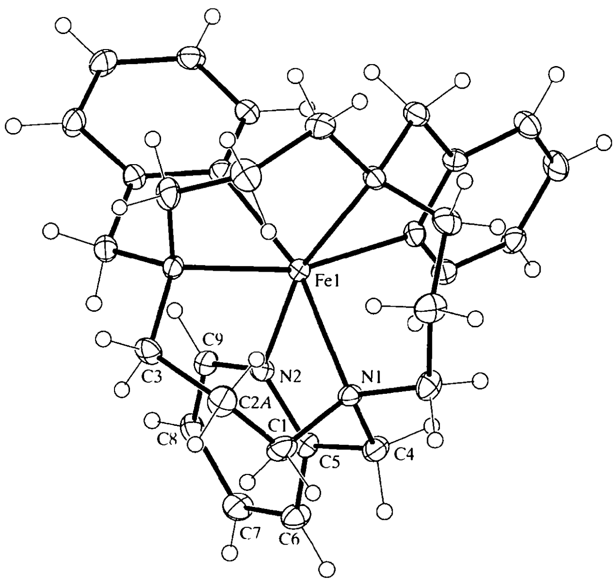

Fig. 1. View of the cation of (I) from a direction close to the threefold axis, showing the atomic numbering. Only the major component of the disordered ring is shown. Displacement ellipsoids are drawn at the 20% probability level.

The ligand rigidity is manifested directly in the N···N distances in the macrocyclic ring; these are 3.37 (1) Å, compared with 2.74 Å in the nine-membered ring. This increase is not the only factor contributing to the lengthening of the Fe—N distances. It might be possible for the metal ion to move closer to the centre of the ring to compensate for the larger N···N distances, but this is prevented by the rigidity of the five-membered Fe—N—C—C—N—(Fe) rings involving the dangling pyridine arms. Any movement of the Fe atom towards the [12]-N3 ring would lengthen the Fe—N(py) distance, with no net gain in stability.

The smaller Cu^{II} ion produces considerably more distortion in the complex geometry than is found with Fe^{II}, with statistically significant variation between the two independent ions. Both have two short Cu—N(py) [2.049 (6)–2.109 (6) Å] and two short Cu—N(ring) distances [2.058 (7)–2.200 (7) Å]. However, the third Cu—N(ring) distance is considerably longer [2.283 (6) and 2.329 (7) Å], while the third Cu—N(py) interaction is clearly very weak [2.420 (7) and 2.473 (7) Å]. As these two longer bonds are *trans* to each other, the octahedron is best described as tetragonally distorted. The variation between the independent ions probably reflects the ease with which these long Cu—N distances can stretch and thus their susceptibility to small variations in packing forces.

The N···N distances in the macrocyclic ring are slightly smaller than in the iron complex [3.23 (3) Å, averaged over both ions]. Cation *A* has the central CH_2 disordered, giving chair/boat conformations, as for the iron complex (0.7 occupancy for the chair form). In cation *B*, all the C atoms are disordered, implying the co-existence of chair, boat and skew conformations. As a result of this disorder, ligand geometry is rather poorly determined.

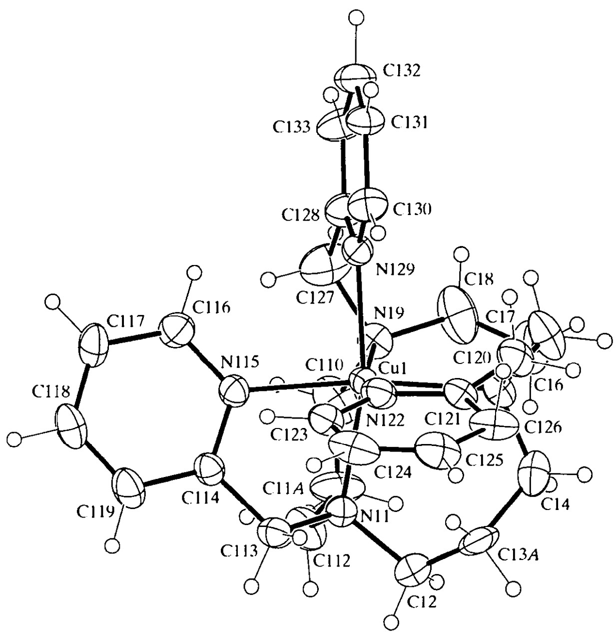

Fig. 2. View of cation *A* of (2), showing the atomic numbering, including only the major disordered component. It is viewed approximately along the tetragonally elongated axis. Displacement ellipsoids are drawn at the 20% probability level. Atom N15 is not labelled.

Confirmation that the solid-state conformations of these complexes are preserved in solution has been obtained from a study of the ^{13}C and ^{1}H NMR spectra of $[Zn(L)](PF_6)_2$ in CD_3CN [*L* is 1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane; Zhang, 1994]. The spectra show dynamic processes which are attributed to rapid exchange between the two alternative positions for C2 (as found in the iron complex), leading to interconversion of the chair and boat conformations, with both these forms co-existing in solution. Cooling the solution to 230 K causes broadening of the ^{13}C peak assigned to C2.

The Fe—Cl distances in the $FeCl_4$ counter-ion of the iron(II) complex are 2.315 (2) and 2.365 (4) Å, compared with a mean value of 2.301 Å in other examples (Orpen *et al.*, 1989).

Experimental

The title complexes were prepared according to Zhang & Busch (1994). Both gave weakly diffracting crystals.

Compound (1)

Crystal data

$[Fe(C_{27}H_{36}N_6)][FeCl_4]$
$M_r = 698.12$
Cubic
$Pa\overline{3}$
$a = 18.793$ (2) Å
$V = 6637.3$ (13) Å^3
$Z = 8$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 10$–$11°$
$\mu = 1.223$ mm^{-1}
$T = 200$ (2) K
Block
0.48 × 0.38 × 0.37 mm
Light brown

Data collection

Siemens *R*3*m* diffractometer
ω–2θ scans
Absorption correction: Gaussian (*SHELXTL-Plus*; Sheldrick, 1990*a*)
$T_{min} = 0.845$, $T_{max} = 0.946$
2262 measured reflections
1461 independent reflections
1098 reflections with $I > 2\sigma(I)$

$R_{int} = 0.127$
$\theta_{max} = 22.54°$
$h = 0 \rightarrow 12$
$k = 1 \rightarrow 20$
$l = 0 \rightarrow 20$
3 standard reflections every 200 reflections intensity decay: 22%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.173$
$S = 1.094$
1461 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0720P)^2 + 17.7800P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.758$ e Å^{-3}
$\Delta\rho_{min} = -0.377$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0012 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe1—N2	2.226 (5)	Fe1—N1	2.257 (5)
N2^i—Fe1—N2	89.3 (2)	N2—Fe1—N1^i	98.7 (2)
N2^i—Fe1—N1	164.0 (2)	N1—Fe1—N1^i	96.57 (18)
N2—Fe1—N1	77.04 (19)		

Symmetry code: (i) *y*, *z*, *x*.

Compound (2)

Crystal data

$[Cu(C_{27}H_{36}N_6)](PF_6)_2\cdot 0.5C_2H_3N$
$M_r = 818.62$
Orthorhombic
Pbca
$a = 24.309$ (5) Å
$b = 13.543$ (3) Å
$c = 41.392$ (8) Å
$V = 13627$ (5) Å^3
$Z = 16$
$D_x = 1.596$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3837 reflections
$\theta = 3$–$15°$
$\mu = 0.833$ mm^{-1}
$T = 293$ (2) K
Block
0.20 × 0.15 × 0.10 mm
Blue–green

Data collection

Delft Instruments FAST TV area-detector diffractometer
φ scans
Absorption correction: none
42132 measured reflections
8385 independent reflections

3837 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 22.83°$
$h = -25 \rightarrow 25$
$k = -10 \rightarrow 13$
$l = -41 \rightarrow 42$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.179$
$S = 0.842$
8385 reflections
930 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1050P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.080$
$\Delta\rho_{max} = 0.457$ e Å^{-3}
$\Delta\rho_{min} = -0.345$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—N129	2.094 (6)	Cu2—N229	2.049 (6)
Cu1—N115	2.109 (6)	Cu2—N215	2.058 (7)
Cu1—N11	2.149 (6)	Cu2—N21	2.063 (8)
Cu1—N15	2.181 (6)	Cu2—N25	2.200 (7)
Cu1—N19	2.283 (6)	Cu2—N29	2.329 (7)
Cu1—N122	2.420 (7)	Cu2—N222	2.473 (7)
N129—Cu1—N115	90.5 (2)	N229—Cu2—N215	91.5 (3)
N129—Cu1—N11	165.8 (2)	N229—Cu2—N21	166.2 (3)
N115—Cu1—N11	78.7 (2)	N215—Cu2—N21	79.3 (3)
N129—Cu1—N15	96.0 (2)	N229—Cu2—N25	93.7 (3)
N115—Cu1—N15	161.3 (2)	N215—Cu2—N25	160.8 (3)
N11—Cu1—N15	97.1 (2)	N21—Cu2—N25	98.4 (3)
N129—Cu1—N19	77.8 (2)	N229—Cu2—N29	78.8 (3)
N115—Cu1—N19	105.0 (2)	N215—Cu2—N29	109.4 (2)
N11—Cu1—N19	95.9 (2)	N21—Cu2—N29	94.4 (4)
N15—Cu1—N19	93.6 (2)	N25—Cu2—N29	89.8 (3)
N129—Cu1—N122	91.0 (2)	N229—Cu2—N222	91.3 (3)
N115—Cu1—N122	85.7 (3)	N215—Cu2—N222	86.6 (2)
N11—Cu1—N122	97.3 (2)	N21—Cu2—N222	98.3 (4)
N15—Cu1—N122	76.6 (3)	N25—Cu2—N222	74.7 (3)
N19—Cu1—N122	164.4 (2)	N29—Cu2—N222	161.2 (2)

For both compounds, no significant diffraction was recorded above a θ value of 22.5° and collection was terminated at this limit. The relatively high R_{int} for the iron complex is understandable in view of the averaging of the large number of low significance observations.

For the iron complex, the temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). For the copper complex, the data collection nominally covered over a hemisphere of reciprocal space by a combination of several sets of exposures. Information on percentage coverage is not available. Crystal decay was found to be negligible by analysing duplicate reflections.

H atoms were added at calculated positions (except as noted below) and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms (except as noted below); H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the carrier atom. In compound (1), the central C atom of the macrocyclic ring is disordered; the two C atoms and the two sets of idealized H atoms attached to C1–C3 were refined with linked occupancies [the refined occupancy for the major component was 0.69 (1)]. Although the largest residual Fourier peaks are considerably less than 1 e Å^{-3} in height, they are located in a large void in the unit cell (160 Å^3) and may indicate the presence of extremely disordered solvent. Compound (2) has two independent cations, four anions and one molecule of acetonitrile in the asymmetric unit. Cation *A* has two disordered CH_2 groups, C13*A*/*B* and C11*A*/*B* [with very similar occupancies, refined together as 0.719 (2):0.281 (2)]. Cation *B* is highly disordered and atoms C22–C24 [occupancies 0.55 (2):0.45 (2)], C26–C28 [0.66 (2):0.34 (2)] and C210–C212 [0.51 (2):0.49 (2)] were all refined as disordered pairs. Only the H atoms of the major components of cation *A* and the non-disordered atoms of cation *B* were included. The second and third $[PF_6]^-$ anions were also modelled with four equatorial F atoms doubled. All P—F and F···F distances were restrained [refined P—F value = 1.549 (3) Å]. Anisotropic displacement parameters were not used for the minor components of cation *A*, the disordered atoms of cation *B* and some of the disordered F atoms. High displacement parameters for some other F atoms suggest additional unmodelled disorder.

Data collection: *R3M* (Siemens, 1986) for (1); *MADNES* (Pflugrath & Messerschmidt, 1992) for (2). Cell refinement: *R3M* for (1); *MADNES* for (2). Data reduction: *R3M* for (1); *MADNES* for (2). Program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990*a*) for (1); *SHELXS*86 (Sheldrick, 1990*b*) for (2). Program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997) for (1); *SHELXL*93 (Sheldrick, 1993) for (2). Molecular graphics: *XP* (Siemens, 1995) for (1); *SHELXTL-Plus* for (2). Software used to prepare material for publication: *XCIF* for (1); *SHELXTL-Plus* for (2).

We thank Professor M. B. Hursthouse, University of Cardiff, for providing data for compound (2). We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). The Warwick–Kansas collaboration has been supported by NATO.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1275). Services for accessing these data are described at the back of the journal.

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Triphenyltin *N*,*N*-dimethylthiocarbamoylacetate, triphenyltin *N*,*N*-pentamethylenecarbamoylthioacetate and cyclopentyldiphenyltin *N*,*N*-dimethylthiocarbamoylacetate

Kong Mun Lo,[a] V. G. Kumar Das[a] and Seik Weng Ng[b]

[a]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and* [b]*Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: h1nswen@cc.um.edu.my*

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Abstract

Carboxylate bridges link two independent molecules of triphenyltin *N*,*N*-dimethylthiocarbamoylacetate, $[Sn(C_6H_5)_3(C_5H_8NO_3S)]$, into a helical chain {*i.e. catena*-poly[triphenyltin-μ-(*N*,*N*-dimethylthiocarbamoylacetato-*O*:*O*′)]}, as do the carboxylate bridges in triphenyltin *N*,*N*-pentamethylenecarbamoylthioacetate, $[Sn(C_6H_5)_3(C_8H_{12}NO_3S)]$ {*i.e. catena*-poly[triphenyltin-μ-(*N*,*N*-

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