Supramolecular organization of the crystals of allylsulfide clathrochelate: influence of the nature of solvate molecules

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The influence of the nature of solvate molecules on the supramolecular organization of the crystals of α-benzyldioximate $FeBd_2((AllylS)_2Gm)(BF)_2$ clathrochelate containing the allylsulfide substituents was studied by X-ray diffraction analysis.

Key words: supramolecular chemistry, clathrochelates, X-ray diffraction analysis.

The preparation of single crystals of complexes with an encapsulated metal ion (in particular, clathrochelates) suitable for X-ray diffraction analysis presents considerable difficulties.[1] In many cases, the use of solvents of different nature does not give the desired results. In an effort to elucidate the influence of various solvents on the crystal packing, we studied the allylsulfide $FeBd_2[(AllylS)_2Gm](BF)_2$ clathrochelate, where Bd^{2-} is the α-benzyldioxime dianion and Gm is the glyoxime residue. The molecular structure of this complex is shown in Fig. 1. The clathrochelate molecule has a disk-like shape and its periphery is formed by the nonpolar Ph and Me groups. Only cross-linking fragments of the clathrochelate framework containing the oxygen and fluorine atoms are polar. One would expect that the solvent molecules would be involved in specific dipole-dipole interactions with these (although insufficiently "open") moieties of the molecule.

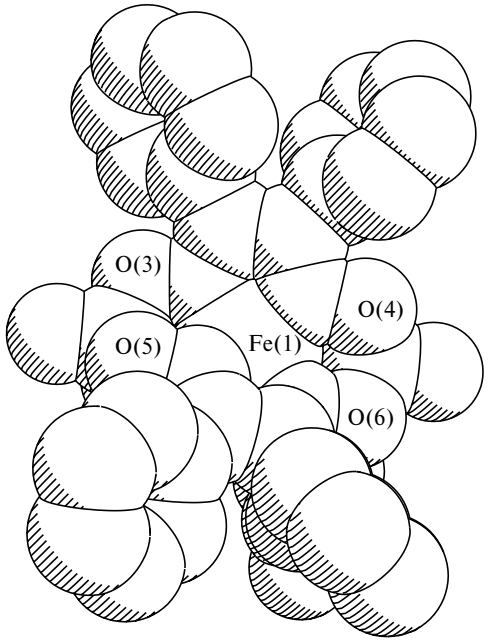

Fig. 1. Molecular structure of the $FeBd_2[(AllylS)_2Gm](BF)_2$ clathrochelate.

Experimental

(1,8-Bis(2-fluorobora)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12-tetraphenyl-17,18-diallylmercaptylbicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene(2−)iron(II), $FeBd_2[(AllylS)_2Gm](BF)_2$. A solution of allylthiol (0.25 mL, 3.14 mmol) and Et_3N (0.44 mL, 3.16 mmol) in CH_2Cl_2 (10 mL) was added with stirring to a solution of the $FeBd_2(Cl_2Gm)(BF)_2$ complex[2] (1.07 g, 1.43 mmol) in CH_2Cl_2 (30 mL) under argon. The reaction mixture was stirred for 2 h and concentrated to dryness. The residue was washed with methanol (15 mL) and dissolved in a small amount of CH_2Cl_2. The solution was filtered through a layer of silica gel SPH-300

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(Chemapol) and precipitated with an excess of hexane. The precipitate was filtered off, washed with hexane, and dried *in vacuo*. The yield was 0.79 g (67%). Found (%): C, 52.69; H, 3.65; N, 10.11; Fe, 6.55. $C_{36}H_{30}N_6O_6B_2S_2F_2Fe$. Calculated (%): C, 52.58; H, 3.65; N, 10.22; Fe, 6.79. MS, *m/z* 822 $[M]^{+\bullet}$. ^1H NMR ($CDCl_3$), δ: 3.96 (d, 4 H, SCH_2); 5.02 (m, 4 H, $=CH_2$); 5.81 (m, 2 H, =CH—); 7.32 (m, 20 H, Ph). ^{13}C NMR $\{^1H\}$ ($CDCl_3$), δ: 36.7 (SCH_2); 119.0 ($=CH_2$); 127.9, 129.0, 130.1, and 130.6 (all Ph); 132.3 (=CH—); 148.4 (S—C=N); 156.6 (Ph—C=N).

Isothermal crystallization of the $FeBd_2((AllylS)_2Gm)(BF)_2$ clathrochelate was carried out at room temperature using the chloroform—heptane (solvate **1**), acetonitrile—isooctane (solvate **2**), and dichloromethane—*n*-hexane (solvate **3**) systems. As a result, we obtained crystals of the compound with polar chloroform solvate molecules characterized by a low donor number (**1**), the crystals with polar and donor acetonitrile solvate molecules (**2**), and the solvate with nonpolar *n*-hexane (**3**).

Low-temperature X-ray diffraction experiments were carried out on automated Bruker SMART and Syntex $P2_1$ diffractometers. Reflection intensities were integrated using the SAINT Plus software and corrected for absorption using the SADABS program.[3,4] The structures were solved by direct methods and refined by full-matrix least-squares against F^2 with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were revealed from the difference Fourier synthesis and refined using the riding model with $U_{iso}(H) = nU_{eq}(C)$, where $n = 1.5$ for the methyl groups and 1.2 for all other groups, and $U_{eq}(C)$ are the equivalent isotropic factors of the corresponding pivot carbon atoms. All calculations were carried out using the SHELXTL-97 program package.[5] The atomic coordinates were deposited with the Cambridge Structural Database. The crystallographic parameters and details of structure refinement of these solvates are given in Table 1.

Results and Discussion

The crystal structures of solvates **1—3** contain the isolated clathrochelate molecules and disordered solvate molecules located in the cavities between the clathrochelate molecules. It should be noted that crystals **1** and **2** with polar solvate molecules ($CHCl_3$ and MeCN, respectively) are isostructural, whereas a different molecu-

Table 1. Crystallographic parameters and details of structure refinement of solvates **1—3**

Parameter	$FeBd_2[(AllylS)_2Gm](BF)_2\cdot$ 0.5 $CHCl_3$ (**1**)	$FeBd_2[(AllylS)_2Gm](BF)_2\cdot$ 0.75 MeCN (**2**)	$FeBd_2[(AllylS)_2Gm](BF)_2\cdot$ 0.5 C_6H_{14} (**3**)
Molecular formula	$C_{36.5}H_{30.5}B_2Cl_1F_2FeN_6O_6S_2$	$C_{37.5}H_{32.25}B_2F_2FeN_6O_6S_2$	$C_{39}H_{37}B_2F_2FeN_6O_6S_2$
Molecular weight	881.93	853.04	865.34
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Temperature/K	120(2)	130(2)	110(2)
a/Å	12.933(3)	12.944(2)	13.892(4)
b/Å	15.505(3)	15.550(3)	17.541(4)
c/Å	19.210(4)	19.133(3)	16.615(4)
β/deg	102.578(5)	102.549(4)	95.34(2)
V/Å^3	3760(1)	3759(1)	4031(2)
Z	4	4	4
d_{calc}/g cm^{-3}	1.558	1.507	1.426
Color, crystal habit	Red needle	Red plate	Red needle
Dimensions/mm	0.30×0.35×0.50	0.35×0.30×0.15	0.45×0.35×0.30
Diffractometer	SMART Bruker	SMART Bruker	Syntex $P2_1$
Radiation		Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	6.85	5.80	5.41
Absorption correction	SADABS	SADABS	
T_{min}/T_{max}	0.472/0.862	0.564/0.862	
Scan mode	φ/ω	φ/ω	*q*/2*q*
$2\theta_{max}$/deg	56.56	58.00	52.74
Total number of reflections	27439	30506	8648
Number of independent reflections (R_{int})	9291 (0.1077)	9970 (0.0817)	8109 (0.0144)
R_1 (based on *F* for reflections with $I > 2\sigma(I)$)	0.0558 (on 3757)	0.0603 (on 5168)	0.0535 (on 6107)
wR_2 (based on F^2 for all reflections)	0.1548	0.1294	0.0895
Number of refinement parameters	523	516	568
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, $P = 1/3(F_o^2 + 2F_c^2)$		
a	0.0554	0.1000	0.0869
b			3.1221
GOOF	0.777	0.859	0.973
F(000)	1804	1754	1788
e_{max}/e_{min} (eÅ^{-3})	0.688/−0.343	0.794/−0.374	1.050/−0.485

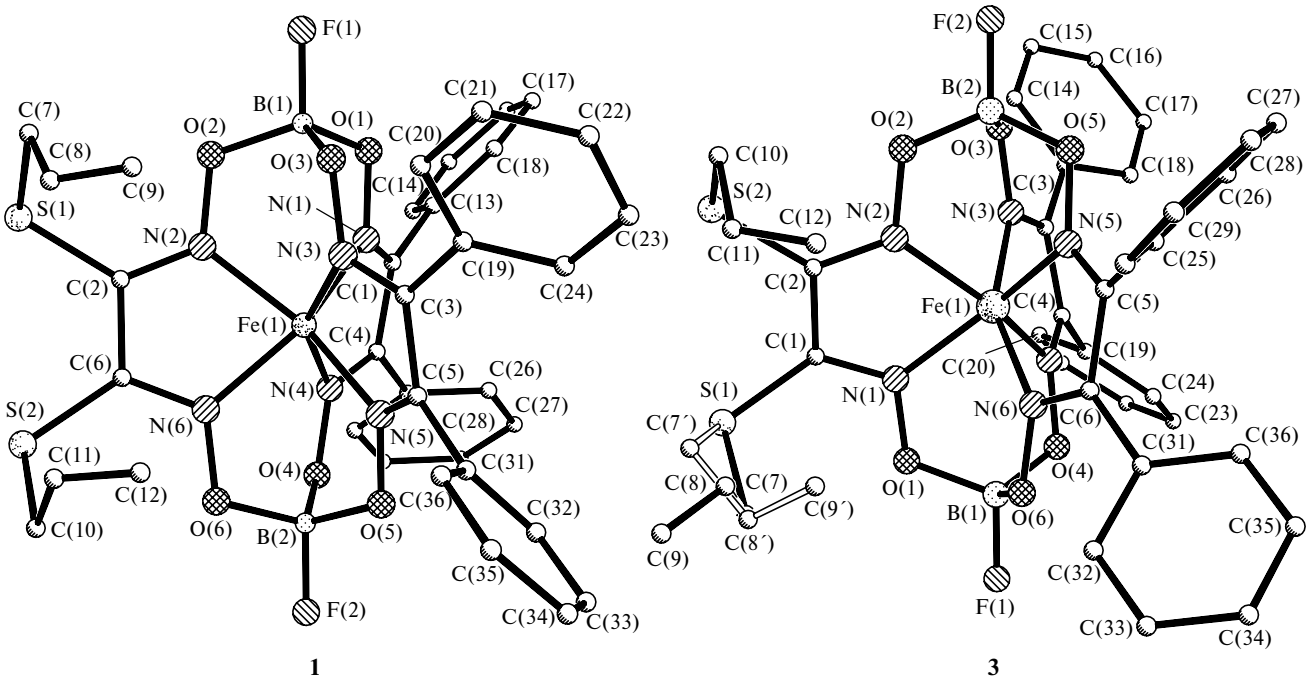


Fig. 2. Clathrochelate molecular structures in solvates **1** and **3**.

lar packing was revealed in crystals **3** with nonpolar *n*-hexane solvate molecules. All these crystals belong to the monoclinic system and have the same space group ($P2_1/n$, $Z = 4$).

The clathrochelate ligand (Fig. 2) is formed by three planar dioximate fragments O—N=C—C=N—O (two fragments contain two Ph groups each, whereas the third fragment contains two allylsulfide substituents) cross-linked with boron atoms. In solvate **3**, the carbon atoms of one of the two allyl fragments are disordered over two positions with occupancies of 0.5 (see Fig. 2). The dihedral angles between the planes of these three fragments are close to 120°. Therefore, the clathrochelate framework of the molecule has a threefold symmetry pseudoaxis. Selected geometric parameters of the clathrochelate molecules in crystals **1—3** are given in Tables 2 and 3. These

Table 2. Selected bond lengths (Å) in clathrochelate molecules **1—3**

Bond	**1**	**2**	**3**
Fe—N	1.905—1.919 (σ 0.003 Å)	1.902—1.918 (σ 0.003 Å)	1.906—1.915 (σ 0.002 Å)
B—F	1.355(5), 1.364(5)	1.359(4), 1.366(4)	1.355(3), 1.361(4)
B—O	1.474—1.489 (σ 0.005 Å)	1.472—1.487 (σ 0.004—0.005 Å)	1.473—1.497 (σ 0.003—0.004 Å)
C=N	1.303—1.324 (σ 0.004 Å)	1.312—1.317 (σ 0.004 Å)	1.304—1.312 (σ 0.003—0.004 Å)
N—O	1.364—1.374 (σ 0.003—0.004 Å)	1.361—1.375 (σ 0.003 Å)	1.369—1.377 (σ 0.003 Å)
C—C(ring)	1.461, 1.447, 1.450 (σ 0.005 Å)	1.450, 1.458, 1.455 (σ 0.004—0.005 Å)	1.460, 1.466, 1.462 (σ 0.003—0.004 Å)
C(ring)—S	1.752(4), 1.751(4)	1.755(3), 1.741(4)	1.753(3), 1.744(3)
S—CH_2	1.818(5), 1.831(4)	1.819(5), 1.830(4)	1.891(8)*, 1.844(4)
CH_2—CH	1.467(6), 1.493(6)	1.449(7), 1.470(6)	1.52(1)*,1.481(6)
CH=CH_2	1.310(6), 1.293(5)	1.282(7), 1.285(6)	1.32(1)*, 1.296(7)
C(ring)—C(Ph)	1.485, 1.475, 1.470, 1.475 (σ 0.005 Å)	1.482, 1.468, 1.478, 1.472 (σ 0.004—0.005 Å)	1.483, 1.478, 1.477, 1.481 (σ 0.004 Å)
C(Ph)—C(Ph)	1.362—1.394	1.370—1.397	1.357—1.403

* Data for the disordered allylsulfide substituent.

Table 3. Main conformational characteristics (angles in deg, distances in Å) of the clathrochelate molecules in crystals **1—3**

Parameter	**1**	**2**	**3**
Dihedral angle between planar chelate rings[a]	I/III 119.1 I/II 112.4 II/III 114.0	I/III 118.9 I/II 112.4 II/III 111.8	I/III 122.7 I/II 118.9 II/III 110.5
Torsion angle F—B—O—N	173.3, 174.2, 170.6 171.0, 172.5, 172.8	171.4, 173.2, 172.2 171.6, 172.4, 173.0	170.6, 173.2, 170.9 172.2, 171.2, 172.9
Fe···B distance	2.968, 2.978	2.975, 2.982	2.976, 2.983
Dihedral angle between phenyl substituents	51.6, 55.3	52.4, 56.2	52.8, 59.7
Torsion angles			
C(ring)—S—CH_2—CH	127.4, 118.1	124.8, 116.1	122.5, 106.5
S—CH_2—CH=CH_2	53.0, 74.9	54.3, 74.3	75.2, 58.7 (77.9, 76.0)[b]

[a] The chelate rings of fragments I and II containing the Ph groups and the chelate ring of the fragment III containing the allylsulfide groups.
[b] Data for the disordered allylsulfide substituent.

molecules have the identical Fe—N, B—O, C=N, N—O, S—C, and S—CH_2 bond lengths (average values are 1.912, 1.482, 1.313, 1.370, 1,749, and 1.824 Å, respectively), which are close to standard values.[6] The conformational parameters of the clathrochelate molecules are also similar (see Table 3). In the structures of solvates **1—3**, the phenyl and allylsulfide substituents, which are rather labile (rotation of the Ph groups about the C(oxime)—C(Ph) bond and rotations about the S—CH_2 and CH_2—CH bonds in the allylsulfide fragments), have nearly identical orientations.

Therefore, the nature of the solvate molecules has no effect on the molecular structure of the $FeBd_2((AllylS)_2Gm)(BF)_2$ clathrochelate. The crystal structures of **1** and **2** are characterized by the same packing of the clathrochelate molecules, which differs substantially from that in crystal **3** (Fig. 3).

In all structures, the solvate molecules are located in the centrosymmetric cavities and are disordered about the corresponding center of symmetry. The structures of **1** and **2** differ substantially from the structure of **3** in that the clathrochelate molecules are shifted along the *c* axis. Besides, the molecules differ in the orientation of the threefold pseudoaxis with respect to the crystallographic *a*, *b*, and *c* axes. In crystals **1** and **2**, this pseudoaxis is perpendicular to the *a* axis and is inclined to the *b* and *c* axes by ~45°. By contrast, this axis in the crystal of **3** is perpendicular to the *a* and *b* axes and parallel to the *c* axis.

In crystals **1—3**, the centrosymmetrical cavities, which are occupied by the solvate molecules, are formed by the atoms of the Ph and allylsulfide substituents and have an ellipsoid shape. Figures 4 and 5 schematically show the structures of these cavities (solvate molecules are denoted by circles in the centers); the contacts determining the sizes of the cavities are also shown. The shortest intermolecular contacts between the molecules of the clathrochelate "host" and the solvate "guest" are given in Table 4. In crystals **1** and **2**, there are Cl...C and N...C contacts smaller than the sums of the van der Waals radii of the corresponding atoms (3.60 and 3.20 Å).[7] These contacts can be considered as weak specific dipole-dipole interactions. In crystal **3**, such interactions are absent and all intermolecular contacts are larger than the sum of the van der Waals radii C...C (3.42 Å).[7]

Table 4. Selected characteristics of the molecular packing of compounds **1—3**

Compound	Orientation*/deg			V/Å^3	Cavity size /Å
	a	*b*	*c*		
1	88.2	127.6	141.2	41.40	10.07×9.16×7.09
2	87.8	127.5	141.4	39.37	10.12×8.70×7.20
3	80.9	94.1	170.4	103.76	16.87×9.60×7.73

* The orientation of the threefold pseudoaxis (B1···B2) relative to the crystallographic axes *a*, *b*, *c*.

In molecule **1**, the centrosymmetrical cavity is formed by atoms of four phenyl groups and two allyl groups of two clathrochelate molecules (see Fig. 4). The oxygen atoms (O(1) and O(1a)) of the clathrochelate framework also form the shortest contacts with the chlorine atom. The C(19)...C(19b) atoms of the Ph rings form the longest diagonal (10.07 Å). Two other diagonals are formed by the C(9a)—C(9c) atoms (9.16 Å) of one of the allyl fragments and the C(18)...C(18b) atoms (7.09 Å) of the Ph rings. Taking into account the van der Waals radius of the carbon atoms, the approximate volume of this cavity is 41.3 Å^3. The $CHCl_3$ molecules, which are

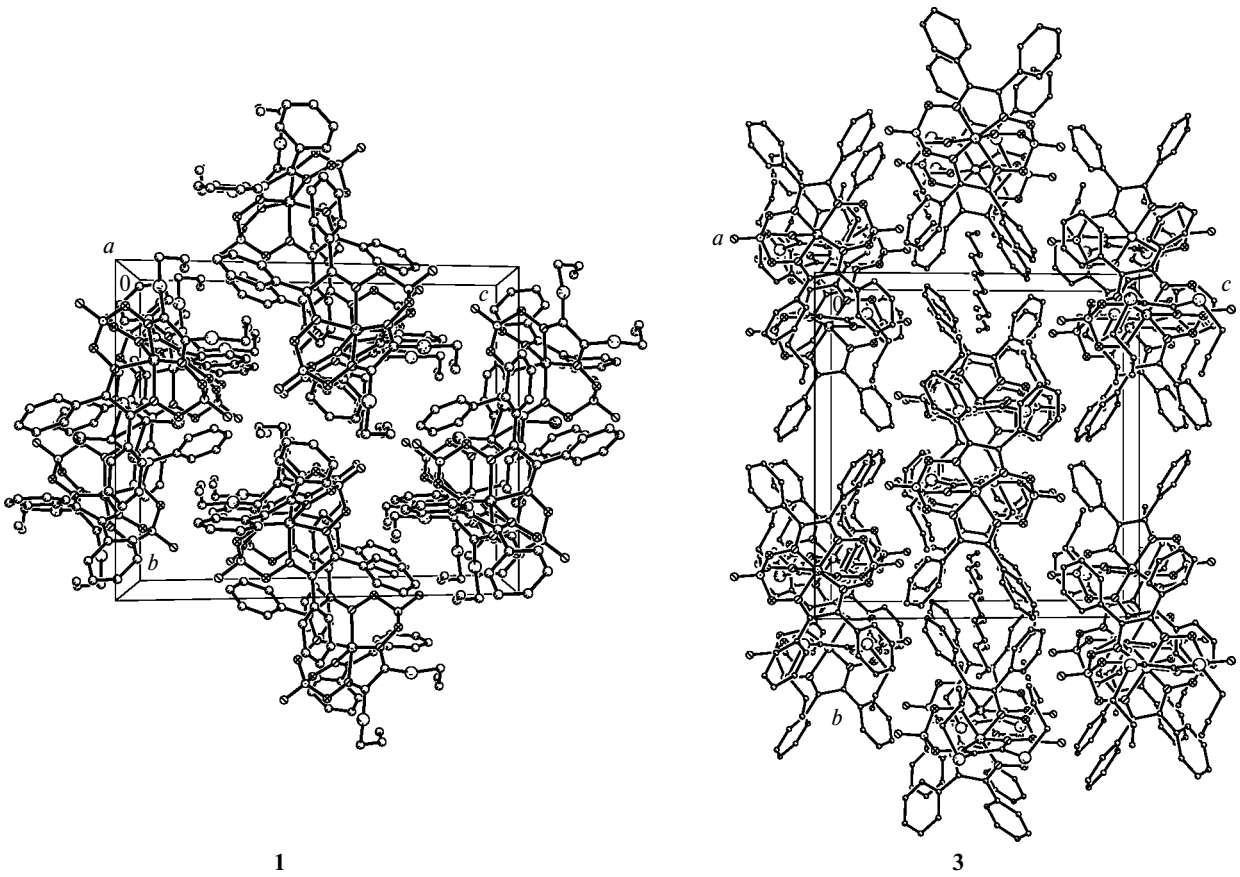


Fig. 3. Crystal packing of solvates **1** and **3** (structure projected onto the 0*yz* plane, the *y* axis is vertical).

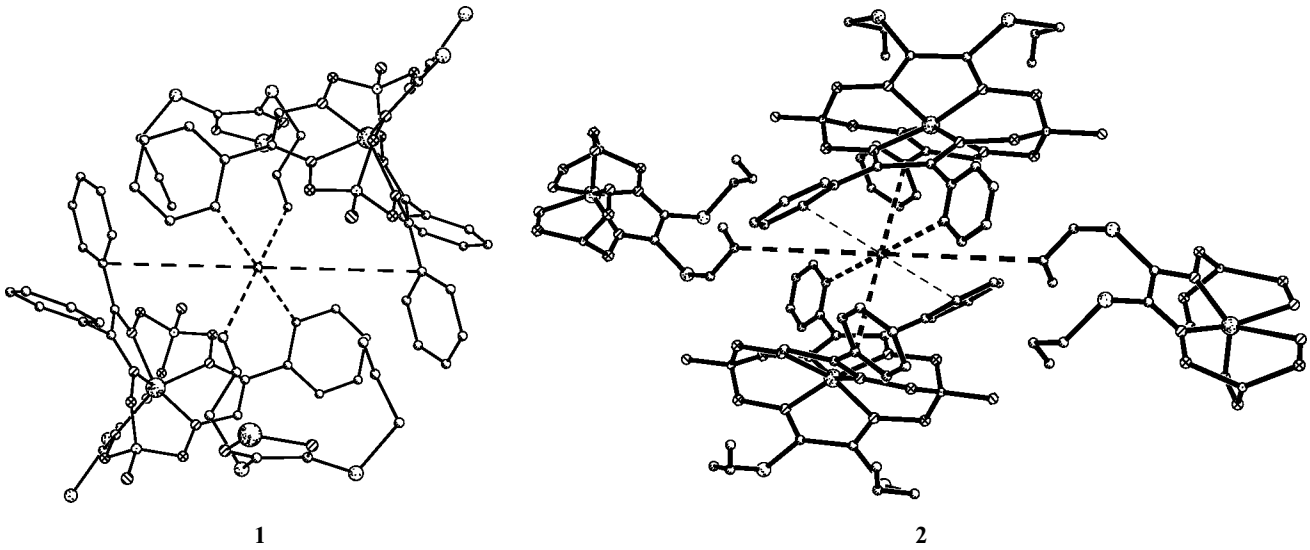
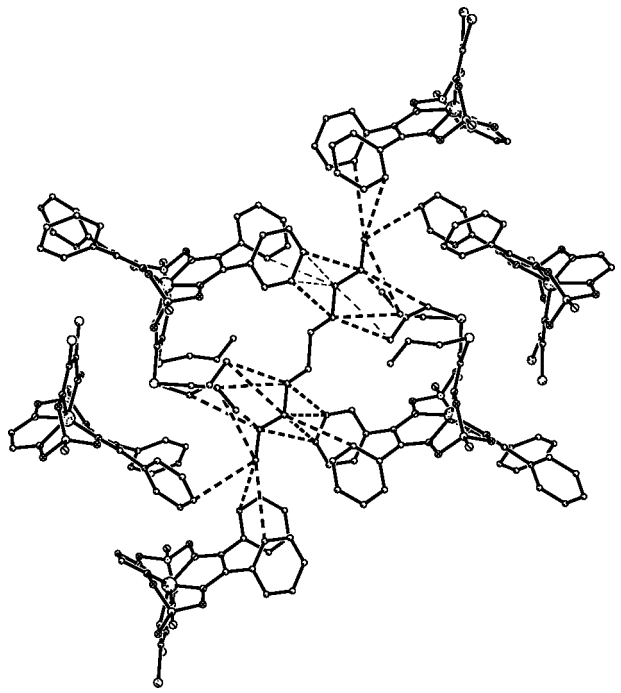


Fig. 4. Schematic representation of the location of the solvate molecules in the cavities of the crystal structures of **1** and **2**.

disordered over two positions, form the dimeric Cl—CH-(μ_2-Cl$_2$)—CH—Cl fragment, in which the distance between two most remote chlorine atoms is 4.94 Å, and the distance between the μ_2-Cl atoms is 2.90 Å. This fragment can be approximated by an ellipsoid with the long and short axes of 4.0 and 2.9 Å, respectively. Taking into account the van der Waals radius of the chlorine atom (1.9 Å), the volume of this ellipsoid is ~29 Å^3.



3

Fig. 5. Schematic representation of the location of the *n*-hexane solvate molecules in the cavities of the crystal structure of **3**.

Therefore, the cavity size in the crystal structure is comparable to the volume of the solvate molecule, whereas the volume of the $CHCl_3$ molecule is substantially smaller. Presumably, that is the reason why the $CHCl_3$ solvate molecules are disordered in the crystal.

In the crystal sructure of **2**, the cavity is formed by the atoms of six Ph rings and two allyl groups of two clathrochelate molecules. Unlike the structure of **1**, the long axis of the ellipsoid (10.12 Å) is formed by the carbon atoms of the allylsulfide substituents (C(13) and C(13a)), and two other axes (7.02 and 8.71 Å) are formed by the atoms of the Ph rings. The volume of the cavity is 37.6 $Å^3$, whereas the volume of the CH_3CN molecule approximates 22 $Å^3$. As a result, the CH_3CN molecule is disordered over four positions.

In the structure of **3**, the cavity is more elongated (see Fig. 5). This cavity is formed by six "host" molecules, *viz.*, the carbon atoms of twelve Ph and four allylsulfide substituents (two of them are disordered). No shortened contacts between the atoms of the solvent and the clathrochelate framework were revealed. The hexane molecule is also disordered about the center of symmetry, which coincides with the midpoint of the C(1s)—C(1sa) bond, *i.e.*, the solvate fragment is a ten-atom planar aliphatic chain, which is extended along the long axis of the cavity and oriented so that its plane is parallel to the plane of the C(31)—C(36) and C(31a)—C(36a) rings. Taking into account the van der Waals radius of the carbon atoms, the volume of the cavity is 75.8 $Å^3$. The long axis of the ellipsoid (C(36c)...C(36d), 17.77 Å) is 14.17 Å, and two other axes are 4.9 and 3.7 Å. The length of the solvate fragment is 11.26 Å (C(5s)...C(5sa) distance), whereas the length of the hexane chain is ~7.5 Å.

Table 5. Shortest intermolecular contacts (*d*) in the crystal structures of compounds **1**—**3**

Bond	*d*/Å	Bond	*d*/Å
Structure **1**		Structure **3**	
C(11s)...O(1b)	3.311	C(5s)...C(16b)	3.789
C(11s)...C(8a)	3.418	C(5s)...C(26c)	3.803
C(11s)...C(9a)	3.500	C(5s)...C(36c)	3.734
C(11s)...C(19b)	3.386	C(4s)...C(7´)	3.802
C(11s)...C(24b)	3.293	C(4s)...C(8´)	3.838
C(11s)...H(18c)	2.76	C(4s)...C(34c)	3.574
C(11s)...H(8aa)	2.76	C(3s)...C(9´)	3.762
C(11s)...H(9ba)	2.96	C(3s)...C(30c)	3.744
Structure **2**		C(3s)...C(33c)	3.565
N(1sa)...C(8c)	3.322	C(3s)...C(34c)	3.627
N(1sa)...C(9c)	3.463	C(2s)...C(8)	3.378
N(1sa)...C(13a)	3.360	C(2s)...C(9´)	3.251
N(1sa)...C(18a)	3.151	C(2s)...C(33a)	3.624

A comparative analysis of the volume of the solvate molecule and the elliptical cavity occupied by the solvate molecules (taking into account the van der Waals radius of the carbon atom) shows (see Table 4) that these cavities in all structures studied are accessible for the solvate molecules (particularly, in the structure of **2**). As a result, the solvate molecules are disordered about the center of symmetry.

The character of packing of the bulky clathrochelate molecules and smaller solvate molecules in crystals **1**—**3** is determined, apparently, not only by the volume and shape of the solvate molecule but also by its polarity. The chlorine and nitrogen atoms are involved in specific dipole-dipole interactions between atoms of the "host" and "guest" molecules. This is, in particular, reflected in the densities of the crystal structures. Thus, d_{calc} for crystals **1** and **2** are substantially higher than that for crystal **3**; the larger value of d_{calc} for solvate **1** compared to d_{calc} for solvate **2** also correlates with the larger number of shortened intermolecular contacts in crystal **1** (see Table 4).

Therefore, weak intermolecular interactions between the clathrochelate "host" molecules provide the possibility of using solvate "guest" molecules for the desired changes in the supramolecular organization of the crystals of these complexes. The hiearhical architecture of the crystals is determined by the electronic properties of the solvate molecule rather than by its geometric parameters. This conclusion can be extended to the polymorphism of molecules containing polar groups: even weak intermolecular contacts involving these groups might play a key role in the crystal packing of these molecules.

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