

A supramolecular analog of cyclohexane sustained by aromatic C–H $\cdots\pi$ interactions between ferrocene moieties: molecular packing of ferrocene-containing thiosemicarbazato metal complexes

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Novel supramolecular cyclohexane-like structures, [NiL₂] (1) and [ZnL₂] (2) (HL = acetylferrocenyl thiosemicarbazone), have been constructed by self-assembly of ferrocene moieties *via* aromatic C–H $\cdots\pi$ interactions. The nickel(II) atom in 1 is coordinated in a distorted square-planar *cis* configuration with two ferrocene-containing ligands positioned on the same side. One of the ferrocene moieties interacts with symmetry-related species to form a supramolecular arrangement that is topologically equivalent to cyclohexane, but in which edge-to-face C–H $\cdots\pi$ interactions between ferrocene moieties serve the same structural functions as the C–C bonds in cyclohexane. The zinc(II) atom in 2 is coordinated in a tetrahedral geometry with two equivalent Zn–S and Zn–N bonds. Each ferrocene moiety interacts with symmetry-related species using C–H $\cdots\pi$ interactions to form a two-dimensional cyclohexane-like network. Powder X-ray diffraction analyses of complexes 1 and 2, together with the palladium(II) complex [PdL₂] (3), copper(II) complex [CuL₂] (4), and cobalt(II) complex [CoL₂] (5) reveal that the supramolecular cyclohexane-like aggregation is robust enough to be exchanged from one network to another. All the results indicate that although C–H $\cdots\pi$ interactions have energies only in the 2–20 kJ mol^{–1} range, these interactions are directional enough in combination that the orientation of molecules in the solid can be predicted with a reasonable degree of accuracy.

Interactions between aromatic molecules represent an important class of intermolecular forces in chemistry, biology, materials science and crystallography.^{1–3} It is generally recognized that,^{4,5} in the absence of strong hydrogen-bond donors and acceptors, aromatic compounds tend to self-assemble *via* π – π (face-to-face) interactions, C–H $\cdots\pi$ interactions (T-shape geometry, edge-to-face or herringbone interactions) or with both. These weak non-covalent bonds can sustain supramolecular synthons that are structure determining.^{6–9} In the present work, we report the self-assembly and structural characterization of a novel robust cyclohexane-like aggregation *via* C–H $\cdots\pi$ interactions between ferrocene moieties. Previous studies of C–H $\cdots\pi$ interactions generally focused on the use of organic compounds.^{10,11} In the assembly of cyclohexane supramolecular analogs here, we have introduced ferrocene moieties for interaction with each other, thereby offering the potential of broadening the scope of further work in this area.

The goal of crystal engineering is to recognize and design synthons that are robust enough to be exchanged from one network to another, which ensures generality and predictability. Such structural predictability leads to the anticipation of one-, two- and three-dimensional patterns formed with intermolecular interactions.^{12–14} It was suggested¹⁵ that although the C–H $\cdots\pi$ interactions have energies that are only in the 2–20 kJ mol^{–1} range, they can still be important for transient processes such as those associated with biomolecular structure and conformation; their effects on crystal structure and packing are just about as predictable as the effects of conventional hydrogen bonding and strong π – π stacking interactions. In order to test this approach, powder X-ray diffraction analyses of several related complexes have been measured for comparison.

Experimental

General

Thiosemicarbazide and acetylferrocene (Aldrich) were used as received. All other chemicals were of reagent grade quality obtained from commercial sources and were used without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 240 analyzer. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{–1} range. Powder X-ray diffraction patterns were recorded on a D/max- γ A rotating anode X-ray diffractometer with graphite-monochromated Cu-K α (mean λ ca 1.542 Å) radiation at room temperature. The cell dimensions were calculated by the least-squares method using the Original 4.1 program.

Syntheses

Acetylferrocenyl thiosemicarbazone, HL. The ligand HL was prepared as described in the literature.¹⁶ Refluxing a methanol solution containing acetylferrocene (0.46 g, 2 mmol) and thiosemicarbazide (0.18 g, 2 mmol) for 2 h resulted in the formation of an orange crystalline solid, which was isolated and dried under vacuum.

Metal complexes. To form the nickel complex [NiL₂] (1), thiosemicarbazone HL (0.42 g, 1 mmol) and nickel acetate (0.25 g, 1 mmol) were mixed in 25 mL of ethanol. After refluxing for 4 h, the dark brown solid formed was isolated, washed with ethanol and dried under vacuum. Complexes [ZnL₂] (2),

Table 1 Elemental analyses and IR data for the complexes 1–5

Complex and chemical formula	Analysis ^a (%)			IR/cm ⁻¹		
	C	H	N	$\nu_{\text{C-H}}$	$\nu_{\text{C=C}}, \nu_{\text{C=N}}, \nu_{\text{C-N}}$	$\delta_{\text{C-H}}$
1 · CH ₃ CH ₂ OH · 2H ₂ O	45.2	4.8	11.8	3080	1601, 1566, 1530	823, 765
C ₂₈ H ₃₈ Fe ₂ N ₆ NiO ₃ S ₂	(45.4)	(5.2)	(11.3)			
2 · CH ₃ CH ₂ OH	47.8	4.5	11.7	3086	1594, 1565, 1497	823, 766
C ₂₈ H ₃₄ Fe ₂ N ₆ OS ₂ Zn	(47.3)	(4.8)	(11.8)			
3 · H ₂ O	42.5	3.4	11.5	3088	1630, 1599, 1531	826, 764
C ₂₆ H ₃₀ Fe ₂ N ₆ OPdS ₂	(43.1)	(4.2)	(11.6)			
4 · 0.5CH ₃ CH ₂ OH · H ₂ O	45.7	4.2	11.9	3087	1611, 1563, 1509	825, 763
C ₂₇ H ₃₃ CuFe ₂ N ₆ O _{1.5} S ₂	(46.0)	(4.7)	(11.9)			
5 · 4H ₂ O	43.0	5.2	11.9	3084	1608, 1561, 1502	825, 765
C ₂₆ H ₃₆ CoFe ₂ N ₆ O ₄ S ₂	(42.8)	(5.0)	(11.5)			

^a Calculated values are given in parentheses. Analyses were performed on powder samples.

[CuL₂] (**4**) and [CoL₂] (**5**) were prepared by the same procedure with the corresponding Zn(II), Cu(II) and Co(II) acetates, while complex [PdL₂] (**3**) was synthesized using Pd(CH₃CN)₂Cl₂ instead of the metal acetate. Elemental analyses and IR spectroscopic data for compounds 1–5 are reported in Table 1. Crystals of **1** and **2** suitable for X-ray structural analyses were obtained by slow evaporation of the dichloromethane solution in air.

Crystallography

Parameters for data collection and refinement of complexes **1** and **2** are summarized in Table 2. Data were collected on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the $\omega-2\theta$ scan mode. Data were corrected for Lorentz polarization effects during data reduction using XSCANS,¹⁷ and a semi-empirical absorption correction from ψ scans was applied. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods in SHELXTL version 5.0.¹⁸ Anisotropic thermal parameters were refined for non-hydrogen atoms. For complex **1**, the atoms of the lattice ethanol molecule were refined isotropically. The lattice water molecule was refined as disordered; the s.o.f. (site occupancy factor) of the oxygen atom was fixed at 0.16667. For complex **2**, the lattice ethanol molecule was refined disordered with the ethanol carbon C(15) situated on a crystallographic twofold axis; the s.o.f. of the C(14), C(15) and O(1) atoms were thus fixed at 0.5.

CCDC reference number 440/197. See <http://www.rsc.org/suppdata/nj/b0/b002590i/> for crystallographic files in .cif format.

Results and discussion

During our study on the nonlinear optical properties of thiosemicarbazones,^{19,20} the ferrocene-containing thiosemicarbazone Schiff base ligand HL was designed and synthesized.

Table 2 Crystallographic data for complexes 1 and 2

	1 · CH ₃ CH ₂ OH · 0.16H ₂ O	2 · CH ₃ CH ₂ OH
Formula	C ₂₈ H _{34.32} Fe ₂ N ₆ NiO _{1.16} S ₂	C ₂₈ H ₃₄ Fe ₂ N ₆ OS ₂ Zn
<i>M</i>	708.14	711.80
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}c$
<i>a</i> /Å	29.293(4)	29.171(3)
<i>c</i> /Å	18.470(4)	19.702(3)
<i>U</i> /Å ³	13 730(4)	14 519(3)
<i>Z</i>	18	18
<i>T</i> /K	293(2)	293(2)
μ /mm ⁻¹	1.719	1.785
Unique reflections	4961 [<i>R</i> (int) = 0.042]	2857 [<i>R</i> (int) = 0.113]
<i>R</i> ₁	0.068	0.071
<i>wR</i> ₂ (all data)	0.194	0.166
Goodness-of-fit	1.089	1.011

Crystal structure analyses and spectroscopic studies revealed that the ligand remains in the thione tautomer both in solution and in the solid state. However, in the presence of metal ions, the Schiff base compound is rapidly converted into the thiol tautomeric form to facilitate the formation of metal complexes, as the deprotonated monoanionic bidentate ligand. Crystal structure analyses show that the cell volumes of the nickel(II) and zinc(II) complexes **1** and **2** are almost the same, and surprisingly larger than 1.0×10^4 Å³. This result may demonstrate the existence of supramolecular analogs controlling the crystallization.

Structure of the nickel(II) complex

Fig. 1 shows an ORTEP plot of the nickel(II) complex **1** with atomic numbering scheme. The nickel atom is coordinated in a distorted square-planar *cis* configuration with two ferrocene moieties positioned on the same side [N(3)–Ni(1)–N(6) 101.3(2)°, S(1)–Ni(1)–S(2) 91.5(1)°]. The mean deviation of the NiSSNN coordination plane is *ca.* 0.20 Å. The crowding between the two ligands in the complex is relieved by the molecule assuming a step conformation.²¹ The dihedral angles between the NiSSNN coordination plane and two SCNN planes are *ca.* 26° on average. It is suggested that the *cis* configuration is stabilized by the intramolecular π – π stacking interaction between the two acetylcyclopentadienyl rings.²² The dihedral angle of the stacked pair is 22°, the shortest interplanar atom···atom separation is 3.47 Å. This distance is comparable with the standard distance for a strong π –stacking

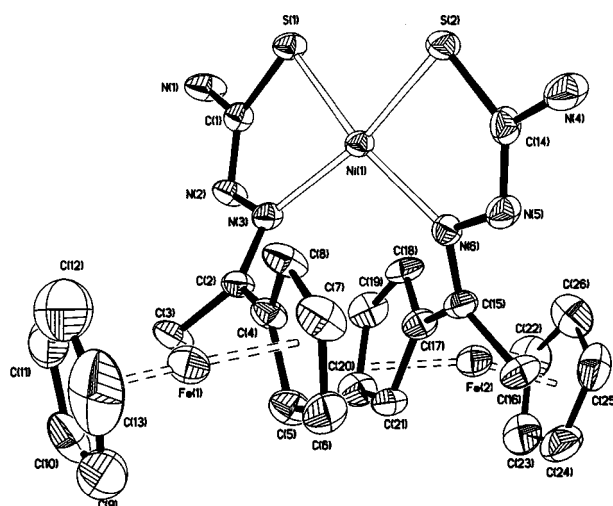
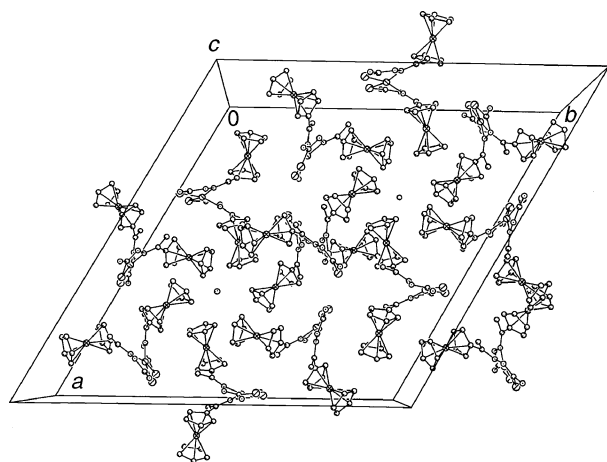


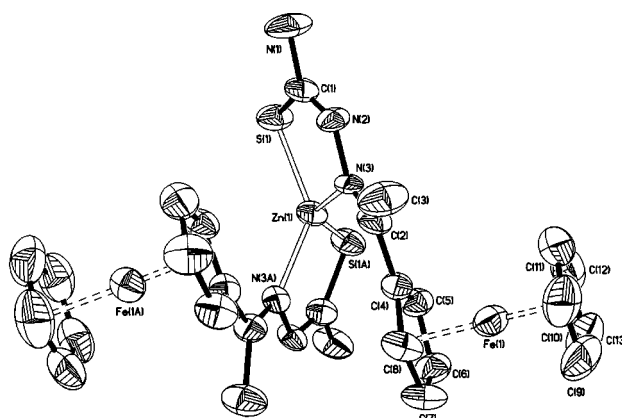
Fig. 1 ORTEP plot of the nickel(II) complex **1** with atomic numbering scheme. The atoms are represented by 50% probability thermal ellipsoids. The solvent molecules and hydrogen atoms are omitted for clarity.

The molecules connect with one another to form a cyclohexane-like hexamer *via* aromatic C-H $\cdots\pi$ interactions between ferrocene moieties (Fig. 2). The cyclic hexamer comprises six symmetry-related Cp rings. Since the hexamer lies on a crystallographic S_3 axis, it adopts a chair geometry. The shortest distance between the centroid of the Cp ring [defined by C(9), C(10), C(11), C(12) and C(13)] in one molecule and the interacting C atom C(11) ($1-x, 1-x+y, 0.66667-z$) in a symmetry-related molecule is 3.85 Å (H \cdots centroid 3.03 Å, C-H \cdots centroid 141°); the inter-plane angle is 69°. It should be noted that this distance is a little longer than those found in the crystal structure of benzene (3.78 Å and 85°)²⁵ and similar to the honeycomb arrangement in the crystal structure



HL		$1 \cdot (\text{CH}_3\text{CH}_2\text{OH}) \cdot (\text{H}_2\text{O})_{0.16}$		$2 \cdot (\text{CH}_3\text{CH}_2\text{OH})$			
S(1)–C(1) N(1)–C(1) N(2)–C(1) N(2)–N(3) N(3)–C(2)	1.693(3) 1.315(4) 1.345(4) 1.387(4) 1.290(4)	Ni(1)–N(3)	1.940(6)	Ni(1)–N(6)	1.946(6)	Zn(1)–N(3)	2.057(5)
		Ni(1)–S(1)	2.154(2)	Ni(1)–S(2)	2.168(2)	Zn(1)–S(1)	2.292(2)
		S(1)–C(1)	1.752(8)	S(2)–C(14)	1.752(8)	S(1)–C(1)	1.759(8)
		N(1)–C(1)	1.341(9)	N(4)–C(14)	1.365(10)	N(1)–C(1)	1.364(9)
		N(2)–C(1)	1.280(9)	N(5)–C(14)	1.278(10)	N(2)–C(1)	1.276(9)
		N(2)–N(3)	1.418(8)	N(5)–N(6)	1.401(8)	N(2)–N(3)	1.417(7)
		N(3)–C(2)	1.274(9)	N(6)–C(15)	1.287(9)	N(3)–C(2)	1.295(9)
		N(3)–Ni(1)–S(1)	84.4(2)	N(6)–Ni(1)–S(2)	86.1(2)	N(3)–Zn(1)–S(1)	86.5(2)
C(1)–N(2)–N(3) C(2)–N(3)–N(2) N(1)–C(1)–N(2) N(1)–C(1)–S(1) N(2)–C(1)–S(1) N(3)–C(2)–C(4) N(3)–C(2)–C(3) C(4)–C(2)–C(3)	118.2(3) 116.9(3) 117.0(3) 122.8(2) 120.1(2) 115.6(3) 125.2(3) 119.3(3)	N(6)–Ni(1)–S(1)	166.2(2)	N(3)–Ni(1)–S(2)	164.3(2)	N(3)–Zn(1)–S(1A)	136.4(2)
		S(1)–Ni(1)–S(2)	91.5(1)			S(1)–Zn(1)–S(1A)	108.6(1)
		N(3)–Ni(1)–N(6)	101.3(2)			N(3)–Zn(1)–N(3A)	110.8(3)
		C(1)–N(2)–N(3)	111.6(6)	C(14)–N(5)–N(6)	112.5(6)	C(1)–N(2)–N(3)	114.7(6)
		C(2)–N(3)–N(2)	115.5(6)	C(15)–N(6)–N(5)	113.2(6)	C(2)–N(3)–N(2)	115.0(6)
		N(2)–C(1)–N(1)	120.0(7)	N(5)–C(14)–N(4)	118.8(7)	N(2)–C(1)–N(1)	117.1(7)
		N(1)–C(1)–S(1)	117.1(6)	N(4)–C(14)–S(2)	116.6(6)	N(1)–C(1)–S(1)	113.5(6)
		N(2)–C(1)–S(1)	122.8(5)	N(5)–C(14)–S(2)	124.6(6)	N(2)–C(1)–S(1)	129.3(5)
N(3)–C(2)–C(4) N(3)–C(2)–C(3) C(4)–C(2)–C(3)	115.6(3) 125.2(3) 119.3(3)	N(3)–C(2)–C(4)	119.1(7)	N(6)–C(15)–C(17)	120.1(7)	N(3)–C(2)–C(4)	118.9(6)
		N(3)–C(2)–C(3)	121.8(7)	N(6)–C(15)–C(16)	121.9(7)	N(3)–C(2)–C(3)	123.1(6)
		C(4)–C(2)–C(3)	119.1(7)	C(17)–C(15)–C(16)	118.1(7)	C(4)–C(2)–C(3)	118.0(7)

The configuration of the zinc complex is different from that of the nickel complex, however, the details of the crystal structure reveal the presence of the honeycomb supramolecular hexamers; each hexamer is connected to six neighbors through the zinc coordination centers to form a honeycomb grid (Fig. 4). The formation of the hexamer is stabilized by C-H $\cdots\pi$ interactions between the Cp rings. The distance between the centroid of the Cp ring and the nearest C atom C(12) ($y, 1-x+y, -z$) of the interacting ring is 3.67 Å (H \cdots centroid 2.95 Å, C-H \cdots centroid 132°) and the interplanar angle is 78.1°. This C \cdots centroid distance is shorter



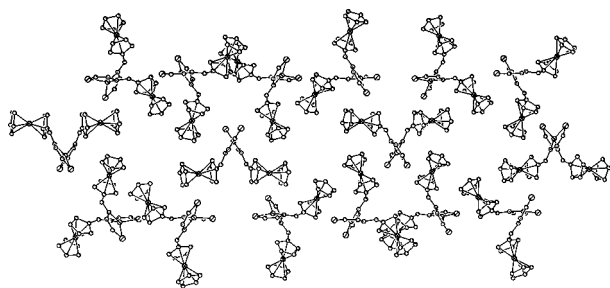


Fig. 4 The molecular packing of the cyclohexane-like network of the zinc(II) complex **2**. The solvent molecules and the methyl groups as well as the hydrogen atoms are omitted for clarity.

than those found in the previous honeycomb complexes, however, the $\text{H}\cdots\text{centroid}$ distance is longer than that in the corresponding honeycomb networks.^{4a}

Powder X-ray diffraction analyses

The aim of crystal engineering is to establish reliable connections between molecular and supramolecular structures on the basis of intermolecular interactions. Ideally, one would like to identify substructural units in a target supramolecule that can be assembled from logically chosen precursors. Therefore, the predictable self-organization of molecules into one-, two- or three-dimensional networks is of importance in crystal engineering. For such rational design, intermolecular interactions, be they strong or not so strong, must be directional enough in combination that the orientation of molecules in the solid can be predicted with a reasonable degree of accuracy. To test this, powder X-ray diffraction analyses of complexes **1** and **2**, together with three other related complexes, **3**, **4** and **5**, were undertaken. As shown in Fig. 5, the powder X-ray diffraction pattern of the palladium complex **3** is quite similar to that calculated from the single crystal data of the nickel(II) complex **1**. This result indicates that the two metal complexes crystallized in a similar lattice, or sometimes, in a similar space group. Table 4 shows the cell dimensions of the five complexes obtained from the powder X-ray data. The measured and calculated values of the inter-planar spacing (d) and diffraction index of the five complexes are also listed in Table 4. It is interesting to find that all of the five complexes crystallize in a hexagonal lattice. This observation is good evidence for the existence of similar supramolecular analogs in the crystallization of the five compounds, although the metal center and coordination geometry of the central metal atoms are dif-

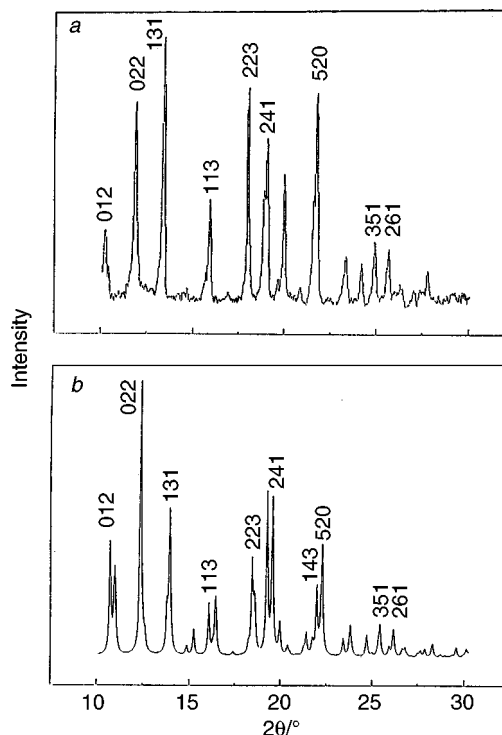


Fig. 5 (a) The powder X-ray diffraction pattern of the palladium complex **3**. (b) The powder X-ray diffraction pattern calculated from the single crystal data of the nickel(II) complex **1**.

ferent. It could be suggested that the five complexes are isomorphous and the potential supramolecular aggregation in these complexes is stabilized by the $\text{C-H}\cdots\pi$ interactions between the Cp rings of the neighboring molecules.

Molecular crystal engineering is the modeling, synthesis and exploitation of crystalline materials with predefined aggregations of molecules or ions.^{7a,27} The powder and single crystal X-ray diffraction analysis studies demonstrate that the synthon sustained by $\text{C-H}\cdots\pi$ interactions between ferrocene moieties is robust enough to be exchanged from one network to another. It ensures generality and predictability in crystal engineering and should extend beyond supramolecular chemistry, since it is anticipated that the structures may aid in the prediction of crystal structures that are sustained by weak interactions such as the aromatic $\text{C-H}\cdots\pi$ interaction. The potential of this research field is enormous and the interest in

Table 4 Selected powder X-ray diffraction data of complexes **1–5** at room temperature

	1	2	3	4	5
Cell dimensions/Å	$a = 29.06$ $c = 18.44$	$a = 28.99$ $c = 19.60$	$a = 29.55$ $c = 18.24$	$a = 29.03$ $c = 19.28$	$a = 28.87$ $c = 19.62$
Volume/Å ³	13 486	14 265	13 793	14 071	14 162
$h\ k\ l$	d_o, d_c^a	d_o, d_c	d_o, d_c	d_o, d_c	d_o, d_c
0 1 2	8.691, 8.659	9.125, 9.129	8.614, 8.592	9.105, 9.001	9.245, 9.129
0 3 0	8.181, 8.389	8.294, 8.368		8.240, 8.379	8.025, 8.333
0 2 2	7.474, 7.438	7.792, 7.725	7.430, 7.428	7.754, 7.649	7.692, 7.715
1 3 1	6.380, 6.528	6.471, 6.561	6.583, 6.615	6.508, 6.556	6.332, 6.537
1 13	5.575, 5.662	5.926, 5.956	5.552, 5.623	5.772, 5.876	6.013, 5.955
0 4 2		5.383, 5.285		5.340, 5.264	5.324, 5.270
2 2 3	4.709, 4.693	4.922, 4.853	4.697, 4.695	4.810, 4.811	4.814, 4.845
2 4 1	4.642, 4.606	4.571, 4.611	4.650, 4.675	4.566, 4.612	4.635, 4.593
1 4 3	4.171, 4.096	4.087, 4.198	4.110, 4.113	4.114, 4.172	4.131, 4.188
5 2 0	4.045, 4.030	4.087, 4.020	4.075, 4.098	4.114, 4.025	4.131, 4.003
3 5 1	3.550, 3.529	3.525, 3.528	3.568, 3.585	3.516, 3.530	
2 6 1	3.453, 3.429		3.463, 3.484		3.472, 3.414

^a d_o : observed (Å), d_c : calculated (Å).

the development of expert synthetic strategies for the preparation of molecular solids is increasing rapidly.

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