Table II. Fractional Coordinates for Non-Hydrogen Atoms of $Cu(C_{16}H_{36}N_4O_4)(PF_6)_2$

atom	*x*	*y*	*z*
Cu1	0.2457 (3)	0.5995 (14)	0.0299 (4)
N1	0.1352 (14)	0.0770 (10)	−0.087 (2)
N2	0.2833 (15)	0.1466 (12)	−0.040 (2)
N3	0.353 (2)	0.0638 (14)	0.173 (32)
N4	0.2276 (13)	−0.0284 (8)	0.138 (2)
O1	0.2566 (13)	−0.0126 (9)	−0.197 (2)
O2	0.361 (2)	−0.1205 (10)	−0.099 (3)
O3	0.2436 (14)	−0.2025 (9)	0.073 (2)
O4	0.0877 (13)	−0.1258 (10)	0.096 (2)
C1	0.145 (2)	0.1421 (14)	−0.164 (3)
C2	0.207 (2)	0.182 (2)	−0.079 (3)
C3	0.342 (2)	0.171 (2)	0.071 (3)
C4	0.404 (2)	0.116 (2)	0.121 (3)
C5	0.378 (2)	0.003 (2)	0.198 (4)
C6	0.304 (2)	−0.0394 (15)	0.228 (3)
C7	0.144 (2)	−0.0353 (12)	0.220 (3)
C8	0.118 (2)	−0.1028 (13)	0.242 (3)
C9	0.091 (2)	−0.1942 (15)	0.073 (3)
C10	0.169 (2)	−0.217 (2)	−0.010 (3)
C11	0.325 (2)	−0.217 (2)	0.005 (3)
C12	0.354 (3)	−0.191 (2)	−0.113 (5)
C13	0.439 (3)	−0.099 (2)	−0.259 (5)
C14	0.331 (2)	−0.038 (2)	−0.269 (3)
C15	0.180 (2)	0.0017 (13)	−0.285 (3)
C16	0.111 (2)	0.0210 (14)	−0.189 (3)
P1	0.0595 (6)	0.1395 (4)	−0.5603 (7)
P2	0.4504 (8)	0.3610 (4)	0.1085 (8)
F1	0.0651 (11)	0.2029 (7)	−0.7519 (13)
F2	0.0327 (12)	0.0981 (8)	−0.7987 (13)
F3	0.0480 (11)	0.0756 (7)	−0.5516 (13)
F4	0.084 (2)	0.1791 (8)	−0.507 (2)
F5	−0.0392 (13)	0.1545 (8)	−0.624 (2)
F6	0.1572 (10)	0.1226 (8)	−0.688 (2)
F7	0.4539 (13)	0.4039 (7)	0.260 (2)
F8	0.467 (2)	0.4234 (8)	0.011 (2)
F9	0.453 (2)	0.3176 (8)	−0.037 (2)
F10	0.435 (2)	0.3003 (8)	0.208 (2)
F11	0.3505 (15)	0.370 (2)	0.099 (3)
F12	0.5531 (14)	0.3535 (11)	0.122 (2)

This deviation from octahedral coordination by elongation along one 4-fold axis, arising from Jahn–Teller distortion, is typical of Cu^{2+} complexes. Figure 2 includes one of the two hexafluorophosphate counteranions present in the unit cell. This figure shows the presence of a weak interaction between a fluorine atom and the central copper atom. Also of interest is the appearance of an apparent hydrogen-bonding interaction in the same hexafluorophosphate anion and the hydrogen presumably attached to a nitrogen atom on the macrocycle. This H-bonding interaction may exert a stabilizing influence and, thus, play a role in orientating this PF_6 anion in the unit cell.

The d^9 configuration makes Cu(II) subject to Jahn–Teller distortion when placed in an environment of octahedral symmetry.[22] The most common distortion is an elongation along one 4-fold axis, resulting in a plane of four short basallike Cu–L bonds and two long apical-type bonds. Depending on the nature of the ligands, the observed geometry can extend anywhere from a pseudooctahedral structure to a limiting case of square planar. In complex **3** the distorted-square-pyramidal geometry observed about copper (Figure 1) could also be considered as pseudooctahedral (Figure 2), with a hexafluorophosphate anion serving to occupy a position trans to atom O1. The large distance (3.07 Å), however, between this fluorine atom and the central copper leads us to consider that five-coordinate square-pyramidal configuration is a more accurate limiting description of the copper coordination geometry in complex **3**. Such a conclusion seems reasonable in light of a variety of earlier structures obtained with a number of other mono- and dinuclear copper-containing complexes derived from unrelated polyaza crown systems.[5,8,23]

Conclusion

We have established the synthesis and structure of a potentially ditopic receptor. Further, its complex with copper has been elucidated. Studies are currently going on to probe the binding of two metals within this cavity. Initial attempts to bind Na^+ to **3**, however, have met with little success: Little or no change was observed in the visible spectrum upon adding Na^+ to **3**. Moreover, no change in the FAB MS was observed following this addition. This suggests that the macrocycle **2** may be too small to accommodate the Coulombic repulsion accruing from the binding of two cations within close cocomplexed proximity. In light of recent work showing the binucleating capability of 1,4,7,10,13,16,19,22-octaazacyclotetracosane,[24] we are continuing to investigate the properties of **2** as a ditopic receptor. Indeed, it has been shown by Busch and co-workers[25] that macrocycle size and metal binding ability are interrelated for aza-crowns. With this in mind, a Ni-containing complex has been synthesized.[26] The slightly smaller size of the Ni(II) cation in comparison to that of the Cu(II) cation[27] may allow for a more favorable interaction with a second, putative cobound cation. We are currently exploring this possibility.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 36384) for financial support of this research.

Supplementary Material Available: Positional and isotropic or equivalent isotropic thermal parameters for the non-H atoms (Table S1), positional and isotropic thermal parameters for the H atoms (Table S2), anisotropic thermal parameters for the Cu, P, F, O, and N atoms (Table S3), bond lengths and angles for the non-H atoms (Table S4), bond lengths and angles for the H atoms (Table S5), and a complete crystallographic summary (Table S6) (16 pages); observed and calculated structure factor amplitudes (Table S7) (22 pages). Ordering information is given on any current masthead page.

---

(22) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 811.

(23) Hoskins, B.; Williams, G. *Aust. J. Chem.* **1975**, *28*, 2607–2614.

(24) Bianchi, A.; Mangani, S.; Micheloni, M.; Nanini, V.; Orioli, P.; Paoletti, P.; Seghi, B. *Inorg. Chem.* **1985**, *24*, 1182–1187.

(25) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392–400.

(26) Sibert, J.; Sessler, J. L. Unpublished results.

(27) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925–946.

Contribution from the Department of Chemistry,
Louisiana State University,
Baton Rouge, Louisiana 70803-1804,
Istituto Chimico, Facoltà di Ingegneria,
Università di Catania, 95125 Catania, Italy,
and Dipartimento di Scienze Chimiche,
Università di Catania, 95125 Catania, Italy

Crystal and Molecular Structure of the (*N*,*N*'-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane)copper Dichloride Monohydrate Complex

Frank R. Fronczek,[†] Antonino Mamo,[‡]
and Sebastiano Pappalardo*[,§]

Received August 17, 1988

The design, synthesis, and ion-binding properties of multiheteromacrocycles, incorporating 2,6-pyridino subunits as part of the macroring, have received much attention in the last decade and remain an active field today.[1] Very little, however, is known about the ligating ability of medium-sized 12-membered [3.3]-

---

[†] Louisiana State University.

[‡] Istituto Chimico, Facoltà di Ingegneria, Università di Catania.

[§] Dipartimento di Scienze Chimiche, Università di Catania.

0020-1669/89/1328-1419$01.50/0

Table I. Crystal Data and Data Collection Parameters

formula	$CuCl_2(C_{16}H_{20}N_4)\cdot H_2O$
fw	420.8
cryst syst	orthorhombic
space group	*Pbca*
cell dimens	
a, Å	13.452 (2)
b, Å	14.9319 (6)
c, Å	18.2366 (14)
V, Å^3	3663.1 (10)
Z	8
d, g cm^{-3}	1.526
cryst color	light green
cryst size, mm^3	0.12 × 0.30 × 0.48
radiation	Cu Kα
μ, cm^{-1}	45.0
T, °C	27
min transmissn, %	64.89
θ limits, deg	2–75
scan rates, deg min^{-1}	0.61–3.30
no. of unique data	3768
no. of observed data	3049
no. of variables	306
final *R*	0.036
final R_w	0.047
GOF	2.139
max residual, e Å^{-3}	0.25
extinction	1.07 (2) × 10^{-6}

(2,6)pyridinophanes,[2] the only studies on these systems having been mainly concerned with their synthesis and conformational behavior in the solid state and in solution.[3] On the other hand, first-row transition metal ion complexes with structurally related 12-membered saturated tetradentate macrocyclic ligands have been studied in detail.[4] Busch has illustrated by means of calculations a relationship between the ring size of a macrocyclic ligand and the amount of strain such ligand would impose on a metal complex on the assumption that the cyclic ligand is bonded in a coplanar manner with the metal ion.[5] Since the cavity size of a 12-membered macrocyclic ligand is too small to accommodate a given metal ion in a coplanar manner (a minimum of 13 atoms is required) without imposing large strain energies, distortion from square-planar coordination will occur.[5,6] Accordingly, most tetradentate 12-membered macrocyclic ligands form square-pyramidal Cu(II) complexes with the metal ion displaced from the basal plane of the four donor atoms,[7-10] even though in some particular case folding of the ligand, so as to form either a cis-octahedral[6,11,12] or a trigonal-bipyramidal structure,[12] has been noticed.

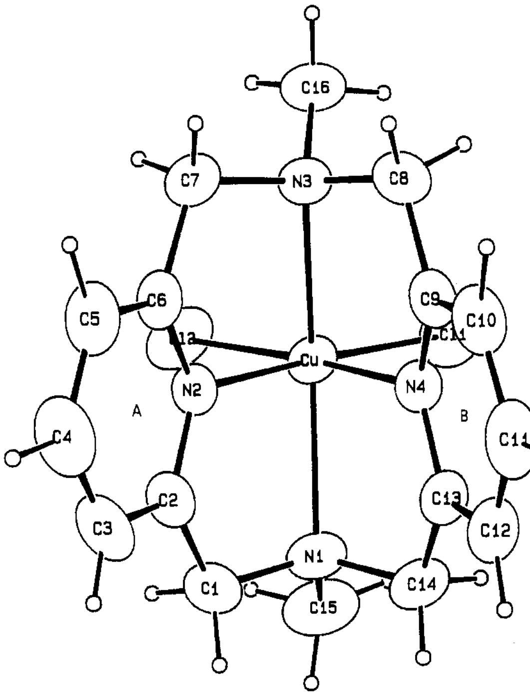


Figure 1. Perspective drawing of the Cu(II) complex.

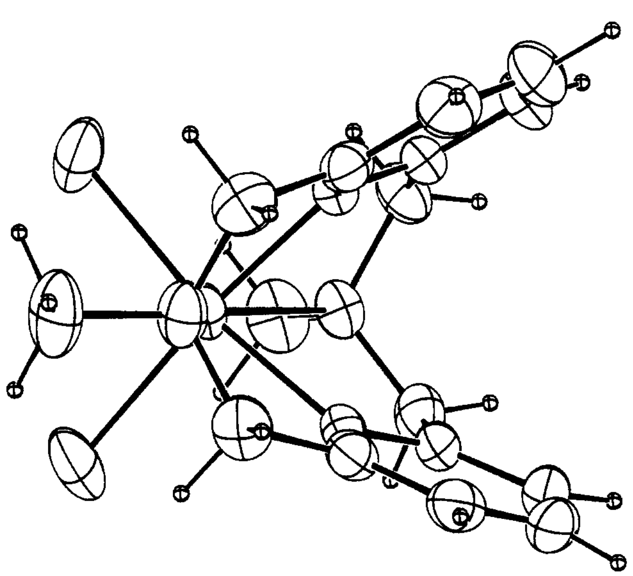
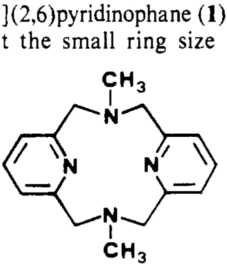


Figure 2. Side view of the Cu(II) complex showing the boat–boat conformation of the bridging chains.

Models of the 12-membered N_4 macrocyclic ligand *N*,*N*′-dimethyl-2,11-diaza[3.3](2,6)pyridinophane (**1**), recently synthesized by us,[3g] suggest that the small ring size and reduced ligand



1

---

(1) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513. Majestic, V. K.; Newkome, G. R. *Top. Curr. Chem.* **1982**, *106*, 79. Weber, E. *Synthesis of Macrocycles: The Design of Selective Complexing Agents*; Izatt, R. M., Christensen, J. J., Ed.; John Wiley & Sons: New York, 1987. Ferguson, G.; Matthes, K. E.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1350.

(2) The nomenclature of Vögtle and Neumann (Vögtle, F.; Neumann, P. *Tetrahedron* **1970**, *26*, 5847) is employed for these macrocyclic ring systems.

(3) (a) Vögtle, F.; Schunder, L. *Chem. Ber.* **1969**, *102*, 2677. (b) Newcomb, M.; Gokel, G. W.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 6810. (c) Bottino, F.; Pappalardo, S. *Chem. Lett.* **1981**, 1781. (d) Newkome, G. R.; Pappalardo, S.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 5152. (e) Pappalardo, S.; Bottino, F.; Di Grazia, M.; Finocchiaro, P.; Mamo, A. *Heterocycles* **1985**, *23*, 1881. (f) Shinmyozu, T.; Hirai, Y.; Inazu, T. *J. Org. Chem.* **1986**, *51*, 1551. (g) Bottino, F.; Di Grazia, M.; Finocchiaro, P.; Fronczek, F. R.; Mamo, A.; Pappalardo, S. *J. Org. Chem.* **1988**, *53*, 3521.

(4) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(5) Martin, L. Y.; Dehayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4046.

(6) Iitaka, Y.; Shina, M.; Kimura, E. *Inorg. Chem.* **1974**, *13*, 2886.

(7) Stika, M. C.; Smierciak, R. C.; Blinn, E. L.; DeSimone, R. E.; Passariello, J. V. *Inorg. Chem.* **1978**, *17*, 82.

(8) Clay, R.; Murray-Rust, P.; Murray-Rust, J. *Acta Crystallogr.* **1979**, *B35*, 1894.

(9) DeSimone, R. E.; Blinn, E. L.; Mucker, K. F. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 23.

(10) Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Corfield, P. W.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661.

(11) Van Remoortere, F. P.; Boer, F. P.; Steiner, E. C. *Acta Crystallogr.* **1975**, *B31*, 1420.

(12) Sarther, C. M.; Blinn, E. L. *Inorg. Chem.* **1976**, *15*, 3083.

Table II. Coordinates of Non-Hydrogen Atoms for $CuCl_2C_{16}H_{20}N_4{\cdot}H_2O$

atom	x	y	z	B,[a] Å^2
Cu	0.01014 (3)	0.18309 (2)	0.63603 (2)	3.115 (7)
Cl(1)	−0.08198 (6)	0.07358 (4)	0.69086 (5)	5.77 (2)
Cl(2)	0.14019 (6)	0.09147 (4)	0.60311 (5)	5.56 (2)
O(1W)	0.3506 (2)	0.3411 (2)	0.1551 (2)	7.96 (7)
N(1)	−0.0737 (2)	0.1928 (1)	0.5243 (1)	4.07 (4)
N(2)	0.0782 (2)	0.2910 (1)	0.5886 (1)	3.13 (4)
N(3)	0.0782 (2)	0.2587 (1)	0.7382 (1)	3.48 (4)
N(4)	−0.0936 (2)	0.2840 (1)	0.6566 (1)	3.14 (4)
C(1)	−0.0096 (2)	0.2496 (2)	0.4785 (2)	4.76 (6)
C(2)	0.0503 (2)	0.3159 (2)	0.5216 (1)	3.69 (5)
C(3)	0.0784 (2)	0.3990 (2)	0.4940 (2)	5.10 (6)
C(4)	0.1343 (3)	0.4552 (2)	0.5363 (2)	5.88 (7)
C(5)	0.1618 (2)	0.4294 (2)	0.6056 (2)	4.96 (6)
C(6)	0.1318 (2)	0.3465 (2)	0.6310 (1)	3.49 (5)
C(7)	0.1581 (2)	0.3133 (2)	0.7064 (2)	4.31 (6)
C(8)	−0.0027 (2)	0.3138 (2)	0.7681 (1)	4.05 (6)
C(9)	−0.0758 (2)	0.3427 (2)	0.7106 (1)	3.38 (5)
C(10)	−0.1249 (2)	0.4251 (2)	0.7136 (2)	4.30 (5)
C(11)	−0.1942 (2)	0.4438 (2)	0.6602 (2)	4.84 (6)
C(12)	−0.2112 (2)	0.3844 (2)	0.6039 (2)	4.32 (6)
C(13)	−0.1581 (2)	0.3045 (2)	0.6029 (1)	3.53 (5)
C(14)	−0.1692 (2)	0.2357 (2)	0.5431 (2)	4.56 (6)
C(15)	−0.0915 (3)	0.1055 (2)	0.4880 (2)	6.18 (7)
C(16)	0.1183 (2)	0.1976 (2)	0.7951 (2)	4.97 (6)

[a] The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}(\cos \gamma) + acB_{13}(\cos \beta) + bcB_{23}(\cos \alpha)]$.

flexibility, due to the insertion of two pyridine rings into a "cyclen" framework, do not permit coplanar coordination of the four nitrogen atoms. From the above considerations, this type of ligand should coordinate around the face of either an octahedron or a trigonal bipyramid. In order to prove this hypothesis and to advance our knowledge on the coordination properties of this new class of pyridine-containing macrocyclic ligands, a single-crystal X-ray structure determination of a Cu(II) complex of **1** was undertaken.

Experimental Section

Synthesis of the Copper(II) Complex. To a stirred solution of **1** (268 mg, 1 mmol) in CH_3CN (10 mL) was added a solution of $CuCl_2{\cdot}2H_2O$ (170 mg, 1 mmol) in the same solvent (10 mL). The mixture was refluxed for 1 h and cooled. The solvent was evaporated to leave a crystalline residue, which on recrystallization from $CH_3CN/(CH_3)_2CO$ gave light green crystals of the desired complex; yield 340 mg, 81%. Anal. Calcd for $CuCl_2C_{16}H_{20}H_4{\cdot}H_2O$: C, 45.66; H, 5.27; N, 13.31. Found: C, 46.06; H, 5.09; N, 13.71.

Crystallography. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Cu Kα (λ = 1.54184 Å) and a graphite monochromator. Crystal data and specifics of data collection are given in Table I. Data were corrected for background, Lorentz, polarization, and absorption effects, the latter based on ψ scans.

The structure was solved by heavy-atom methods and refined by full-matrix least-squares techniques based upon F with weights $w = \sigma^{-2}(F_0)$, treating non-hydrogen atoms anisotropically, using the Enraf-Nonius SDP package.[13] Hydrogen atoms, including those of the water molecule, were located in difference maps and refined isotropically. Coordinates for non-hydrogen atoms are given in Table II, while further crystallographic data are given in the supplementary material.

Results and Discussion

Reaction of **1** with $CuCl_2{\cdot}2H_2O$ in CH_3CN produced a light green complex that displayed a 1:1 metal to ligand stoichiometry, as indicated by the elemental analysis. Slow evaporation of a solution of the complex in $CH_3CN/(CH_3)_2CO$ gave crystals suitable for X-ray diffraction studies.

Perspective and side views of the Cu(II) complex with the atomic numbering scheme are shown in Figures 1 and 2, respectively. Crystals of the complex consist of neutral molecules containing Cu(II) N-chelated by the four nitrogens and two chloro ligands. The dichloro complex has symmetry C_{2v} and somewhat distorted cis-octahedral coordination geometry, in which the nitrogens in the bridge (N(1) and N(3)) span axial positions approximately normal to the square plane formed by the two pyridine nitrogens (N(2) and N(4)) and the chloro ligands. Cu–Cl distances average 2.291 Å, equatorial Cu–N distances 2.067 Å, and axial Cu–N distances 2.347 Å. Individual distances and angles within the coordination sphere are given in Table III.

Table III. Coordination Geometry of $CuCl_2C_{16}H_{20}N_4{\cdot}H_2O$

Distances (Å)			
Cu–Cl(1)	2.2824 (5)	Cu–N(2)	2.045 (1)
Cu–Cl(2)	2.3004 (5)	Cu–N(3)	2.362 (1)
Cu–N(1)	2.333 (2)	Cu–N(4)	2.089 (1)
Angles (deg)			
Cl(1)–Cu–Cl(2)	95.81 (2)	Cl(2)–Cu–N(4)	169.87 (4)
Cl(1)–Cu–N(1)	99.46 (4)	N(1)–Cu–N(2)	78.38 (6)
Cl(1)–Cu–N(2)	173.12 (4)	N(1)–Cu–N(3)	147.81 (5)
Cl(1)–Cu–N(3)	101.97 (4)	N(1)–Cu–N(4)	77.83 (5)
Cl(1)–Cu–N(4)	94.32 (4)	N(2)–Cu–N(3)	77.48 (5)
Cl(2)–Cu–N(1)	100.17 (4)	N(2)–Cu–N(4)	78.86 (5)
Cl(2)–Cu–N(2)	91.01 (4)	N(3)–Cu–N(4)	76.86 (5)
Cl(2)–Cu–N(3)	101.24 (4)		

Equatorial N(sp^2)–Cu distances are similar to those found in several Cu(II)–pyridyl complexes,[14] while axial N(sp^3)–Cu distances are significantly longer than those generally observed (1.99–2.11 Å) in medium-sized[8,9,15] and large-ring[16] polyazacycloalkane–Cu(II) complexes. This is a direct consequence of the steric constraints imposed by the planarity of the pyridine rings, which reduce the energy of Cu–N(sp^3) interactions.[17]

The largest deviation from ideal octahedral coordination is found in the N(1)–Cu–N(3) angle [147.81 (5)°], which bends by ca. 32° to accommodate the [5.5.5.5] chelate ring system. The five-membered chelate rings are decidedly nonplanar, with intraannular torsion angles varying up to 38° in magnitude. The average intrachelate angles are as follows: N–Cu–N, 77.63°; N(sp^2)–C(sp^2)–C(sp^3), 116.4°, N(sp^3)–C(sp^3)–C(sp^2), 112.5°; Cu–N(sp^3)–C(sp^3), 104.7°; Cu–N(sp^2)–C(sp^2), 119.2°.

The Cu atom and the four equatorial donor atoms are planar to within 0.009 Å. Pyridine rings A and B (Figure 1) are also planar to within 0.009 and 0.017 Å, respectively, and form a dihedral angle of 50.60° with each other and a mean dihedral angle of 87.62° with the best plane containing N(2), N(4), Cl(1), Cl(2), and Cu atoms. The metal atom lies −0.427 and 0.558 Å apart from the best planes of pyridine rings A and B, respectively.

The Cu(II) complex crystallizes as the monohydrate. The water molecule forms intermolecular links between complex molecules via hydrogen bonds to the chloro ligands. The O···Cl contacts are O(1W)···Cl(1) = 3.215 (3) and O(1W)···Cl(2′) = 3.151 (2) Å, with Cl···O···Cl angle = 112.96 (6)°. The hydrogen bonds are essentially linear, with O–H···Cl(1) angle = 159 (3)° and O–H···Cl(2′) angle = 177 (3)°.

The macrocyclic ligand in the complex assumes a syn geometry with the bridging chains in a boat–boat conformation.[18] This is, to our knowledge, a rare example of a *syn*-[3.3]heteroheterophane existing in this specific conformation. Such a conformation was first noticed for 1,3,10,12-tetrathia[3.3](2,6)pyridinophane (**2**).[3d] While in **2** hydrogen-bonding interactions of the methylene protons to the pyridine nitrogens (N···H contacts 2.5 Å) may play

---

[13] Frenz, B. A. "Enraf-Nonius Structure Determination Package SDP/VAX, Version 3.0"; Enraf-Nonius: Delft, Holland, 1985.

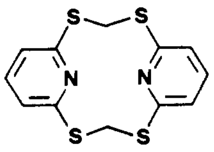
[14] Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Gupta, V. K. *Inorg. Chem.* **1986**, *25*, 1149. Basu, A.; Bhaduri, S.; Sapre, N. J.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 1724.

[15] Bauer, R. A.; Robinson, W. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1973**, 289. Clay, R.; Murray-Rust, J.; Murray-Rust, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1135. Gahan, L. R.; Kennard, C. H. L.; Smith, G.; Mak, T. C. W. *Transition Met. Chem.* (*Weinheim, Ger.*) **1986**, *11*, 465.

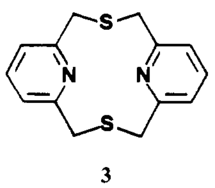
[16] Bencini, A.; Bianchi, A.; Garcia-España, E.; Giusti, M.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 1243.

[17] Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Chem. Commun.* **1978**, 833; *J. Chem. Soc., Dalton Trans.* **1979**, 1581.

[18] Semmelhack, M. F.; Harrison, J. J.; Young, D. C.; Gutiërrez, A.; Rafii, S.; Clardy, J. *J. Am. Chem. Soc.* **1985**, *107*, 7508.



2



3

an important role on the stabilization of the boat–boat conformer, in the present case this conformation is attained by complex formation. Its geometry is characterized by dramatically diminished NCCN torsion angles of ca. 35° as compared to the corresponding NCSC torsion angles of ca. 48° in **2**, and NCCS torsion angles of 112–121° in 2,11-dithia[3.3](2,6)pyridinophane (**3**). Macrocycle **3** was found to exist as the syn chair–chair conformer in the solid state.[3d]

Finally, bond distances and angles of the N_4 ligand in the Cu(II) complex agree well with accepted values. The mean C–C and C–N interatomic distances in the pyridine rings are 1.382 (3) and 1.339 (2) Å, respectively. The mean C(sp^2)–C(sp^3) distance is 1.502 (3) Å, and the mean C(sp^3)–N(sp^3) distance is 1.475 (3) Å.

Further studies on the structural modification of the N_4 ligand for specific applications are in progress.

Acknowledgment. We wish to thank the Italian Ministry of Education (MPI funds) for partial support of this work.

Supplementary Material Available: Tables SI–SVIII, listing coordinates and isotropic thermal parameters for hydrogen atoms, bond distances and angles, bond distances and angles involving H atoms, least-squares planes, torsion angles, and anisotropic thermal parameters for $CuCl_2(\mathbf{1})\cdot H_2O$ (15 pages); Table SIX, listing observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Additions and Corrections

1988, Volume 27

Pierre Braunstein,* Claude de Méric de Bellefon, Michel Ries, Jean Fischer, Salah-Eddine Bouaoud, and Daniel Grandjean: Tri- and Tetranuclear Palladium–Cobalt Clusters Containing Bridging $Ph_2PCH_2PPh_2$ (dppm) Ligands. Crystal Structures of $[Pd_2Co_2(\mu_3\text{-}CO)_2(CO)_5(\mu\text{-dppm})_2]$ and $[Pd_2Co(\mu_3\text{-}CO)_2(CO)_2(\mu\text{-dppm})_2][PF_6]$.

Page 1331. The Cambridge Crystallographic Data Centre has drawn our attention to typing errors in bond distances pertaining to the crystal structure of $[Pd_2Co(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})_2][PF_6]\cdot C_3H_6O$, i.e. $C_{54}H_{44}CoO_4P_4Pd_2F_6P\cdot C_3H_6O$. In Table I, third column, the distance for Co(1)–C(51) should read 1.92 (7) and that for Pd(1)–C(51) should read 2.40 (4) Å. The same corrections apply to Table S-IX of the supplementary material, in which additionally O(1)–C(51) should read 1.11 (6) Å (the latter value was not published in Table I).—Pierre Braunstein

P. L. Bogdan, M. Sabat, S. A. Sunshine, C. Woodcock, and D. F. Shriver*: Anionic Iron Carbido Carbonyl Clusters with Sulfur Dioxide Ligands.

Pages 1904–1910. For the compound $[PPN]_2[Fe_5(CO)_{13}C(SO_2)]$, the unit cell parameters should be a = 19.984 (5) Å, b = 15.644 (6) Å, c = 26.612 (4) Å, $\alpha = \gamma = 90°$, and β = 109.09 (2)°. The formula weight should be 1796.614. The bond distances and angles reported in the paper are correct. We thank the Cambridge Crystallographic Data Center for calling this to our attention.—D. F. Shriver, M. Sabat, and P. Bogdan.

W. E. Garwood,* P. Chu, N. Y. Chen, and J. C. Bailar, Jr.: Stability of Synthetic Zeolite ZSM-5 to Dealumination with Chromium(III) Salt Solutions.

Page 4331. In the third paragraph of the Experimental Section, last line, SiO_2/Al_2O_3 ratio 8.1 should be SiO_2/Al_2O_3 ratio 81/1.—W. E. Garwood