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FULL PAPER

Self-assembled macrocyclic tetranuclear molecular square $[Ni(HL)]_4^{4+}$ and molecular rectangle $[Cu_2Cl_2L]_2$ {H_2L = bis[phenyl(2-pyridyl)methanone] thiocarbazone}

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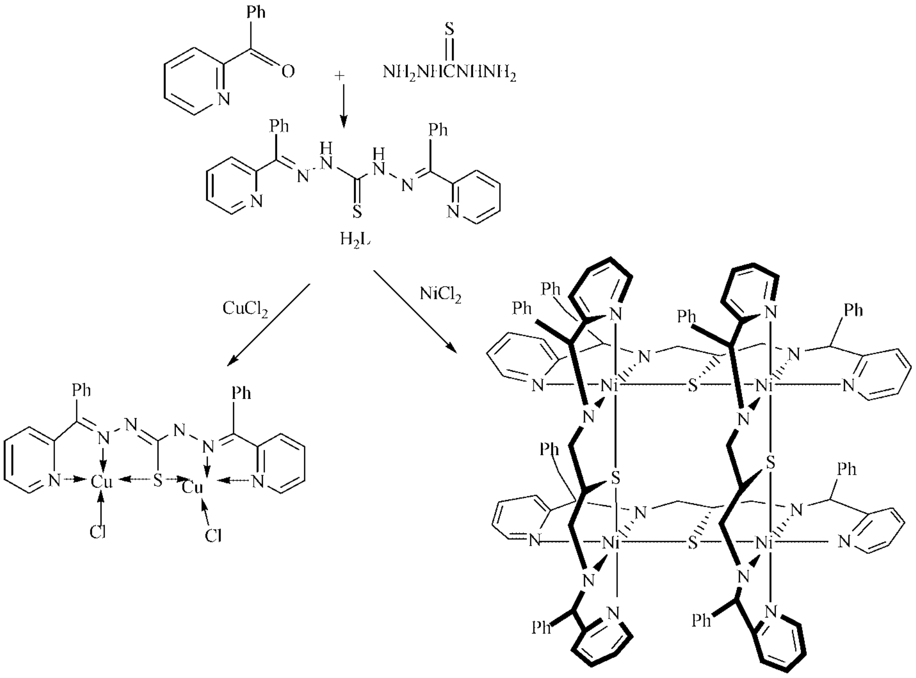
The conformationally rigid, nickel(II)-based cationic molecular square $[Ni(HL)]_4^{4+}$ and copper(II)-based neutral molecular rectangle $[Cu_2Cl_2L]_2$ were achieved *via* self-assembly from novel rigid pentadentate N_4S ligand bis[phenyl(2-pyridyl)methanone] thiocarbazone (H_2L). Crystal structure analyses show that the tetranuclear nickel(II) cation $[Ni(HL)]_4^{4+}$ is located at the inversion center with four nickel atoms in the corners of a square with edge length Ni · · · Ni *ca.* 4.8 Å, each metal center being octahedrally coordinated by sulfur atoms, pyridine nitrogen and carbazone nitrogen atoms from two perpendicular HL^- ligands. Relative to the square of metal cations the sulfur atoms are midway between the edges of the square, each being connected to two nickel atoms with the angles Ni–S–Ni *ca.* 163°. The tetranuclear copper(II) complex $[Cu_2Cl_2L]_2$ is also located in the inversion center with four copper atoms in the corners of a rectangle. Two edges of the rectangle are Cu–S–Cu bridges with edge length Cu · · · Cu of 4.51 Å, the other two edges are double Cu–Cl–Cu bridges with Cu · · · Cu distance of 3.41 Å. Each metal center is coordinated in a tetragonal-pyramid with the sulfur atom, pyridine nitrogen atom, carbazone nitrogen atom and one chlorine atom comprising the basal plane, whereas the other chlorine atom of the symmetry-related half of the molecule occupies the apical position. The crystal structure of the free ligand is also reported for comparison.

The design and study of well-arranged metal-containing macrocycles is one of the major current research areas in modern supramolecular chemistry.[1] Such complexes are of interest not only for their unusual structures and the simple synthetic methods used to prepare them, but also for their special functional properties such as luminescence,[2] redox activity[3] and magnetism.[4] Here we report a new conformationally rigid, nickel-based cationic molecular square $[NiHL]_4^{4+}$ (Scheme 1) and a new conformationally rigid, copper-based neutral molecular rectangle $[Cu_2LCl_2]_2$ achieved *via* self-assembly from bis[phenyl(2-pyridyl)methanone] thiocarbazone.

Incorporation of such a pentadentate ligand into a supramolecular macrocyclic square or rectangle *via* self-assembly is attractive for several reasons. Since 1990, Fujita *et al.*[5] and Stang *et al.*[6] have reported many different molecular square complexes based on square planar coordinated metal centers,



Scheme 1

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these 90° bonding angles between ligands in transition metal complexes provide an attractive feature for constructing macrocyclic structures,[5–7] however, there are only a few examples of self-assembled molecular squares based on an octahedral geometry or tetragonal pyramidal geometry at the metal center,[2,8] this is especially rare for multidentate ligands.[7,8] This work introduced a newly designed, rigid pentadentate N_4S ligand for binding to an octahedrally coordinated first-row transition metal, thereby offering the potential of broadening the scope of further work in this area. Polydentate ligands containing thiocarbazone and thiosemicarbazone groups are known to form a variety of mononuclear, dinuclear and multinuclear metal complexes,[9] and a number of thiosemicarbazones, thiocarbazones and their metal complexes have been found to be active in cell destruction, as well as in the inhibition of DNA systems.[10] The molecular square and rectangle reported here can add a new dimension not only to supramolecular, but also to biomimetic chemistry.

Experimental

General

All chemicals were of reagent grade and used without further purification. The IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. ^{1}H-NMR spectra were recorded on Am5600 Bruker spectrometers at 298 K using TMS as the internal standard. The magnetic measurements were carried out on a powder sample with a CHAN 2000 Faraday-type magnetometer in the temperature range 75–300 K. Electrospray mass spectra were recorded on a LCQ system (Finnigan MAT, USA) using methanol as the mobile phase.

Preparations

Bis[phenyl(2-pyridyl)methanone] thiocarbazone H_2L. Thiocarbonohydrazide (0.21 g, 2 mmol), 2-benzoylpyridine (0.80 g, 4.4 mmol) and five drops of 6 M HCl were mixed in methanol (25 mL). The solution was refluxed for 3 hours, then evaporated to a small volume (10 mL). After cooling to room temperature, the yellow crystalline solid formed was isolated and dried under vacuum to give the ligand H_2L. Anal. Found: C, 68.2; H, 4.8; N, 18.9; Calc. for $C_{25}H_{20}N_6S$: C, 68.8; H, 4.6; N, 19.3%. IR (cm^{-1}): 3319, 3205 (ν_{N-H}), 3051 (ν_{C-H}), 2937, 1498, 1469, 1456, 1422 ($\nu_{C=C}$, ν_{C-N}), 1228 (ν_{N-N}), 1115 ($\nu_{C=S}$), 842, 796, 760, 735 (δ_{C-H}). ^{1}H NMR (ppm) (CD_3Cl): 8.92 (2H, py), 8.45 (2H, NH), 8.03 (2H, py), 7.86 (4H, py), 7.65 (2H, Ph), 7.45–7.53 (8H, Ph). Crystals suitable for X-ray diffraction determination were obtained by slowly evaporating a methanol solution in air.

$[Ni(HL)]_4[PF_6]_4\cdot 4EtOH\cdot H_2O$ 1. The thiocarbazone H_2L (0.22 g, 0.5 mmol) and $NiCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) were mixed in 15 mL methanol. After refluxing for one hour and cooling to room temperature, KPF_6 (0.18 g, 1.0 mmol) was added and refluxing was resumed for over two hours. The brown precipitate formed was isolated and recrystallized from acetonitrile–ethanol (1 : 1) solution. Found: C, 46.4; H, 3.8; N, 12.0; Calc. for $C_{108}H_{102}N_{24}S_4Ni_4P_4F_{24}O_5$: C, 47.0; H, 3.7; N, 12.2%. IR (cm^{-1}): 3622, 3329 (ν_{N-H}), 3060 (ν_{C-H}), 2896, 1593, 1559, 1506, 1460, 1444 ($\nu_{C=C}$, ν_{C-N}), 1264 (ν_{N-N}), 1095 ($\nu_{C=S}$), 841 (s) (ν_{P-F}), 760 (m), 746 (m) (δ_{C-H}). Crystals suitable for crystal determination were obtained by slowly evaporating an acetonitrile–ethanol (1 : 1) solution in air.

$[Cu_2LCl_2]_2$ 2. The thiocarbazone (0.22 g, 0.5 mmol) and $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) were mixed in 10 mL DMF. After stirring for 3 h, the solution was evaporated in air, the dark green crystalline solid formed was isolated, washed by diethyl ether, and dried under vacuum. Found: C, 47.5; H, 3.2; N, 13.5; Calc. for $C_{50}H_{36}N_{12}S_2Cu_4Cl_4$: C, 47.6; H, 2.8; N, 13.4%). IR (cm^{-1}): 3052 (ν_{C-H}), 3020, 1493, 1463 (m), 1440, 1389 ($\nu_{C=C}$, ν_{C-N}), 1292 (ν_{N-N}), 1096 ($\nu_{C=S}$), 845, 758, 740 (δ_{C-H}). ^{1}H NMR (ppm) [$(CD_3)_2SO$]: 9.03 (2H, py), 7.97 (2H, py), 7.73 (2H, py), 7.48 (2H, py), 7.44 (4H, Ph), 7.30 (4H, Ph), 7.20 (2H, Ph). Crystals suitable for crystal determination were obtained by slowly evaporating DMF solution in air.

Table 1 Crystallographic data for compounds H_2L, **1** and **2**

	H_2L	**1**	**2**
Molecular formula	$C_{25}H_{20}N_6S$	$C_{108}H_{102}N_{24}Ni_4$-$O_5P_4F_{24}S_4$	$C_{50}H_{36}Cl_4Cu_4$-$N_{12}S_2$
M	436.53	2759.08	1264.98
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$
a/Å	8.677(3)	27.045(9)	12.142(3)
b/Å	21.385(9)	16.385(7)	10.625(2)
c/Å	12.229(5)	29.595(9)	19.535(6)
V/Å^3	2157(2)	12372(8)	2520.1(11)
Z	4	4	2
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	0.176	0.815	2.010
No. reflections measured	4870	8968	3559
No. unique reflections	3804 [R(int) = 0.05]	8081 [R(int) = 0.12]	3365 [R(int) = 0.10]
$R1$	0.062	0.079	0.073
$wR2$	0.12	0.16	0.11
Goodness of fit	1.03	0.82	1.03

Crystallography

Parameters for data collection and refinement of compounds H_2L, **1** and **2** are summarized in Table 1, selected bond lengths and angles in the three structures are listed in Table 2. Intensities were collected on a Siemens P4 four circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the $\omega - 2\theta$ scan mode. The data were corrected for Lorentz-polarization effects during data reduction using XSCANS.[11] The structures were solved by direct methods and refined on F^2 using full-matrix least squares methods using SHELXTL version 5.0.[12] Anisotropic thermal parameters were refined for the non-hydrogen atoms.

In complex **1**, The PF_6 anions and the ethanol solvent molecules are considered disordered. One of the anions is $D4$ disordered, with a linear F(1)–P(1)–F(6) not disordered. The other four fluorine atoms are disordered over two positions F(2), F(3), F(4) and F(5), as well as F(2′), F(3′), F(4′) and F(5′), these two atom positions refined to occupancies of 0.68(1) and 0.32(1), respectively. Another anion is disordered over two positions, P(2), F(7) to F(12), and P(2′), F(7′) to F(12′), these two positions refined to occupancies of 0.80(1) and 0.20(1), respectively. The ethanol solvent molecules were also disordered over two positions, C(51), C(52), O(1) and C(51′), C(52′), O(1′). These two positions refined to occupancies of 0.68(1) and 0.32(1), respectively. The structure was refined with distance restraints of P–F = 1.57 ± 0.01 Å, $F\cdots F = 2.20 \pm 0.02$ Å, for the disordered anions. Thermal parameters were also restrained as for the disordered atoms in the anions and solvent molecules. One of the phenyl rings of complex **3** is also disordered over two positions, C(21), C(22), C(23), C(24), C(25) and C(21′), C(22′), C(23′), C(24′), C(25′). These two positions refined to occupancies of 0.79(1) and 0.21(1), respectively.

CCDC reference number 186/1823.

See http://www.rsc.org/suppdata/dt/a9/a909604c/ for crystallographic files in .cif format.

Results and discussion

The new Schiff base H_2L was prepared by the reaction of thiocarbonohydrazide with 2-benzoylpyridine. It can, in principle,

Table 2 Selected bond lengths (Å) and angles (°)[a]

H_2L			
C(13)–N(3)	1.370(4)	C(13)–N(4)	1.347(4)
N(3)–N(2)	1.362(4)	N(4)–N(5)	1.369(4)
C(13)–S(1)	1.649(4)		
Complex **2**			
Ni(1)–S(1)	2.388(3)	Ni(2)–S(1)	2.419(3)
Ni(1)–S(2)	2.450(2)	Ni(2)–S(2A)	2.451(2)
Ni(1)–N(5)	2.001(7)	Ni(2)–N(1)	2.066(7)
Ni(1)–N(6)	2.063(6)	Ni(2)–N(2)	2.020(7)
Ni(1)–N(7)	2.057(6)	Ni(2)–N(11A)	2.008(7)
Ni(1)–N(8)	2.029(7)	Ni(2)–N(12A)	2.108(6)
S(1)–C(13)	1.713(9)	S(2)–C(38)	1.723(9)
C(13)–N(3)	1.374(10)	C(38)–N(9)	1.341(9)
C(13)–N(4)	1.349(10)	C(38)–N(10)	1.362(10)
N(2)–N(3)	1.373(9)	N(8)–N(9)	1.314(8)
N(4)–N(5)	1.373(9)	N(10)–N(11)	1.369(8)
N(5)–Ni(1)–N(6)	78.6(3)	N(1)–Ni(2)–N(2)	78.3(3)
N(5)–Ni(1)–N(7)	100.7(2)	N(1)–Ni(2)–N(11A)	101.7(3)
N(5)–Ni(1)–N(8)	177.0(3)	N(1)–Ni(2)–N(12A)	94.6(2)
N(5)–Ni(1)–S(1)	82.1(2)	N(1)–Ni(2)–S(1)	159.0(2)
N(5)–Ni(1)–S(2)	99.0(2)	N(1)–Ni(2)–S(2A)	92.4(2)
N(6)–Ni(1)–N(7)	93.9(3)	N(2)–Ni(2)–N(11A)	178.3(2)
N(6)–Ni(1)–N(8)	104.4(3)	N(2)–Ni(2)–N(12A)	103.9(2)
N(6)–Ni(1)–S(1)	160.7(2)	N(2)–Ni(2)–S(1)	81.0(2)
N(6)–Ni(1)–S(2)	88.3(2)	N(2)–Ni(2)–S(2A)	98.0(2)
N(7)–Ni(1)–N(8)	79.2(2)	N(11A)–Ni(2)–N(12A)	77.8(2)
N(7)–Ni(1)–S(1)	91.3(2)	N(11A)–Ni(2)–S(1)	99.1(2)
N(7)–Ni(1)–S(2)	160.2(2)	N(11A)–Ni(2)–S(2A)	80.3(2)
N(8)–Ni(1)–S(1)	94.9(2)	N(12A)–Ni(2)–S(1)	87.0(2)
N(8)–Ni(1)–S(2)	81.3(2)	N(12A)–Ni(2)–S(2A)	157.9(2)
S(1)–Ni(1)–S(2)	93.1(1)	S(1)–Ni(2)–S(2A)	93.9(1)
Ni(1)–S(1)–Ni(2)	159.4(1)	Ni(1)–S(2)–Ni(2A)	167.5(1)
Complex **2**			
Cu(1)–S(1)	2.270(2)	Cu(2)–S(1)	2.286(2)
Cu(1)–N(1)	2.007(6)	Cu(2)–N(5)	1.950(6)
Cu(1)–N(2)	1.947(6)	Cu(2)–N(6)	2.029(6)
Cu(1)–Cl(1)	2.219(2)	Cu(2)–Cl(2)	2.250(2)
Cu(1)–Cl(2B)	2.724(2)	Cu(2)–Cl(1B)	2.729(3)
C(13)–N(3)	1.318(9)	C(13)–N(4)	1.347(9)
N(2)–N(3)	1.359(8)	N(4)–N(5)	1.369(8)
S(1)–C(13)	1.786(7)		
N(1)–Cu(1)–N(2)	82.2(3)	N(5)–Cu(2)–N(6)	81.1(2)
N(1)–Cu(1)–Cl(1)	95.7(2)	N(5)–Cu(2)–Cl(2)	173.3(2)
N(1)–Cu(1)–S(1)	161.2(2)	N(5)–Cu(2)–S(1)	83.0(2)
N(1)–Cu(1)–Cl(2B)	97.4(2)	N(5)–Cu(2)–Cl(1B)	93.1(2)
N(2)–Cu(1)–S(1)	84.0(2)	N(6)–Cu(2)–S(1)	160.2(2)
N(2)–Cu(1)–Cl(1)	175.6(2)	N(6)–Cu(2)–Cl(2)	96.2(2)
N(2)–Cu(1)–Cl(2B)	90.2(2)	N(6)–Cu(2)–Cl(1B)	94.0(2)
S(1)–Cu(1)–Cl(1)	97.16(9)	S(1)–Cu(2)–Cl(2)	98.35(9)
S(1)–Cu(1)–Cl(2B)	95.34(8)	S(1)–Cu(2)–Cl(1B)	98.58(8)
Cl(1)–Cu(1)–Cl(2B)	93.96(8)	Cl(2)–Cu(2)–Cl(1B)	93.14(8)
Cu(1)–Cl(1)–Cu(2B)	86.59(8)	Cu(2)–Cl(2)–Cu(1B)	86.08(8)
Cu(1)–S(1)–Cu(2)	163.71(11)		

[a] Symmetry code A: $-x, y, 0.5 - z$; B: $-x, -y, 1 - z$.

exhibit thione–thiol tautomerism, since it contains a thioimide –N–C=S functional group.[13] The ν(S–H) band at 2570 cm^{-1} is absent from the IR spectrum of the Schiff-base, but ν(N–H) at *ca.* 3205 cm^{-1} is present, indicating that in the solid state the ligand remains as the thione tautomer. The ^1H NMR spectrum does not show any peak at *ca.* 4.0 ppm attributable to the SH proton, suggesting that the thiol tautomeric form is absent even in solution.

Fig. 1 shows an ORTEP[22] plot of the molecule with atom numbering scheme. The thiocarbazone shows a *Z-Z* configuration about both the C(6)–N(2) and C(19)–N(5) double bond, with the two pyridine rings positioned on the opposite side. Although non-planar as a whole, the molecule consists of five planar fragments (see Table 3), namely the two pyridine rings I and II, the two benzene rings III and IV plus the thiocarbazone moiety V. The mean deviations of sets of atoms from their best planes and the dihedral angles between them are given in Table 3. The non-planarity of the thiocarbazone moiety apparently arises from steric strain and possibly intramolecular hydrogen bonds.

The C–S bond distance (Table 2) of 1.649(4) Å agrees well with those in related compounds, being intermediate between 1.82 Å for a C–S single bond and 1.56 Å for C=S double bond.[14] The corresponding C(13)–N(3) and C(13)–N(4) [1.370(4), 1.347(4) Å] bond distances are indicative of some double bond character, suggesting the extensive delocalization of the whole thiocarbazone moiety. This suggestion is also supported by the N–N bond distances and other C–N bond distances. The H(3N)···N(1) (2.42 Å) and H(4N)···N(6) (2.57 Å) distances are less than normal van der Waals contacts,[15] suggesting possible intramolecular hydrogen bonds, the N–H···N bond angles [124° and 118° about H(3N) and H(4N), respectively] indicate that these hydrogen bonds are very weak.

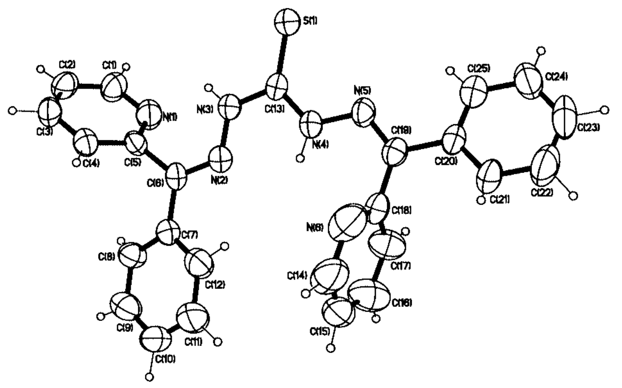

Fig. 1 Molecular structure and atom numbering of $[(C_6H_5)(C_5H_4N)C{=}NNH]_2CS$ [H_2L]. Thermal ellipsoids are drawn at the 50% probability level.

Structure and magnetic properties of $[Ni(HL)]_4[PF_6]_4$

Interaction of the $NiCl_2 \cdot 6H_2O$ with H_2L in boiling methanol gave the tetranuclear metal macrocyclic cation $[NiHL]_4^{4+}$ *via* self-assembly as shown in Scheme 1. ESI-MS (electrospray ionization mass spectroscopy) exhibits three peaks at 493.3, 659.1 and 987.4 which correspond to $[Ni_4(H_4L_4)]^{4+}$, $[Ni_4(H_3L_4)]^{3+}$ and $[Ni_4(H_2L_4)]^{2+}$, respectively, suggesting that the tetranuclear square fragment is the most stable conformation.

As shown in Fig. 2, the tetranuclear cation is located at an inversion center with four nickel(II) atoms at the corners of a square with edge length Ni···Ni *ca.* 4.8 Å [4.73 Å for Ni(1)···Ni(2) and 4.87 Å for Ni(1)···Ni(2A) ($-x$, $1 - y$, $0.5 - z$)]. Each metal center is octahedrally coordinated by the sulfur atoms, the thiocarbazone nitrogen atoms and the pyridine nitrogen atoms from the two different ligands. These two ligands bond to nickel(II) in the *mer* configuration (with pairs of sulfur atoms and pyridine nitrogen atoms each bearing a *cis*-relationship, whereas the thiocarbazone nitrogen atoms are *trans* to each other), as found in related octahedral coordinated metal thiosemicarbazone complexes.[16] The sulfur atoms lie at the mid-points of the edges of square, each being connected to two nickel atoms with bond angles of 159.4 and 167.5° for Ni(1)–S(1)–Ni(2) and Ni(1)–S(2)–Ni(1A) respectively with an average S–Ni–S bond angle *ca.* 93.5°. The C–S bond lengths of 1.713(9) and 1.723(9) Å for C(13)–S(1) and C(38)–S(2) respectively, are within the normal range of a C–S single bond, indicating that the thiocarbazone moiety HL^- adopts the thiol tautomeric form acting as a mono-negative ligand. The C–N and N–N bond distances in HL^- are intermediate between

Table 3 Least-squares planes, mean deviations of atoms from individual planes, and dihedral angles between pairs of planes

H_2L

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle/° I	II	III	IV
I	C(1), C(2), C(3), C(4), C(5), N(1)	0.01				
II	C(14), C(15), C(16), C(17), C(18), N(6)	0.01	68.6			
III	C(7), C(8), C(9), C(10), C(11), C(12)	0.01	67.8	96.7		
IV	C(20), C(21), C(22), C(23), C(24), C(25)	0.01	39.8	79.4	28.7	
V	C(6), N(2), N(3), C(13), S(1), N(4), N(5), C(19)	0.03	59.5	75.0	21.6	22.4

Complex **1**

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle/° I	II	III
I	C(1), C(2), C(3), C(4), C(5), N(1), C(6), N(2), Ni(2), N(3), C(13), S(1)	0.08			
II	C(14), C(15), C(16), C(17), C(18), N(6), Ni(1), N(5), C(19), N(4), S(1), C(13)	0.10	22.0		
I′	C(26), C(27), C(28), C(29), C(30), N(7), Ni(1), N(8), C(31), N(9), C(38), S(2)	0.02	79.5	95.5	
II′	C(39), C(40), C(41), C(42), C(43), N(12), Ni(2A), N(11), C(44), N(10), S(2), C(38)	0.09	88.7	101	14.1

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle/° III	IV	IIIA
III	C(7), C(8), C(9), C(10), C(11), C(12)	0.03			
IV	C(20), C(21), C(22), C(23), C(24), C(25)	0.10	22.8		
IIIA	C(7A), C(8A), C(9A), C(10A), C(11A), C(12A)		31.4	18.6	
IVA	C(20A), C(21A), C(22A), C(23A), C(24A), C(25A)		18.6	5.5	22.8

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle/° III′	IV′	III′A
III′	C(32), C(33), C(34), C(35), C(36), C(37)	0.03			
IV′	C(45), C(46), C(47), C(48), C(49), C(50)	0.01	6.0		
III′A	C(32A), C(33A), C(34A), C(35A), C(36A), C(37A)		10.8	4.9	
IV′A	C(45A), C(46A), C(47A), C(48A), C(49A), C(50A)		4.9	1.1	6.0

Complex **2**

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle/° I	II	III
I	C(1), C(2), C(3), C(4), C(5), N(1)	0.01			
II	C(14), C(15), C(16), C(17), C(18), N(6)	0.02	17.8		
III	C(7), C(8), C(9), C(10), C(11), C(12)	0.02	64.3	82.0	
IV	C(6), N(2), Cu(1), N(3), C(13), S(1), N(4), N(5), Cu(2), C(19)	0.07	13.3	5.1	77.4

formal single and double bonds, pointing to extensive delocalization over the entire molecular skeleton. The thiocarbazone hydrogen atoms of the mono-anions HL^- could not be located from the difference Fourier map, and are most likely disordered over N(4) and N(5), N(9) and N(10) for the two mono-negative ligands, respectively. Although non-planar as a whole, the atoms in each of the mono-anions are divided into two planar parts I and II, I′ and II′ for the two mono-negative ligands respectively, the benzene rings lie out of the planes (Table 3). The mean deviation of each part is *ca.* 0.08 Å on average, whereas, the dihedral angle between the two HL^- ligands coordinated to the same nickel atom is *ca.* 92° on average. The closest intermolecular distance between two HL^- ligands coordinated to different nickel centers is 3.69 Å, indicating weak π–π interactions.[17]

It is interesting to note that the eight uncoordinated benzene rings can also be divided into two groups (III, IV, IIIA, IVA and III′, IV′, III′A, IV′A). Planes in the group defined as the planes III′, IV′, III′A, IV′A are almost parallel to each other (dihedral angles between pairs of planes *ca.* 5° on average) and surprisingly these are stacked as shown in Fig. 3. The closest intermolecular distance between stacked pairs is 3.68 Å, and the dihedral angle between the planes in different groups is *ca.* 90° on average. Although these stacking interactions are weak compared to the metal–nitrogen and metal–sulfur coordinating bonds, it could be suggested that these kinds of interactions were important in the molecular assembly of the tetranuclear metal macrocyclic molecular square.

The temperature dependence of the molar magnetic susceptibility χ_m (4Ni) and the effective magnetic moment μ_{eff} (4Ni) for a polycrystalline sample of the tetranuclear complex **1** in the range of 75–300 K are displayed in Fig. 4. As the temperature is lowered, χ_m increases from 5.7×10^{-3} cm^3 mol^{-1} at room temperature and reaches a maximum of 9.3×10^{-3} cm^3 mol^{-1}. The effective magnetic moment at room temperature of 3.69 μ_B, which is very low compared to that expected for four independent nickel(II) ions, decreases with decreasing temperature and reaches 2.37 μ_B. The shapes of both curves are characteristic of strong antiferromagnetic coupling among the nickel(II) ions.

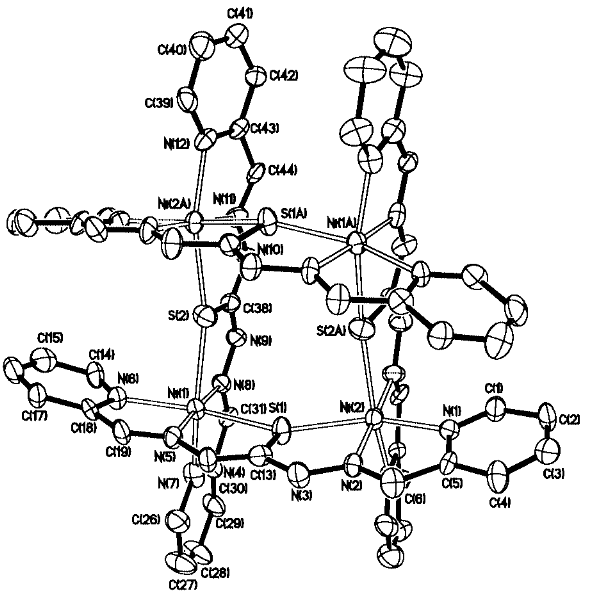

Fig. 2 Perspective view of the molecular skeleton of the square macrocyclic $[Ni(HL)]_4^{4+}$ in **1**, showing the non-hydrogen atoms of 50% probability thermal ellipsoids. The phenyl rings and hydrogen atoms are omitted for clarity.

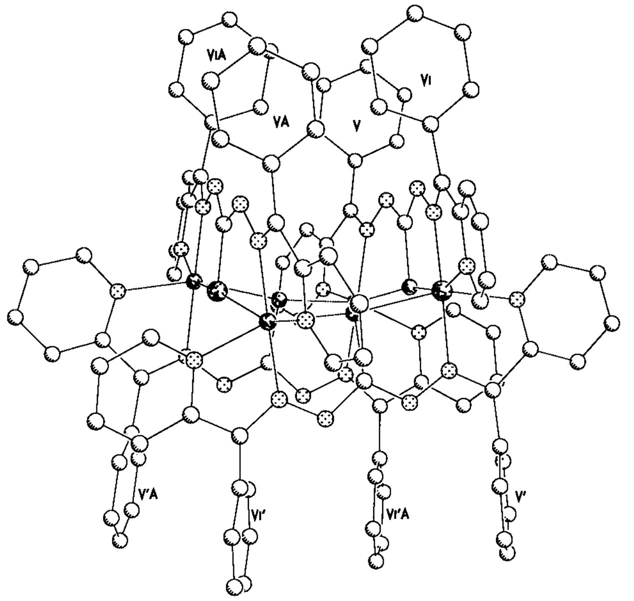

Fig. 3 Molecular structure showing the potential π–π stacking interactions between the phenyl rings. Hydrogen atoms are omitted for clarity.

The structure of $[Cu_2LCl_2]_2$

Interaction of $CuCl_2·2H_2O$ with H_2L in DMF at ambient temperature gave a tetranuclear neutral metal complex *via* self-assembly as shown in Scheme 1. No obvious magnetic susceptibility χ_m was measured from 75–300 K, indicating the strong antiferromagnetic coupling among the copper(II) ions.

As shown in Fig. 5, the neutral tetranuclear copper(II) complex can be described as a centric symmetric dimer of dicopper(II) moieties. The geometry of copper atoms is five-coordinate (4 + 1) square pyramidal with the pyridine nitrogen atom, the thiocarbazone nitrogen atom, the sulfur atom and the chlorine atom comprising the basal plane, whereas the apical position is occupied by the chlorine atom from the symmetry related ($-x$, $-y$, $1 - z$) half of the dimeric molecule, as found in the related thiosemicarbazone copper(II) N_2S-tridentate thiosemicarbazone complex.[18] The basal plane shows a very slight tetrahedral distortion, Cu(1) lies 0.16 Å out of the plane towards the chlorine atom at the apical position of the pyramid [while for Cu(2) the deviation is 0.18 Å]. The bond lengths in the basal plane agree well with those generally found in

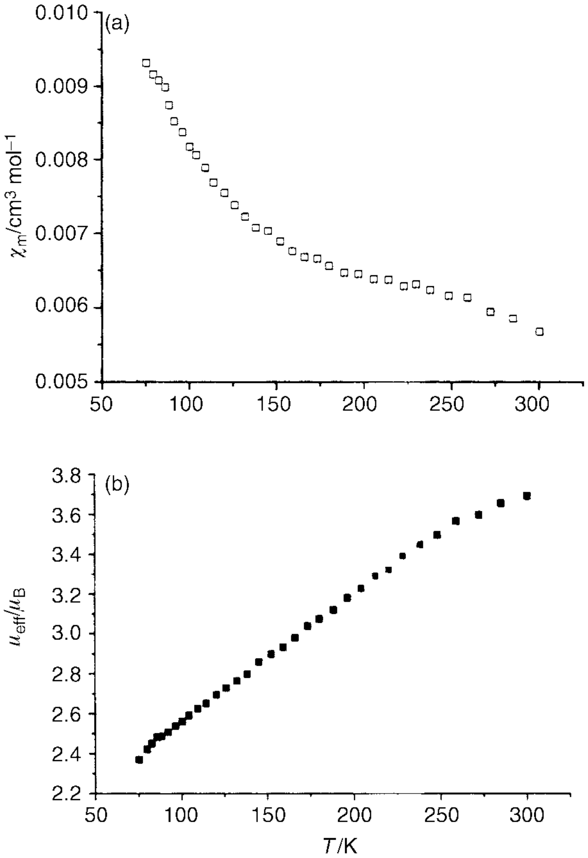

Fig. 4 Thermal dependence of the molar magnetic susceptibility χ_m (a) and effective magnetic moment μ_{eff} (b) for the tetra nickel(II) square.

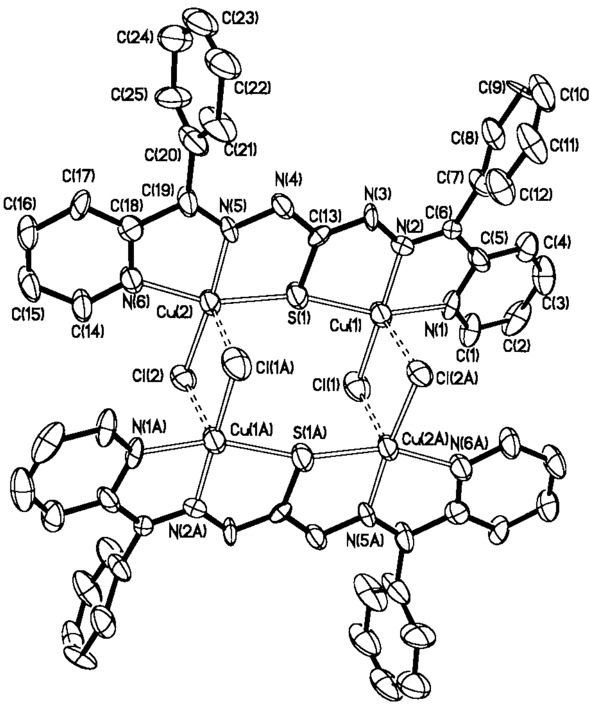

Fig. 5 Perspective view of the molecular skeleton of the rectangular $[Cu_2LCl_2]_2$ in **2**, showing the non-hydrogen atoms of 50% probability thermal ellipsoids. The minor parts of the disordered phenyl rings and hydrogen atoms are omitted for clarity.

copper(II) complexes containing thiosemicarbazone derivatives.[19] The Cu(1)–Cl(2B) apical bond length (2.72 Å) falls within the range of other metal-chloride bridged systems.[20] The Cu · · · Cu distances are 4.51 and 3.41 Å for the sulfur bridged pairs and chlorine bridged pairs respectively. The sulfur atom is coordinated to two Cu(II) ions with a Cu–S–Cu bond angle of 163.7(1)°. It is suggested that this shorter Cu · · · Cu distance and the larger Cu–S–Cu angle contribute to the strong magnetic exchange between the copper(II) centers.

Except the two benzene rings and the apex coordinated chlorine atoms, the atoms in one half of the dimeric molecule are nearly coplanar, the mean deviation from the best plane being 0.08 Å. The C–S bond distance is 1.786(7) Å, this agrees well with the normal range of a C–S single bond,[21] indicating that the thiocarbazone moiety adopts the thiol tautomeric form acting as a negative ligand, the C–N and N–N bond distances are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire molecular skeleton. Although the loss of one or two protons from the ligand might influence the skeleton of the molecule and especially the C–N and N–N distances, the extensive delocalization over the whole molecule means that this difference is not too significant to the crystal structure.

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References

1 (*a*) J. M. Lehn, *Supramolecular Chemistry*, VCH Publishers, New York, 1995 and references therein; (*b*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*c*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502.

2 (*a*) R. V. Slone, K. D. Benkstein, S. Belanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, **171**, 221; (*b*) S. Bélanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson and T. G. Carrell, *J. Am. Chem. Soc.*, 1999, **121**, 557; (*c*) S. S. Sun and A. J. Lees, *Inorg. Chem.*, 1999, **38**, 4181.

3 (*a*) F. S. McQuillan, T. E. Berridge, H. Chen, T. A. Hamor and C. J. Jones, *Inorg. Chem.*, 1998, **37**, 4959; (*b*) C. J. Matthews, Z. Q. Xu, S. K. Mandal, L. K. Thompson, K. Biradha, K. Poirier and M. J. Zaworotko, *Chem. Commun.*, 1999, 347; (*c*) M. Lahav, R. Gabai, A. N. Shipway and I. Willner, *Chem. Commun.*, 1999, 1937.

4 (*a*) E. Solari, W. Lesueur, A. Klose, K. Schenk, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1996, 807; (*b*) I. M. Atkinson, C. Benelli, M. Murrie, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 1999, 285; (*c*) E. Colacio, C. Lopes-Magana, V. McKee and A. Romerosa, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2923.

5 (*a*) M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645; (*b*) M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720; (*c*) M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249.

6 (*a*) P. J. Stang, *Chem. Eur. J.*, 1998, **4**, 19; (*b*) J. A. Whiteford, C. V. Lu and P. J. Stang, *J. Am. Chem. Soc.*, 1997, **119**, 2524; (*c*) P. J. Stang, B. Olenyuk, D. C. Muddiman and R. D. Smith, *Organometallics*, 1997, **16**, 3094.

7 (*a*) G. S. Hanan, D. Volkmer, V. S. Schubert, J. M. Lehn, G. Baum and D. Fenske, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1842; (*b*) Y. S. Zhang, S. Wang, G. D. Enright and S. R. Breeze, *J. Am. Chem. Soc.*, 1998, **120**, 9398; (*c*) R. W. Saalfrank and I. Bernt, *Curr. Opin. Solid State Mater.*, 1998, **3**, 407.

8 (*a*) C. Y. Duan, Z. H. Liu, X. Z. You, F. Xue and T. C. W. Mak, *Chem. Commun.*, 1997, 381; (*b*) J. C. Jeffery, P. L. Jones, K. L. V. Mann, E. Psillakis, J. A. McCleverty, M. D. Ward and C. M. White, *Chem. Commun.*, 1997, 175; (*c*) H. A. Cruse and N. E. Leadbeater, *Inorg. Chem.*, 1999, **38**, 4149.

9 (*a*) C. Y. Duan, B. M. Wu and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3485; (*b*) Z. H. Liu, C. Y. Duan, S. H. Yang and X. Z. You, *Chem. Lett.*, 1999, 1734; (*c*) E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1251.

10 (*a*) E. Lukevics, D. Jansone, K. Rubina, E. Abele, S. Germane, L. Leite, M. Shymanska and J. Popelis, *Eur. J. Med. Chem.*, 1995, **30**, 983; (*b*) M. Diaz-Guerra, M. C. Rivas and M. Esteban, *Virology*, 1997, **236**, 354; (*c*) G. Strote, I. Bonow, M. Kromer, T. R. De Kromer, S. Attah and N. Opoku, *Trop. Med. Int. Health*, 1998, **3**, 397.

11 Siemens, XSCANS (Version 2.1), Siemens, Analytical X-Ray Instruments Inc., Madison, USA, 1994.

12 Siemens, SHELXTL (Version 5.0) Analytical X-Ray Instruments Inc., Madison, USA, 1995.

13 S. Padhýe and G. B. Kauffman, *Coord. Chem. Rev.*, 1985, **63**, 127.

14 (*a*) L. E. Sutton, *Tables of Interatomic Distance and Configuration in Molecules and Ions*, *Supplement*, The Chemical Society, London, 1965; (*b*) A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, G. G. Watson and R. Taylor, in *Structure Correlation*, ed. H. B. Burgi and J. D. Dunitz, VCH, Weinheim, 1994, Vol. 2, Appendix A, pp. 751–857.

15 (*a*) W. Fuller, *J. Phys. Chem.*, 1959, **63**, 1705; (*b*) G. R. Desiraju, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2311.

16 (*a*) M. B. Ferrari, G. G. Fava, G. Pelosi, M. C. Rodriguez-Argüelles and P. Tarasconi, *J. Chem. Soc.*, *Dalton. Trans.*, 1995, 3035; (*b*) E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2125.

17 (*a*) C. A. Hunter, *Chem. Soc. Rev.*, 1994, **23**, 101; (*b*) G. R. Desiraju, *Chem. Commun.*, 1997, 1475; (*c*) Z. H. Liu, C. Y. Duan, J. Hu and X. Z. You, *Inorg. Chem.*, 1999, **38**, 1719.

18 (*a*) M. B. Ferrari, G. G. Fava, C. Pelizzi, P. Tarasconi and G. Tosi, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 227; (*b*) M. B. Ferrari, G. G. Fava, P. Tarasconi and C. Pelizzi, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 361; (*c*) A. G. Bingham, H. Bogge, A. Müller, E. W. Ainscough and A. M. Brodie, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 493.

19 (*a*) J. Garcia-Tojal, M. K. Urtiaga, R. Cortés, L. Lezama, M. I. Arriortua and T. Rojo, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2233; (*b*) E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1737.

20 (*a*) W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1982, **21**, 2679; (*b*) D. J. Hodgson, P. K. Hale and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1061.

21 (*a*) J. S. Casas, M. V. Castaño, M. C. Rodriguez-Argüelles, A. Sánchez and J. Sordo, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1253; (*b*) K. V. Katti, P. R. Singh and C. L. Barnes, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2153; (*c*) E. W. Ainscough, E. N. Baker, A. M. Brodie, R. J. Cresswell, J. D. Ranford and J. M. Waters, *Inorg. Chim. Acta*, 1990, **172**, 185.

22 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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