Structural dependence of π–π interactions in dithiocarbazato and thiosemicarbazato nickel complexes

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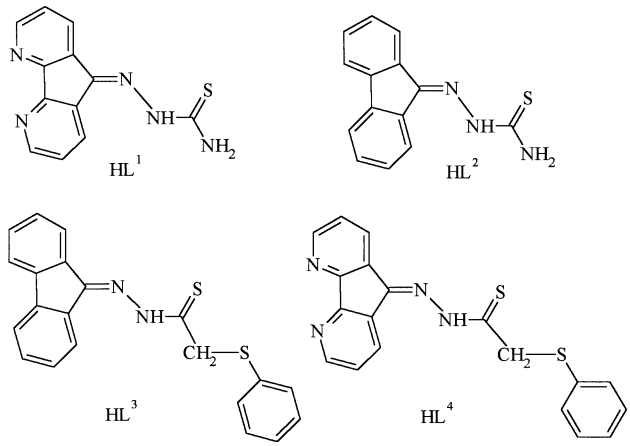
Structures and stabilization due to π–π interactions of N_2S_2 coordinated nickel(II) complexes NiL_2 have been investigated by ESI-MS spectrometry and X-ray diffraction methods. For the systems with HL = 4,5-diazafluoren-9-one thiosemicarbazone (HL^1), fluoren-9-one thiosemicarbazone (HL^2), fluoren-9-one dithiocarbazone (HL^3) and 4,5-diazafluoren-9-one dithiocarbazone (HL^4), the Ni(II) atom in each complex is coordinated in a distorted square-planar geometry with two aromatic rings positioned on the same side. This *cis* configuration is stabilized by π–π stacking interactions between the aromatic rings. Detailed structural analyses reveal that whereas the intermolecular π–π stacking interactions connect NiL_2^1 molecules into a one-dimensional screw chain, the intermolecular π–π stacking interactions and the C–H···π interactions link NiL_2^2 molecules into a dimer. The π–π stacking interactions and the C–H···π interactions among the two phenyl rings and two fluorene rings of NiL_2^3 form a closed hydrophobic brick. In NiL_2^1 one of the two phenyl rings interacts with the two 4,5-diazafluorene rings to give an opened hydrophobic cavity; the edge-to-face interactions about another phenyl ring arrange the molecules into a one-dimensional network.

Interactions between aromatic units represent an important class of intermolecular force in chemistry, biology and materials science.[1–3] It is generally recognized that,[4] in the absence of strong hydrogen-bond donors and acceptors, aromatic compounds tend to self-assemble *via* π–π (face-face) interactions, C–H···π interactions (T-shape geometry, edge-face or herringbone interactions) or both. Examples illustrating the importance and diversity of these interactions include the base pair association that stabilizes the double helical structure of DNA,[5] the tertiary structures of proteins,[6] packing of aromatic molecules in crystals,[7] host–guest binding[8] and aggregation of porphyins in solution.[9] Offset, face-to-face stacking interactions have been the subject of a number of investigations.[10,11] These studies have addressed the role of molecular geometry,[12] the influence on UV charge-transfer bands[13] and the chemical shift in the ^{1}H-NMR spectra,[14] and electrostatic factors in promoting aromatic association.[15] Edge-to-face aromatic interactions have been invoked to explain the stability of certain protein folding motifs,[16] Observations and speculations involving these interactions have been reported in many papers in chemistry and structural biology.[17] Recent studies on crystal structures sustained by π–π interactions reveal that the effects of π–π interactions on molecular structure and molecular packing are just about as predictable as the effects of conventional hydrogen bonds.

In our previous work,[18] we have discussed the molecular structure and crystal packing of the palladium complex $PdL_2^1 \cdot 3H_2O$ (HL^1 = 4,5-diazafluoren-9-one thiosemicarbazone). It is believed that the π–π stacking interactions between the aromatic rings are not only the main factor controlling complex formation as a polarizable rigid molecular clip, but also an important factor controlling the molecular packing into the polarizable $P3_2$ space group. In order to verify that this synthon is robust enough to be exchanged from one network to another, Ni(II) complexes NiL_2 with this ligand and three other related ligands were designed and synthesized to systemically study the structural dependence of the π–π stacking interactions and C–H···π interactions in the molecular structures and crystal packing.



Experimental

Materials

All chemicals were of reagent grade and were used without further purification. Thiosemicarbazide and 4,5-diazafluoren-9-one (Aldrich) were used as received. (*S*)-Phenyldithiocarbazate was synthesized according to the literature method.[19] 4,5-Diazafluoren-9-one thiosemicarbazone HL^1 was prepared according to our previous work.[18] Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin–Elmer 240 analyzer. Electrospray mass spectra were performed on a LCQ system (Finnigan MAT, USA) using methanol as mobile phase.

Bis(4,5-diazafluoren-9-one thiosemicarbazato)nickel, NiL_2^1 (1). Ethanol solutions of sodium acetate (0.16 g, 2 mmol), 4,5-diazafluoren-9-one thiosemicarbazone (0.53 g, 2 mmol) and

$NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) were mixed. The black crystalline solid formed after refluxing for 2 h was isolated and dried under vacuum, yield 85%. Anal. calc. for $C_{24}H_{22}N_{10}O_3S_2Ni$: C: 46.4; H: 3.6; N: 22.5. Found: C: 46.8; H: 3.3; N: 22.4%. Crystals suitable for X-ray structural analysis were obtained by slowly evaporating a DMF–*n*-C_4H_9OH (1 : 1, v/v) solution in air.

Bis(fluoren-9-one thiosemicarbazato)nickel, NiL^2_2 (2). The ligand HL^2 was synthesized according to the literature method using fluoren-9-one to replace the 4,5-diazafluoren-9-one.[18] To the ethanol solution containing HL^2 (0.53 g, 2 mmol) and sodium acetate (0.16 g, 2 mmol), 10 ml of an ethanol solution containing $NiCl_2 \cdot 6H_2O$ (0.25 g, 1 mmol) was added. The black powder formed after refluxing for 2 h was isolated and dried under vacuum to give $NiL^2_2 \cdot H_2O$ in a yield of 64%. Anal. calc. for $C_{28}H_{20}N_6S_2Ni \cdot H_2O$: C: 57.8; H: 3.8; N: 14.5. Found: C: 57.6; H: 3.7; N: 14.4%. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a methanol solution of $NiL^2_2 \cdot H_2O$ in air.

Bis(fluoren-9-one dithiocarbazato)nickel, NiL^3_2 (3). Five drops of acetic acid were added to a mixture of (*S*)-phenyldithiocarbazate (2.1 g, 10 mmol) and fluoren-9-one (1.86 g, 10 mmol) in ethanol (30 mL). The resulting solution was heated to reflux for 3 h and on cooling, a yellowish white solid (HL^3) was formed and separated. Ethanol solutions (20 ml) of HL^3 (0.75 g, 2 mmol), sodium acetate (0.16 g, 2 mmol) and $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) were mixed. The dark-brown crystalline solid formed after refluxing for 2 h was isolated and dried under vacuum to give NiL^4_2 in a yield of 58%. Anal. calc. for $C_{42}H_{30}N_4S_4Ni$: C, 64.8; H, 3.9; N, 7.2. Found: C, 65.3; H, 4.0; N, 6.9%. Crystals suitable for X-ray structural analysis were obtained by slowly evaporating a CH_2Cl_2 solution in air.

Bis(4,5-diazonefluoren-9-one dithiocarbazato)nickel, NiL^4_2 (4). Five drops of acetic acid were added to a mixture of (*S*)-phenyldithiocarbazate (2.1 g, 10 mmol) and 4,5-diazafluoren-9-one (1.86 g, 10 mmol) in ethanol (30 mL). The resulting solution was heated to reflux for 3 h and on cooling, a yellowish white solid (HL^4) was formed and separated. Complex NiL^4_2 was synthesized by combining 10 ml of a methanol solution of HL^4 (0.75 g, 2 mmol), sodium acetate (0.16 g, 2 mmol) and $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol). The black powder formed after refluxing for 2 h was isolated and dried under vacuum to give NiL^4_2 in a yield of 64%. Anal. calc. for $C_{38}H_{26}N_8NiS_4$: C, 58.4; H, 3.5; N, 14.3. Found: C, 58.3; H, 3.3; N, 14.3%. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a benzene solution of NiL^4_2 in air.

Crystallography

The relevant crystal data and structural parameters are summarized in Table 1. Intensity data for the four compounds were measured on a Siemens P4 four-circle diffractometer with monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) radiation using $\omega/2\theta$ scan mode with a variable scan speed of 4.0–60.0° per min in ω. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[20]

The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms of the ligands were placed in their calculated positions with C–H = 0.96 Å (except for the hydrogen atoms of the water molecules, which were found in the Fourier difference map), assigned fixed isotropic thermal parameters (1.2 times that of the atom attached to), and allowed to ride on their respective parent atoms. In complex **1**, since the water oxygen atom O(2W) occupies a special position with sof = 0.5, the hydrogen atoms attached to it were refined disordered with sof fixed at 0.5. And since the hydrogen atom H(1WB) [attached to water oxygen atom O(1W)] occupies a special position with sof = 0.5, hydrogen atom H(1WC) was also refined disordered with sof fixed at 0.5. Refinement in $P3_112$ and $P3_1$ of the *P* helicity for the packed molecules produced worse refinement statistics. All computations were performed on a PC-586 using the SHELXTL-PC program package.[21]

CCDC reference number 440/213. See http://www.rsc.org/suppdata/nj/b0/b0048461/ for crystallographic files in .cif format.

Nonlinear optical property measurement. The second-order nonlinear optical intensities were estimated using powdered crystals (particle diameters of 76 to 154 nm) in a 10 mm diameter pellet. The thickness of each pellet was about 0.8 mm. The experimental arrangement for the nonlinear optical properties utilized a M200 high power mode-locked Nd : YAG laser operating at 1064 with 200 ps pulses at a repetition rate of 5 Hz. The laser beam was split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference (KDP pellet). According to the principle proposed by Kurtz and Perry,[22] the SHG efficiency of **1** can be estimated to be comparable with that of KDP.

Results and discussions

Structure of $NiL^1_2 \cdot 3H_2O$ (1)

Fig. 1 shows an ORTEP plot of the nickel(II) complex **1** with the atomic numbering scheme. The Ni(II) atom is coordinated

Table 1 Crystallographic data for the four Ni(II) compounds

Empirical	$NiL^1_2 \cdot 3H_2O$ (**1**)	$NiL^2_2 \cdot H_2O$ (**2**)	NiL^4_2 (**4**)	NiL^3_2 (**3**)
Formula	$C_{24}H_{22}N_{10}O_3S_2Ni$	$C_{28}H_{22}N_6OS_2Ni$	$C_{42}H_{30}N_4S_4Ni$	$C_{38}H_{26}N_8S_4Ni$
Formula weight	621.35	581.35	777.65	781.62
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	$P3_121$	$P1$	$P2_1/n$	$P2_1/c$
a/Å	10.696(4)	12.294(1)	8.924(1)	10.594(3)
b/Å	10.696(4)	14.670(2)	21.696(3)	8.500(4)
c/Å	19.748(6)	15.508(2)	18.933(2)	38.598(7)
α/°		91.44(1)		
β/°		99.31(1)	100.77(1)	96.79(2)
γ/°	120	106.95(1)		
U/Å^3	1956.6(12)	2632.5(6)	3600.9(8)	3451.1(18)
Z	3	4	4	4
μ/mm^{-1}	0.953	0.930	0.808	0.842
Refl. collected	6084	7281	7019	6322
Refl. unique	3723	6890	6247	5991
R_{int}	0.058	0.022	0.029	0.104
Final R [$I > 2\sigma(I)$]	0.037	0.042	0.049	0.071
Final wR_2	0.088	0.111	0.110	0.159

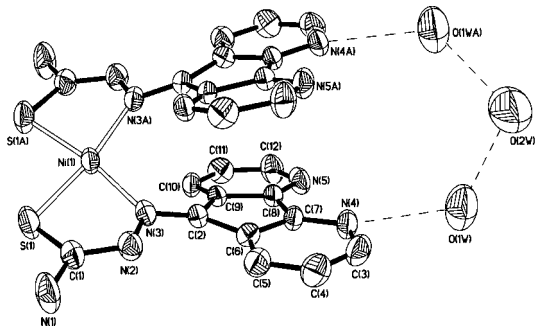


Fig. 1 Molecular structure with atomic numbering of the nickel complex **1**. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Symmetry code A: $1 - x + y$, y, $5/3 - z$.

in a distorted square-planar configuration with two equivalent Ni–N and Ni–S bonds. The mean deviation of the NiSSNN plane (d_0) is *ca.* 0.05 Å. Since the molecule lies on a crystallographic twofold axis, the asymmetric unit therefore contains only one-half of the nickel complex and one and a half water molecules. The crowding between the two ligands in the complex is relieved by the molecule assuming a step conformation, which is characterized by the dihedral angles (β) between the NiSSNN plane and the two SCNN planes that are *ca.* 30° on average.[23] As can be expected,[18,24] the π–π stacking interaction between the two diazafluorene rings controls the positioning of these two rings on the same side to form a rigid molecular clip. The dihedral angle of the stacking pair is 7.2°, the center-to-center separation between the two aromatic rings is *ca.* 3.6 Å, the shortest interplanar atom···atom separation is 3.4 Å. Similar results have been found in related stacked complexes.[25,26] Bond distances and angles are in the normal ranges (Table 2).

The most distinctive structural feature of the complex in the solid state is that it forms a one-dimensional 3_2 screw chain (Fig. 2) with the axis at $x = 1$, $y = 1$; the helical pitch, given by one full rotation of the 3_2 screw axis, is 19.75 Å. It is suggested that the screw aggregate is achieved by intermolecular π–π stacking interactions between the extensively delocalized π-system of the two ligands of adjacent molecules. The members of the stacking pair are almost parallel to each other with the shortest interplanar atom···atom separation being *ca.* 3.3 Å. The average distance of atoms in one plane to the stacked one is 3.4 Å. This distance is comparable to the average distance for a strong π-stacking interaction between two aryl rings (3.35 Å) in graphite. On the basis of previous work on π–π stacking interactions, it seems reasonable to assume a stacked geometry for the aggregates in which the π–π stacking interaction includes the delocalization of the

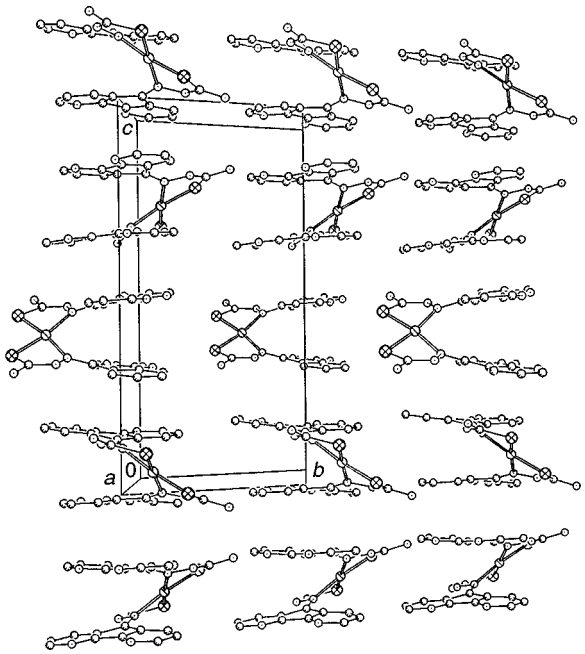


Fig. 2 Side view of the intermolecular π–π stacking interaction of two diazafluorene ligands along the 3_2 screw chain of complex **1**.

thiosemicarbazone moieties. This assumption is further supported by the intermolecular atom···atom separation of C(1)···C(4B) (*ca.* 3.56 Å) and N(2)···C(5B) (*ca.* 3.43 Å) (symmetry code B: x, $1 + x - y$, $2 - z$). Such a stacked scheme contributes to the molecules assembling in a polarizable 3_2 screw.

There are also substantial screw–screw contacts in the crystal lattice. Most importantly, each one-dimensional π-stacked 3_2 screw combines six neighbors through hydrogen bonds between the pyridine nitrogen atoms and the amino nitrogen atoms (Table 3). The inter-screw hydrogen bonds, which link the molecules together in the solid state, lead to a three-dimensional network with channels between the screws. The radius of the channel is *ca.* 6.0 Å. The crystal pattern is further stabilized by the inclusion of water molecules in the channeled structure. The three lattice water molecules connect one by one using hydrogen bonds to form an infinite 3_2 screw chain with the axis position at $x = 1/3$, $y = 2/3$. Each of the channels includes one hydrogen-bonded water screw controlling the molecular packing in the polarizable space group $P3_212$.

It is interesting to note that this structure is isostructural with the Pd(II) complex $PdL_2^1 \cdot 3H_2O$. Powder SHG measurements showed that both compounds exhibit obvious SHG

Table 2 Selected bond distances (Å) and angles (°) for the four Ni(II) compounds

	1	**2**[a]	**3**	**4**	
Ni–N	1.951(4)	1.923(3)	1.928(3)	1.939(3)	1.928(6)
		1.929(3)	1.924(3)	1.936(3)	1.912(6)
Ni–S	2.137(2)	2.146(1)	2.147(1)	2.151(1)	2.144(2)
		2.142(1)	2.137(1)	2.148(1)	2.155(2)
C–S	1.740(5)	1.745(4)	1.742(4)	1.733(4)	1.747(8)
		1.745(5)	1.738(4)	1.738(4)	1.702(9)
				1.745(4)	1.746(8)
				1.742(4)	1.748(8)
N–Ni–N	103.7(2)	100.3(1)	99.8(1)	100.7(1)	99.2(3)
S–Ni–S	87.17(7)	90.32(5)	91.92(5)	89.73(5)	95.3(9)
N–Ni–S	84.7(1)	85.7(1)	85.7(1)	85.5(1)	86.7(2)
		85.0(1)	85.6(1)	85.5(1)	86.1(2)
	170.8(1)	170.9(1)	165.6(1)	169.4(1)	158.4(2)
	170.8(1)	169.3(1)	166.8(1)	169.4(1)	161.2(2)

[a] The crystal of complex **2** contains two different molecules.

Table 3 Hydrogen bonds in complex **1**

D	H[a]	A[a]	D···A/Å	H···A/Å	D–H···A/Å
O(1W)	H(1WA)	N(4)	2.904(7)	2.09	161
O(1W)	H(1WB)	O(2W)	2.752(8)	2.17	126
O(1W)	H(1WC)	O(1WB)	2.745(9)	1.37	177
O(2W)	H(2WA)	O(1WA)	2.752(8)	1.94	159
O(2W)	H(2WB)	N(2C)	3.354(8)	2.83	121
N(1)	H(1B)	N(5D)	3.000(6)	2.14	144
N(1)	H(1A)	O(1D)	2.948(8)	2.21	143

[a] Symmetry codes: A: $1-x+y, y, 5/3-z$, B: $x, 1+x-y, 2-z$, C: $1-x+y, 1+y, 5/3-z$, D: $1+x, y, z$.

efficiency (5 times that of urea for the Pd(II) complex and the same as that of KDP for the Ni(II) complex). This result clearly indicates that there is only one enantiomer in each of the crystals. Crystal structure studies show that the nickel complex is a *M* helix while the Pd complex is a *P* helix; studies of the factors influencing the absolute conformation of these complexes are in progress.

Structure of NiL^2_2 (2)

Using fluoren-9-one to replace 4,5-diazafluoren-9-one to construct the Schiff-base ligand HL^2 and nickel complex **2**, a black crystalline solid also formed. Elemental analysis and spectral characterization agree well with the formula of $NiL^2_2 \cdot H_2O$. The X-ray crystal structure determination of **2** reveals that an asymmetric unit consists of two different molecules and two lattice water molecules. Like complex **1**, both molecules are rigid molecular clips (Fig. 3). Each Ni(II) atom is coordinated in a step distorted square-planar configuration with two Ni–N bonds and two Ni–S bonds ($d_0 = 0.15$ Å, $\beta = 29°$ on average). Whereas the fluorene rings of the molecule containing Ni(2) stack upon each other to stabilize the molecular clips (dihedral angle of the stacked pair is 17°, the center-to-center separation is *ca.* 3.65 Å), the dihedral angle between the two aromatic rings of the molecule containing Ni(1) is *ca.* 48°; this value is too large for the two aromatic rings to be considered as stacked above each other. It is suggested that the *cis* configuration of Ni(1) is not stabilized by intramolecular π–π stacking interactions between the two fluorene rings directly. Detailed structure analysis reveals that this clip molecule has a U-shaped cavity similar to that of some glycoluril derived clips.[27] The clip molecule dimerizes to give a 'head-to-head' packing, with the wall of one clip molecule being buried in the cavity of a symmetry related clip $(2-x, -y, -z)$ (Fig. 4). Although no further evidence supports the existence of C–H···π interactions to stabilize the dimerization, it seems reasonable to say that the dimerization and the *cis* configuration of the Ni(1) atom are stabilized by cooperative intermolecular π–π stacking interactions and C–H···π interactions. The π–π stacking interactions between the parallel aromatic rings is characterized by a shortest interplanar atom···atom separation of *ca.* 3.3 Å. The C–H···π interactions are characterized by a H(C14)···M (midpoint of the aromatic group C(17A)–C(22A) (symmetry code A; $2-x, -y, -z$) distance of 2.93 Å with a θ (C(14)–H(14A)···M) angle of 141°.[28] It should be noted that the aromatic interaction is quite similar to the P4PE (parallel fourfold phenyl embrace) motif described by Scudder and Dance[11] for tetraphenylphosphonium cations in which two of the four phenyl rings are approximately parallel and the motif comprises one offset face-to-face attractive phenyl···phenyl interaction and two edge-to-face interactions.

The dimerization in solution can also be observed by electrospray ionization mass spectrometry (ESI-MS). This soft ionization method has been successfully applied for the direct characterization of weakly bonded species containing non-covalent supramolecular systems.[29] The presence of several pseudo-molecular peaks corresponding to successive loss of the counter ions is clear and easy to interpret. By carefully controlling the ionization energies,[30] non-covalent molecular architectures, the stability of which depends on weak interactions, are not destroyed so that the ion distribution in the mass spectra reflects with confidence the species arrangement in solution. ESI-MS spectrum (Fig. 5) recorded at a cone voltage of 120 V shows two major peaks at *m*/*z*, 563.2 and

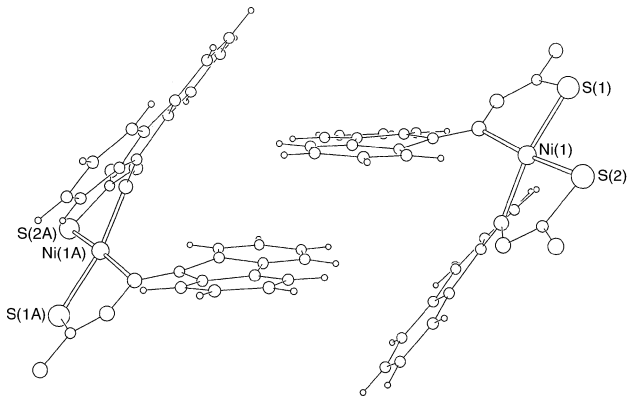


Fig. 4 Intermolecular π–π stacking and C–H···π interactions for dimerization of the molecular clip in complex **2**. Symmetry code A: $2-x, -y, -z$.

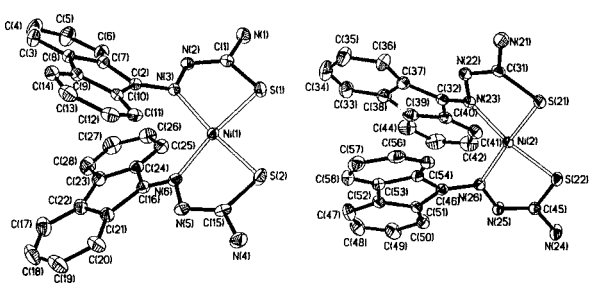


Fig. 3 Molecular structure with atomic numbering of the two molecules of the nickel complex **2**. The thermal ellipsoids are drawn at the 30% probability level. H atoms and water molecules are omitted for clarity.

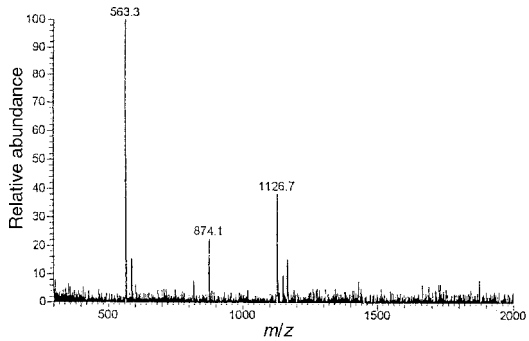


Fig. 5 ESI-MS spectrum of complex **2** at a capillary tube temperature of 120 °C.

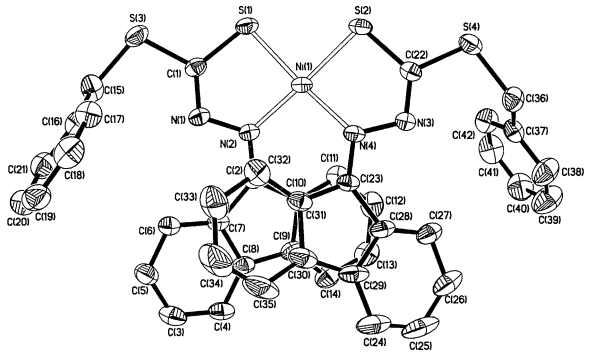


Fig. 6 Molecular structure with atomic numbering of the nickel complex **3**. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

1124.7, corresponding to the pseudo-monomolecular ions $[NiL^2_2]^+$ and $[(NiL^2_2)_2]^+$, respectively. The peak at *m*/*z* 563.2 is clearly an isotropically resolved overlap of $[NiL^2_2]^+$ and $[(NiL^2_2)_2]^{2+}$ species. This result suggested that a dimeric neutral nickel(II) complex $\mathbf{2}_2$ was formed in solution. Simultaneously, partial fragmentation of the dinuclear complex $\mathbf{2}_2$ appeared as a novel peak at *m*/*z* 874.1, assigned to the fragmentation product $[(NiL^2_2)(NiL^2)]^+$.

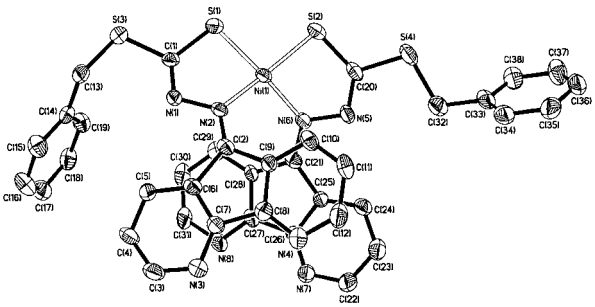


Fig. 7 Molecular structure with atomic numbering of the nickel complex **4**. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

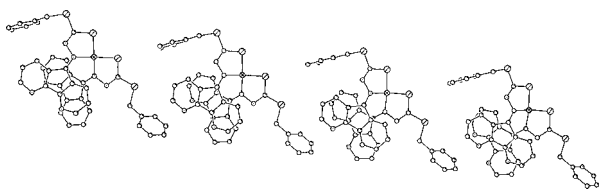


Fig. 8 Intermolecular π–π stacking and C–H···π interactions in the one-dimensional chain in complex **4**.

Structure of NiL^3_2 (3)

When the amino group in ligand HL^2 was substituted by a $-CH_2SPh$ group, a new ligand HL^3 was formed. It is clear that there is no hydrogen atom having the potential to form hydrogen bonds. In the absence of strong hydrogen-bond donors and acceptors, aromatic compounds tend to self-assemble *via* π–π (face-face) interactions, C–H···π interactions (T-shape geometry, edge-face or herringbone interactions) or both. As shown in Fig. 6, the nickel(II) complex **3** surprisingly forms of a hydrophobic brick. Two fluorene rings positioned on the same side form two longer walls of the brick and two phenyl rings also positioned on the same side form the two shorter walls of the cavity. The size of the cavity is *ca.* 12.8 × 3.4 × 3.6 Å^3. The Ni(II) atom is coordinated in a slight distorted step square-planar configuration (d_0 *ca.* 0.13 Å and β *ca.* 26°) with two Ni–N bonds and two Ni–S bonds. It is clear that the *cis* configuration of the aromatic rings is stabilized by the π–π stacking between the two fluorene rings and edge-to-face interactions of the two fluorene rings and two phenyl rings. The dihedral angle between the two stacked fluorene rings is *ca.* 12°, the center-to-center distance of the stacking pair is *ca.* 3.45 Å. The shortest interplanar atom···atom separation is *ca.* 3.56 Å. Dihedral angles between the fluorene rings and phenyl rings, listed in Table 4, range from 82.0°–109°. The shortest interplanar atom···atom separation is *ca.* 3.5 Å, indicating strong edge-to-face π–π interactions. Similar edge-to-face interactions are also find in the cavity structure of $[Cu(phen)(H_2O)(phenylpropionate)]_2(NO_3)_2 \cdot 2H_2O$.[31]

Structure of NiL^4_2 (4)

Substituting the amino group in ligand HL^1 by a $-CH_2SPh$ group gives the new ligand HL^4. This ligand is quite similar to HL^3, in which there are no strong hydrogen-bond donors and acceptors; the π–π (face-face) interactions and C–H···π interactions should be the main factor controlling the molecular structure and packing. Fig. 7 shows an ORTEP plot of the Ni(II) complex **4**. The Ni(II) atom is coordinated in a distorted step square-planar configuration (d_0 *ca.* 0.28 Å and β *ca.* 22°). Intramolecular π–π stacking interactions also connect the two 4,5-diazafluorene rings positioned on the same side with a shortest atom···atom separation of 3.42 Å and a dihedral angle of 24.8°. Unlike the hydrophobic brick structure in complex **3**, NiL^4_2 does not assemble into a closed brick, the intramolecular edge-to-face interactions only connect the two 4,5-diazafluorene rings and one phenyl ring, forming an opened brick with three walls. The shortest atom···atom distance of atoms in the phenyl ring to atoms in two diazafluorene rings is *ca.* 3.60 Å for C(5)···C(15), and 3.69 for C(30)···C(18), respectively. The dihedral angles between the diazafluorene and phenyl rings are listed in Table 4.

It is interesting to find that *inter*molecular edge-to-face interactions about the second phenyl ring (not involved in an *intra*molecular edge-to-face interaction) link the molecules together (Fig. 8) to make an infinite chain. The phenyl ring

Table 4 Dihedral angles for complexes **3** and **4**

Plane	Atoms defining the plane	Mean dev./Å	Dihedral angle/°		
			I	II	III
Complex **3**					
I	C(2)–C(14)	0.056			
II	C(23)–C(35)	0.047	12.0		
III	C(16)–C(21)	0.005	82.4	87.7	
IV	C(37)–C(42)	0.006	93.7	102.3	108.8
Complex **4**					
I	N(3), N(4), C(2)–C(12)	0.049			
II	N(7), N(8), C(21)–C(31)	0.055	158.1		
III	C(14)–C(19)	0.011	80.5	87.0	
IV	C(33)–C(38)	0.010	44.3	114.1	54.0

interacts with the stacked diazafluorene rings of the symmetry related molecule (symmetry code: $-1+x, 1+y, z$) with the shortest atom···atom separation being *ca.* 3.17 Å.

Conclusions

The above results show that the interactions between aromatic groups are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. The origin of these interactions is imperfectly understood. (i) This result clearly indicates that although these types of weak interactions, which only have energies in the 2–20 kJ mol^{-1} range, they have effects on molecular structure and packing that are just about as important as the effects of conventional hydrogen bonds. (ii) Interconnected systems of aromatic–aromatic interactions possess the property of being co-operative, that is the contacts enhance the strengths of each other, and the interaction energy per contact is greater than the energy of an isolated interaction. These results complement our earlier studies in crystal engineering studies on SHG materials based on aromatic stacking interactions. This contribution adds several new features to the fast developing field of supramolecular chemistry and aids in the fundamental understanding of molecular recognition and systematic rationalization of molecular aggregation in inorganic crystal engineering.

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