C(45)	0.5731	0.2945	−0.1359	0.058 (2)
C(46)	0.4810	0.2300	−0.1261	0.038 (1)
C(51)	0.5020 (2)	0.2315 (2)	−0.3437 (2)	0.050 (2)
C(52)	0.5382	0.1959	−0.4398	0.063 (2)
C(53)	0.4558	0.1439	−0.4642	0.070 (2)
C(54)	0.3373	0.1275	−0.3925	0.075 (2)
C(55)	0.3011	0.1631	−0.2963	0.055 (2)
C(56)	0.3834	0.2150	−0.2719	0.040 (1)
C(61)	0.3257 (3)	0.4367 (2)	−0.2561 (2)	0.049 (2)
C(62)	0.3216	0.5383	−0.2726	0.061 (2)
C(63)	0.3367	0.6018	−0.2063	0.059 (2)
C(64)	0.3560	0.5637	−0.1234	0.058 (2)
C(65)	0.3602	0.4620	−0.1069	0.049 (2)
C(66)	0.3450	0.3985	−0.1732	0.038 (1)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Te(1)—Fe(1)	2.531 (1)	Te(1)—Fe(2)	2.539 (1)
Te(1)—Fe(3)	2.545 (1)	Te(2)—Fe(1)	2.544 (1)
Te(2)—Fe(2)	2.549 (1)	Te(2)—Fe(3)	2.565 (1)
Fe(1)—Fe(3)	2.800 (1)	Fe(1)—P(1)	2.274 (1)
Fe(1)—C(1)	1.792 (3)	Fe(1)—C(2)	1.749 (4)
Fe(2)—Fe(3)	2.707 (1)	Fe(2)—P(2)	2.214 (1)
Fe(2)—C(3)	1.779 (5)	Fe(2)—C(4)	1.775 (4)
Fe(3)—C(5)	1.775 (5)	Fe(3)—C(6)	1.786 (4)
Fe(3)—C(7)	1.771 (3)		
Fe(1)—Te(1)—Fe(2)	98.9 (1)	P(2)—Fe(2)—C(4)	97.6 (1)
Fe(2)—Te(1)—Fe(3)	64.3 (1)	Te(1)—Fe(3)—Te(2)	80.9 (1)
Fe(1)—Te(2)—Fe(3)	66.5 (1)	Te(1)—Fe(3)—Fe(2)	57.7 (1)
Te(1)—Fe(1)—Te(2)	81.5 (1)	Te(1)—Fe(3)—C(6)	86.0 (1)
Te(1)—Fe(1)—P(1)	94.0 (1)	Te(2)—Fe(3)—Fe(1)	56.4 (1)
Te(1)—Fe(1)—C(2)	99.4 (1)	Te(2)—Fe(3)—C(5)	86.8 (1)
Te(2)—Fe(1)—P(1)	172.4 (1)	Te(2)—Fe(3)—C(7)	99.8 (1)
Te(2)—Fe(1)—C(2)	94.5 (1)	Fe(1)—Fe(3)—C(5)	141.4 (1)
Fe(3)—Fe(1)—C(1)	104.2 (1)	Fe(1)—Fe(3)—C(7)	77.5 (1)
P(1)—Fe(1)—C(1)	93.6 (1)	Fe(2)—Fe(3)—C(6)	106.7 (1)
C(1)—Fe(1)—C(2)	97.8 (2)	C(5)—Fe(3)—C(6)	95.7 (2)
Te(1)—Fe(2)—Fe(3)	57.9 (1)	C(6)—Fe(3)—C(7)	95.7 (2)
Fe(1)—Te(1)—Fe(3)	67.0 (1)	Te(1)—Fe(2)—C(4)	89.9 (2)
Fe(1)—Te(2)—Fe(2)	98.3 (1)	Te(2)—Fe(2)—P(2)	109.1 (1)
Fe(2)—Te(2)—Fe(3)	63.9 (1)	Te(2)—Fe(2)—C(4)	152.8 (1)
Te(1)—Fe(1)—Fe(3)	56.8 (1)	Fe(3)—Fe(2)—C(3)	107.7 (1)
Te(1)—Fe(1)—C(1)	160.9 (1)	P(2)—Fe(2)—C(3)	94.2 (1)
Te(2)—Fe(1)—Fe(3)	57.1 (1)	C(3)—Fe(2)—C(4)	96.5 (2)
Te(2)—Fe(1)—C(1)	88.9 (1)	Te(1)—Fe(3)—Fe(1)	56.3 (1)
Fe(3)—Fe(1)—P(1)	115.3 (1)	Te(1)—Fe(3)—C(5)	135.2 (1)
Fe(3)—Fe(1)—C(2)	143.0 (1)	Te(1)—Fe(3)—C(7)	124.0 (2)
P(1)—Fe(1)—C(2)	92.3 (1)	Te(2)—Fe(3)—Fe(2)	57.7 (1)
Te(1)—Fe(2)—Te(2)	81.3 (1)	Te(2)—Fe(3)—C(6)	163.5 (1)
Te(1)—Fe(2)—P(2)	98.5 (1)	Fe(1)—Fe(3)—Fe(2)	88.7 (1)
Te(1)—Fe(2)—C(3)	164.9 (1)	Fe(1)—Fe(3)—C(6)	122.8 (2)
Te(2)—Fe(2)—Fe(3)	58.3 (1)	Fe(2)—Fe(3)—C(5)	79.3 (1)
Te(2)—Fe(2)—C(3)	86.9 (1)	Fe(2)—Fe(3)—C(7)	157.5 (1)
Fe(3)—Fe(2)—P(2)	153.2 (1)	C(5)—Fe(3)—C(7)	100.4 (2)
Fe(3)—Fe(2)—C(4)	95.2 (1)		

The structure was solved by direct methods. The phenyl rings were constrained as rigid groups. All H atoms were included in idealized riding positions, with fixed isotropic *U*. The *SHELXTL-Plus* (Sheldrick, 1990) program library was used throughout.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71208 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1039]

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Copper(II) and Nickel(II) Octabromo-tetrakis(pentafluorophenyl) Porphyrin Complexes

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Abstract

The copper and nickel complexes of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ({4,5,9,10,14,15,19,20-octabromo-2,7,12,17-tetrakis(pentafluorophenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1,3(22),4,6,8(23),9,11,13(24),14,16,18(21),19-dodecaene}copper(II) 0.5-dichloromethane solvate and {4,5,9,10,14,15,19,20-octabromo-2,7,12,17-tetrakis(pentafluorophenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1,3(22),4,6,8(23),9,11,13(24),14,16,18(21),19-dodecaene}nickel(II) 0.5-dichloromethane solvate) form isostructural crystals. There is significant distortion from planarity of the porphyrin ring caused by the octabromo substituents interacting with the *meso*-pentafluorophenyl groups and with each other, with departures of the Br atoms from the plane defined by the four N atoms of up to 2.36 Å. This tetrahedral distortion of the molecule does not result in any significant changes in bond distances from those in non-halogenated tetraphenylporphyrin complexes.

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† Contribution No. 8624.

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Comment

Metalloporphyrin complexes function as catalysts for the oxygenation of light alkanes to alcohols with negligible catalyst decomposition (Lyons, Ellis, Wagner, Thompson, Hughes, Hodge & Gray, 1992). The two compounds reported here were studied to determine if there were unusual structural features to account for this activity. After this paper was submitted, the structure of the Ni complex was independently reported (Mandon, Ochsenbein, Fischer, Weiss, Jayaraj, Austin, Gold, White, Brigaud, Battioni & Mansuy, 1992). The geometry we find for this compound is essentially the same as was found by Mandon *et al.* (1992).

$Zn[TF_{20}PP\beta\text{-}Br_8]$ [$TF_{20}PP\beta\text{-}Br_8$ = the dianion of tetrakis(pentafluorophenyl)-β-octabromoporphyrin] was synthesized according to published procedures (Lyons & Ellis, 1991) and demetallated at room temperature by bubbling HCl gas through a stirred $CHCl_3$ solution for 2–3 min. The free ligand was metallated in a stirred room-temperature methanol solution by the slow addition of an excess of the corresponding metal acetate and the product was purified on silica gel by elution with a hexane–dichloromethane solution. Dark-purple crystals of each compound were grown by evaporation at room temperature of CH_2Cl_2 solutions over a period of 7–10 d.

A diagram of the Ni complex in Fig. 1 shows the numbering for both compounds. The central cavity holding the metal is larger in the Cu complex than in the Ni complex [*CT*—N 1.969 (6) *vs* 1.902 (4) Å for Ni; *CT* is the average of the coordinates of the four N atoms] and both metal atoms are within 0.01 Å of the four N-atom plane. This plane shows some tetrahedral distortion; in the Ni complex the N atoms are ± 0.19 Å from their plane and in the Cu complex, ± 0.15 Å. As one moves farther from the metal atom, the tetrahedral distortions increase; they are comparable in the two structures (Fig. 2). Table 3 lists the average deviation of selected atoms from the four N-atom plane (averaged according to $\bar{4}$ symmetry). The *meso* C atoms (attached to the phenyl groups) are least affected by this saddling; in these compounds they are on the 'node' of the effect. The Br atoms actually form two groups in which the odd-numbered Br atoms on each pyrrole ring are farther out of the plane than the even-numbered Br atoms. These large displacements from the plane increase the Br···C(phenyl)···Br distances which are still extremely short. A Br···C van der Waals contact is expected to be 3.60 Å; here we find approaches as short as 3.13 Å, with the average being 3.18 (3) Å for both compounds. The Br···C(*ortho*) distances are slightly longer, averaging 3.46 (16) Å for the Cu compound and 3.49 (13) Å for the Ni compound. Even the Br···Br contacts are 0.45 Å shorter than expected [average 3.444 (10) Å for Ni, 3.438 (12) Å for Cu]. The molecule has apparently adjusted as much as it could to increase the distances between the atoms involved in these close interactions. The macrocyclic distortion found upon β-octabromo substitution is approximately equal in magnitude to that observed for the Zn complex of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin (Barkigia, Berber, Fajer, Medforth, Renner & Smith, 1990). This similarity is not unexpected if the saddling of the macrocycle originates merely from steric interactions (a methyl group and a Br atom are about the same size) and not from electronic factors. Most of the adjusting involves bond angles and torsion angles; bond distances are in

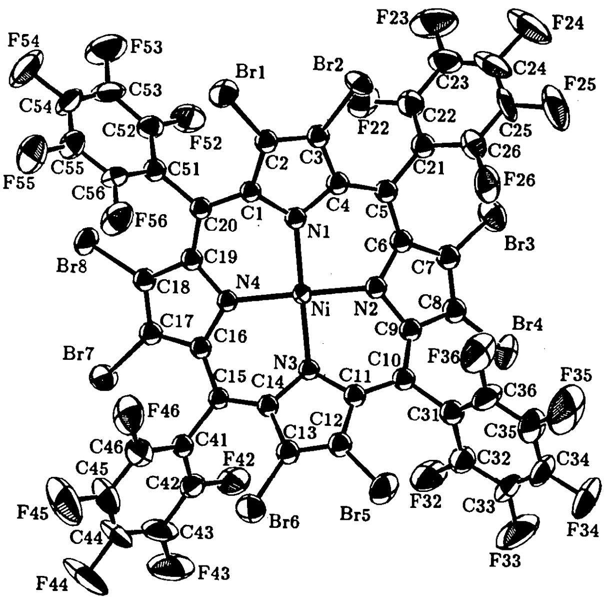

Fig. 1. An *ORTEP* drawing of the Ni complex with 50% probability ellipsoids showing the numbering system used for both compounds.

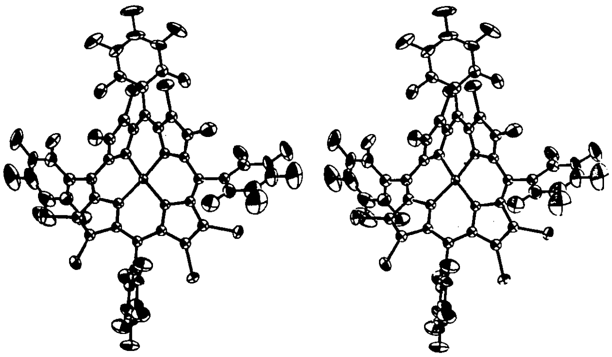

Fig. 2. A stereo drawing of the Ni complex with 50% probability ellipsoids showing the pronounced tetrahedral distortion. Note that the phenyl rings are approximately perpendicular to the vector between their neighboring Br atoms.

general comparable to those in undistorted porphyrins.

The intermolecular approaches are at van der Waals distances or longer with three exceptions: two Br···F contacts at 3.03 and 3.18 Å (3.30 Å expected) and one F···F contact at 2.64 Å (2.70 Å expected). These are not so close as to arouse suspicion. There are two Br atoms from adjacent molecules in axial positions above and below the metal atom, about 3.42 and 3.53 Å distant in the Ni complex and 3.36 and 3.48 Å in the Cu complex: these separations are so large as to preclude any formal bonding interaction.

Experimental

Nickel(II) compound

Crystal data

$[Ni(C_{44}Br_8F_{20}N_4)].\frac{1}{2}CH_2Cl_2$
$M_r = 1704.88$
Monoclinic
$C2/c$
$a = 18.178\ (7)$ Å
$b = 22.160\ (11)$ Å
$c = 24.421\ (8)$ Å
$\beta = 93.64\ (4)^\circ$
$V = 9818\ (7)$ Å^3
$Z = 8$
$D_x = 2.31$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13\text{-}18^\circ$
$\mu = 7.02$ mm^{-1}
$T = 295$ K
Thin parallelepiped
$0.55 \times 0.55 \times 0.07$ mm
Dark purple

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical
$T_{min} = 0.04$, $T_{max} = 0.58$
16 471 measured reflections
8602 independent reflections
8602 observed reflections [all reflections used]

$R_{int} = 0.046$
$\theta_{max} = 25^\circ$
$h = 0 \rightarrow 20$
$k = -23 \rightarrow 26$
$l = -29 \rightarrow 29$
3 standard reflections
frequency: 167 min
intensity variation: within counting statistics

Refinement

Refinement on F^2(all F^2, positive and negative, used in refinement)
Final $R(F) = 0.042$ for 4055 reflections with $F_o^2 > 3\sigma(F_o^2)$
$wR(F^2) = 0.005$
$S = 1.22$
8602 reflections
570 parameters

H-atom parameters not refined
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 1.68$ e Å^{-3}
$\Delta\rho_{min} = -1.55$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Copper(II) compound

Crystal data

$[Cu(C_{44}Br_8F_{20}N_4)].\frac{1}{2}CH_2Cl_2$
$M_r = 1709.72$
Monoclinic
$C2/c$
$a = 18.099\ (4)$ Å
$b = 22.326\ (4)$ Å
$c = 24.303\ (5)$ Å
$\beta = 92.31^\circ$
$V = 9812\ (3)$ Å^3
$Z = 8$
$D_x = 2.32$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6\text{-}18^\circ$
$\mu = 7.07$ mm^{-1}
$T = 294$ K
Irregular plate
$0.41 \times 0.40 \times 0.11$ mm
Dark purple

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: analytical
$T_{min} = 0.09$, $T_{max} = 0.51$
18 304 measured reflections
8610 independent reflections
8610 observed reflections [all reflections used]

$R_{int} = 0.070$
$\theta_{max} = 25^\circ$
$h = -21 \rightarrow 21$
$k = -26 \rightarrow 26$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 150 min
intensity variation: within counting statistics

Refinement

Refinement on F^2
Final $R(F) = 0.047$ for 3625 reflections with $F_o^2 > 3\sigma(F_o^2)$
$wR(F^2) = 0.007$
$S = 1.18$
8610 reflections
570 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 1.82$ e Å^{-3}
$\Delta\rho_{min} = -2.32$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

An asterisk indicates an isotropic displacement parameter, B; for others $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B or U_{eq}
Nickel(II) compound				
Ni	0.32110 (4)	0.09900 (3)	0.97460 (3)	0.0287 (2)
Br1	0.29730 (4)	0.35540 (3)	0.93000 (3)	0.0567 (2)
Br2	0.43380 (4)	0.33560 (3)	1.03330 (3)	0.0536 (2)
Br3	0.62430 (4)	0.09180 (3)	1.05940 (3)	0.0609 (2)
Br4	0.54010 (4)	−0.03720 (3)	1.10320 (3)	0.0590 (2)
Br5	0.19620 (4)	−0.06110 (4)	1.12960 (3)	0.0650 (2)
Br6	0.08080 (4)	−0.06570 (4)	1.01190 (3)	0.0640 (2)
Br7	0.16680 (4)	0.01180 (3)	0.77550 (3)	0.0601 (3)
Br8	0.21810 (4)	0.15760 (3)	0.75030 (3)	0.0528 (2)
N1	0.3549 (2)	0.1787 (2)	0.9617 (2)	2.4 (1)*
N2	0.3991 (2)	0.0873 (2)	1.0293 (2)	2.5 (1)*
N3	0.2747 (2)	0.0273 (2)	0.9974 (2)	2.3 (1)*
N4	0.2559 (2)	0.1028 (2)	0.9104 (2)	2.2 (1)*
C1	0.3167 (3)	0.2217 (2)	0.9299 (2)	2.3 (1)*
C2	0.3385 (3)	0.2813 (3)	0.9503 (3)	2.8 (1)*
C3	0.3935 (3)	0.2737 (3)	0.9887 (3)	2.7 (1)*
C4	0.4074 (3)	0.2092 (3)	0.9951 (3)	2.7 (1)*
C5	0.4666 (3)	0.1807 (3)	1.0223 (2)	2.6 (1)*
C6	0.4653 (3)	0.1191 (3)	1.0316 (2)	2.6 (1)*
C7	0.5226 (3)	0.0802 (3)	1.0556 (3)	2.9 (1)*
C8	0.4900 (3)	0.0301 (3)	1.0733 (3)	3.0 (1)*
C9	0.4119 (3)	0.0349 (3)	1.0592 (2)	2.7 (1)*
C10	0.3544 (3)	0.0003 (3)	1.0766 (2)	2.6 (1)*
C11	0.2855 (3)	0.0015 (2)	1.0493 (2)	2.5 (1)*
C12	0.2197 (3)	−0.0305 (3)	1.0610 (3)	2.9 (1)*
C13	0.1743 (3)	−0.0312 (3)	1.0155 (3)	2.8 (1)*

C14	0.2093 (3)	0.0035 (2)	0.9745 (2)	2.3 (1)*
C15	0.1884 (3)	0.0093 (2)	0.9196 (2)	2.2 (1)*
C16	0.2171 (3)	0.0541 (3)	0.8872 (2)	2.3 (1)*
C17	0.2022 (3)	0.0657 (3)	0.8299 (3)	2.8 (1)*
C18	0.2234 (3)	0.1226 (3)	0.8202 (3)	2.6 (1)*
C19	0.2547 (3)	0.1472 (3)	0.8710 (2)	2.4 (1)*
C20	0.2753 (3)	0.2066 (3)	0.8827 (2)	2.4 (1)*
C21	0.5338 (4)	0.2151 (3)	1.0405 (3)	3.1 (1)*
C22	0.5765 (4)	0.2426 (3)	1.0036 (3)	0.0497 (21)
C23	0.6423 (5)	0.2704 (3)	1.0183 (4)	0.0677 (30)
C24	0.6656 (5)	0.2723 (4)	1.0728 (5)	0.0838 (40)
C25	0.6248 (5)	0.2467 (4)	1.1116 (4)	0.0655 (27)
C26	0.5584 (4)	0.2192 (3)	1.0962 (3)	0.0523 (23)
F22	0.5560 (2)	0.2422 (2)	0.9501 (2)	0.0733 (14)
F23	0.6836 (3)	0.2961 (2)	0.9827 (2)	0.1156 (19)
F24	0.7303 (3)	0.2971 (2)	1.0892 (2)	0.1289 (22)
F25	0.6467 (3)	0.2475 (2)	1.1648 (2)	0.1088 (17)
F26	0.5192 (2)	0.1931 (2)	1.1333 (2)	0.0695 (15)
C31	0.3695 (3)	−0.0375 (3)	1.1268 (3)	3.1 (1)*
C32	0.3740 (4)	−0.0996 (3)	1.1268 (3)	0.0515 (23)
C33	0.3900 (4)	−0.1321 (4)	1.1740 (4)	0.0637 (27)
C34	0.3985 (4)	−0.1025 (4)	1.2224 (4)	0.0734 (29)
C35	0.3911 (5)	−0.0413 (4)	1.2244 (3)	0.0797 (39)
C36	0.3771 (4)	−0.0102 (3)	1.1763 (3)	0.0610 (28)
F32	0.3666 (3)	−0.1281 (2)	1.0790 (2)	0.0863 (18)
F33	0.3950 (3)	−0.1909 (2)	1.1730 (2)	0.1245 (23)
F34	0.4126 (3)	−0.1332 (2)	1.2687 (2)	0.1182 (19)
F35	0.3980 (4)	−0.0130 (2)	1.2728 (2)	0.1504 (31)
F36	0.3706 (3)	0.0498 (2)	1.1794 (2)	0.1066 (22)
C41	0.1325 (3)	−0.0336 (3)	0.8942 (2)	2.5 (1)*
C42	0.1487 (4)	−0.0930 (3)	0.8867 (3)	0.0435 (20)
C43	0.0965 (6)	−0.1336 (3)	0.8644 (3)	0.0694 (30)
C44	0.0277 (5)	−0.1126 (5)	0.8495 (4)	0.0835 (32)
C45	0.0107 (5)	−0.0551 (5)	0.8564 (4)	0.0821 (33)
C46	0.0621 (4)	−0.0155 (3)	0.8791 (3)	0.0544 (22)
F42	0.2173 (2)	−0.1130 (2)	0.8996 (2)	0.0669 (13)
F43	0.1171 (3)	−0.1908 (2)	0.8566 (2)	0.1108 (20)
F44	−0.0206 (3)	−0.1521 (3)	0.8279 (3)	0.1623 (23)
F45	−0.0584 (3)	−0.0360 (3)	0.8429 (2)	0.1379 (24)
F46	0.0422 (2)	0.0418 (2)	0.8877 (2)	0.0795 (14)
C51	0.2545 (4)	0.2546 (3)	0.8414 (3)	2.6 (1)*
C52	0.3047 (4)	0.2812 (3)	0.8107 (3)	0.0430 (20)
C53	0.2870 (5)	0.3247 (3)	0.7725 (4)	0.0670 (28)
C54	0.2144 (6)	0.3404 (3)	0.7637 (3)	0.0686 (31)
C55	0.1624 (4)	0.3146 (3)	0.7931 (3)	0.0542 (24)
C56	0.1824 (4)	0.2730 (3)	0.8317 (3)	0.0443 (21)
F52	0.3759 (2)	0.2645 (2)	0.8178 (2)	0.0676 (13)
F53	0.3375 (3)	0.3512 (2)	0.7442 (2)	0.1040 (17)
F54	0.1945 (3)	0.3816 (2)	0.7248 (2)	0.1050 (18)
F55	0.0903 (3)	0.3300 (2)	0.7837 (2)	0.0927 (15)
F56	0.1300 (2)	0.2488 (2)	0.8612 (2)	0.0715 (13)
C(*S*)	0	0.1890 (6)	0.7500	0.1339 (58)
Cl(*S*)	0.0038 (2)	0.1464 (2)	0.6925 (1)	0.1750 (14)
H(*S*1)	−0.0427	0.2140	0.7464	12.8*
Copper(II) compound				
Cu	0.32200 (5)	0.09950 (4)	0.97550 (4)	0.0306 (3)
Br1	0.29980 (5)	0.35590 (4)	0.93210 (4)	0.0512 (3)
Br2	0.43400 (5)	0.33560 (4)	1.03520 (4)	0.0492 (3)
Br3	0.62550 (5)	0.09380 (4)	1.06230 (5)	0.0563 (3)
Br4	0.54180 (5)	−0.03620 (4)	1.10290 (5)	0.0572 (3)
Br5	0.19680 (6)	−0.06730 (5)	1.12920 (4)	0.0584 (3)
Br6	0.08120 (5)	−0.06810 (5)	1.01310 (5)	0.0597 (3)
Br7	0.16320 (6)	0.01750 (4)	0.77580 (4)	0.0554 (3)
Br8	0.21680 (5)	0.16170 (4)	0.75110 (4)	0.0484 (3)
N1	0.3590 (3)	0.1809 (3)	0.9617 (3)	2.6 (1)*
N2	0.4008 (3)	0.0879 (3)	1.0332 (3)	2.3 (1)*
N3	0.2752 (3)	0.0241 (3)	0.9979 (3)	2.3 (1)*
N4	0.2532 (3)	0.1045 (3)	0.9109 (3)	2.2 (1)*
C1	0.3202 (4)	0.2227 (3)	0.9308 (4)	2.7 (2)*
C2	0.3422 (4)	0.2813 (3)	0.9514 (3)	2.4 (2)*
C3	0.3952 (4)	0.2742 (3)	0.9892 (4)	2.5 (2)*
C4	0.4093 (4)	0.2106 (3)	0.9959 (4)	2.7 (2)*
C5	0.4672 (4)	0.1815 (3)	1.0240 (4)	3.0 (2)*
C6	0.4662 (4)	0.1201 (3)	1.0350 (3)	2.5 (2)*
C7	0.5230 (4)	0.0811 (3)	1.0593 (4)	3.1 (2)*
C8	0.4911 (4)	0.0301 (3)	1.0751 (4)	2.9 (2)*
C9	0.4128 (4)	0.0349 (3)	1.0608 (4)	2.7 (2)*
C10	0.3550 (4)	−0.0018 (3)	1.0767 (4)	2.5 (2)*
C11	0.2858 (4)	−0.0026 (3)	1.0492 (3)	2.5 (2)*
C12	0.2211 (4)	−0.0350 (3)	1.0619 (4)	2.8 (2)*
C13	0.1761 (4)	−0.0335 (3)	1.0158 (4)	2.7 (2)*
C14	0.2097 (4)	0.0015 (3)	0.9754 (3)	2.2 (2)*
C15	0.1877 (4)	0.0108 (3)	0.9205 (4)	2.4 (2)*
C16	0.2147 (4)	0.0570 (3)	0.8881 (4)	2.5 (2)*
C17	0.2000 (4)	0.0703 (3)	0.8309 (4)	2.4 (2)*
C18	0.2220 (4)	0.1255 (3)	0.8206 (4)	2.8 (2)*
C19	0.2540 (4)	0.1495 (3)	0.8712 (3)	2.3 (2)*
C20	0.2775 (4)	0.2084 (3)	0.8840 (4)	2.4 (2)*
C21	0.5346 (5)	0.2163 (4)	1.0436 (4)	3.0 (2)*
C22	0.5779 (5)	0.2435 (4)	1.0039 (5)	0.0504 (30)
C23	0.6443 (6)	0.2705 (4)	1.0198 (6)	0.0662 (44)
C24	0.6668 (6)	0.2694 (5)	1.0760 (7)	0.0810 (52)
C25	0.6231 (6)	0.2456 (5)	1.1140 (6)	0.0667 (39)
C26	0.5570 (5)	0.2181 (4)	1.0985 (5)	0.0500 (30)
F22	0.5579 (3)	0.2440 (3)	0.9517 (3)	0.0726 (19)
F23	0.6862 (3)	0.2958 (3)	0.9836 (3)	0.1179 (27)
F24	0.7321 (3)	0.2943 (3)	1.0912 (3)	0.1283 (29)
F25	0.6464 (3)	0.2448 (3)	1.1664 (3)	0.1015 (22)
F26	0.5179 (3)	0.1928 (3)	1.1364 (2)	0.0579 (21)
C31	0.3694 (4)	−0.0403 (4)	1.1261 (4)	2.6 (2)*
C32	0.3758 (5)	−0.1012 (4)	1.1246 (5)	0.0481 (29)
C33	0.3914 (6)	−0.1349 (5)	1.1716 (6)	0.0709 (42)
C34	0.3983 (7)	−0.1076 (6)	1.2206 (6)	0.0769 (42)
C35	0.3900 (7)	−0.0473 (6)	1.2242 (5)	0.0823 (50)
C36	0.3753 (6)	−0.0149 (4)	1.1776 (5)	0.0638 (37)
F32	0.3714 (4)	−0.1289 (2)	1.0758 (3)	0.0902 (25)
F33	0.3985 (4)	−0.1934 (3)	1.1692 (3)	0.1248 (30)
F34	0.4117 (4)	−0.1390 (3)	1.2668 (3)	0.1223 (25)
F35	0.3936 (5)	−0.0193 (3)	1.2729 (3)	0.1558 (44)
F36	0.3673 (4)	0.0447 (3)	1.1812 (3)	0.1071 (29)
C41	0.1314 (4)	−0.0307 (4)	0.8957 (4)	2.5 (2)*
C42	0.1473 (5)	−0.0908 (4)	0.8865 (4)	0.0419 (26)
C43	0.0952 (7)	−0.1295 (4)	0.8659 (4)	0.0624 (39)
C44	0.0251 (6)	−0.1088 (5)	0.8525 (5)	0.0786 (39)
C45	0.0086 (6)	−0.0508 (5)	0.8589 (5)	0.0719 (37)
C46	0.0608 (5)	−0.0134 (4)	0.8812 (4)	0.0526 (29)
F42	0.2155 (3)	−0.1113 (2)	0.8993 (2)	0.0633 (17)
F43	0.1134 (3)	−0.1871 (2)	0.8587 (3)	0.0974 (25)
F44	−0.0241 (4)	−0.1477 (3)	0.8318 (3)	0.1414 (27)
F45	−0.0602 (3)	−0.0316 (3)	0.8466 (3)	0.1287 (30)
F46	0.0423 (3)	0.0446 (2)	0.8893 (2)	0.0690 (17)
C51	0.2588 (5)	0.2566 (3)	0.8425 (4)	2.3 (2)*
C52	0.3097 (5)	0.2820 (4)	0.8120 (4)	0.0410 (27)
C53	0.2946 (6)	0.3255 (4)	0.7739 (4)	0.0575 (33)
C54	0.2215 (7)	0.3428 (4)	0.7650 (5)	0.0614 (38)
C55	0.1679 (5)	0.3177 (4)	0.7952 (5)	0.0508 (32)
C56	0.1872 (5)	0.2751 (4)	0.8344 (4)	0.0421 (28)
F52	0.3808 (3)	0.2635 (2)	0.8177 (2)	0.0649 (17)
F53	0.3458 (4)	0.3525 (3)	0.7457 (3)	0.1012 (23)
F54	0.2042 (4)	0.3844 (3)	0.7271 (3)	0.1082 (25)
F55	0.0971 (3)	0.3345 (2)	0.7862 (3)	0.0911 (20)
F56	0.1330 (3)	0.2526 (2)	0.8635 (3)	0.0705 (18)
C(*S*)	0	0.1918 (7)	0.7500	0.1069 (63)
Cl(*S*)	0.0036 (2)	0.1500 (2)	0.6912 (2)	0.1397 (15)
H(*S*)	0.0429	0.2164	0.7528	10.2*

Table 2. *Selected bond distances* (Å) *and angles* (°)

Nickel(II) compound			
Ni—N1	1.902 (4)	Br3—C7	1.863 (6)
Ni—N2	1.904 (4)	Br4—C8	1.871 (6)
Ni—N3	1.898 (4)	Br5—C12	1.880 (6)
Ni—N4	1.906 (4)	Br6—C13	1.861 (6)
Br1—C2	1.858 (6)	Br7—C17	1.870 (6)
Br2—C3	1.872 (6)	Br8—C18	1.871 (6)
N2—Ni—N1	90.5 (2)	N3—Ni—N2	90.3 (2)
N3—Ni—N1	168.4 (2)	N4—Ni—N2	168.5 (2)
N4—Ni—N1	90.8 (2)	N4—Ni—N3	90.8 (2)
Copper(II) compound			
Cu—N1	1.969 (6)	Br3—C7	1.874 (8)
Cu—N2	1.977 (6)	Br4—C8	1.857 (8)
Cu—N3	1.971 (6)	Br5—C12	1.856 (8)
Cu—N4	1.968 (6)	Br6—C13	1.882 (8)

Br1—C2	1.884 (7)	Br7—C17	1.885 (8)
Br2—C3	1.887 (8)	Br8—C18	1.870 (8)
N1—Cu—N2	90.1 (2)	N2—Cu—N3	89.9 (2)
N1—Cu—N3	171.0 (2)	N2—Cu—N4	171.5 (2)
N1—Cu—N4	91.2 (2)	N3—Cu—N4	90.2 (2)

Table 3. *Average distance* (Å) *of selected atoms from the plane of the* N *atoms*

	Cu	Ni
meso C	0.163	0.187
pyrrole C	1.12 (9)	1.18 (10)
Br	1.99 (22)	2.05 (24)
Br(1,3,5,7)	2.16 (10)	2.25 (11)
Br(2,4,6,8)	1.82 (15)	1.86 (13)

The structure of the nickel(II) compound was solved by *MULTAN*88 (Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988). The structure of the copper(II) compound was solved by using coordinates from the Ni compound. For each compound, F^2 magnitudes were used in full-matrix least-squares refinement of 570 parameters: coordinates and anisotropic displacement parameters of the Ni/Cu, Br, F atoms, five C atoms of each phenyl ring, and the C and Cl atoms of the solvent, coordinates and isotropic displacement parameters of the remaining atoms of the complex, and a scale factor. The H atom of the solvent was positioned by calculation and not refined. Weights were calculated as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$. Atomic scattering factors and values for f' were taken from Cromer & Waber (1974) and Cromer (1974). For the nickel(II) compound, the largest peaks and valleys in the final difference map were mostly near the C_6F_5 groups, with five (>1 e Å^{-3}) near Br atoms and one (1.3 e Å^{-3}) 1.2 Å from Ni. For the copper(II) compound, the largest peaks and valleys in the difference map were near Br atoms and F atoms. Programs used were those of the *CRYM Crystallographic Computing System* (Duchamp, 1964) and *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71204 (80 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1023]

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Structure of (2,5,8,11,14-Pentaazapentadecane)copper(II) Diperchlorate Monohydrate

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Abstract

The coordination geometry about the Cu^{II} ion is a distorted trigonal bipyramid. There is variation in the five Cu—N bond distances. The four chiral nitrogen centers are in the (2*SR*,5*RS*,11*RS*,14*RS*) configuration. The ligand is in its most stable conformation with all four five-membered chelate rings in a stable *gauche* form.

Comment

The crystal structures of open-chain tetraamine complexes have been studied extensively (Lee *et al.*, 1986;

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