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THE CRYSTAL STRUCTURES OF [6-NITRO-12,14-DIMETHYL-3,9-BIS(PROPYLSULPHONYL)-1,2,4,8,10,11-HEXAAZACYCLOTETRA-DECA-2,4,6,9,12,14-HEXAENATO(2-)-N^1, N^4, N^8, N^{11}]NICKEL(II) AND [12,14-DIMETHYL-3,9-BIS(ETHYLSULPHONYL)-1,2,4,8,10,11-HEXAAZACYCLOTETRA-DECA-2,4,6,9,12,14-HEXAENATO(2-)-N^1, N^4, N^8, N^{11}]NICKEL(II)

ALEXANDR DVORKIN, POLINA BOUROSH and YURI SIMONOV

Institute of Applied Physics of the Academy of Sciences of Moldova,
277028 Kishinev, Moldova

and

VLADIMIR ARION,†‡ JULIETA GRADINARU and NICOLAE GERBELEU

Institute of Chemistry of the Academy of Sciences of Moldova, 277028 Kishinev, Moldova

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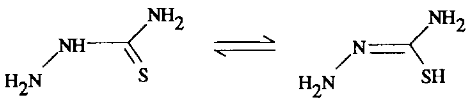
Abstract—Hexaazamacrocyclic complexes [6-nitro-12,14-dimethyl-3,9-bis(sulphonyl)-1,2,4,8,10,11-hexaazacyclotetra-deca-2,4,6,9,12,14-hexaenato(2-)-N^1, N^4, N^8, N^{11}]nickel(II) and [12,14-dimethyl-3,9-bis(ethylsulphonyl)-1,2,4,8,10,11-hexaazacyclotetra-deca-2,4,6,9,12,14-hexaenato(2-)-N^1, N^4, N^8, N^{11}]nickel(II) have been synthesized by a template procedure starting from an open-chain precursor. The crystal structure of both macrocyclic products showed a square planar coordination geometry with *cis*-positioned-SR groups relative to the nickel atom.

Among the hydrazine derivatives S-alkylated isothiosemicarbazides, containing non-equivalent end NH_2 groups, are of special interest for the design and synthesis of macrocyclic compounds.[1]

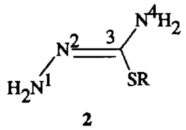
It is well known that thiosemicarbazide in its thione (**1a**) or thiol (**1b**) forms gives a number of complexes with transition metals.[2–7] It is noteworthy that in all cases the sulphur atom is involved in the binding to the metal ion.



1a **1b**

When passing to thioether (**2**)*, which is easily prepared by alkylation of the thiosemicarbazide in its isoform (**1b**) with corresponding alkyl iodide in ethanol, the mode of ligand coordination is radically changed.

In binding to the metal ion the nitrogen atoms N^1 and N^4 are involved, while the sulphur atom remains uncoordinated.[8] This peculiarity, along with the ability of the end NH_2 groups to react with



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† Author to whom correspondence should be addressed.

‡ Present address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany.

ketones and/or aldehydes, permitted us to use these compounds as building blocks in template assemblation of macrocyclic species.

Taking into account a different reactivity of NH_2 end groups and using various β-dicarbonyl compounds, two kinds of nickel(II) mono- and bis-hexaazamacrocyclic species (**3**–**5** and **6**, **7**) shown in Scheme 1, which are different in the arrangement of SR groups relative to the nickel atom, were obtained and characterized by X-ray diffraction.[9–13] In 1991 we reported the template synthesis and physico-chemical characterization of nickel(II) macrocyclic complexes with *cis*-arrangement of SR-groups according to Scheme 2.[14] The formation of closed species **8** and **9** was proved by elemental analysis, IR, ^1H NMR and EI mass spectra.

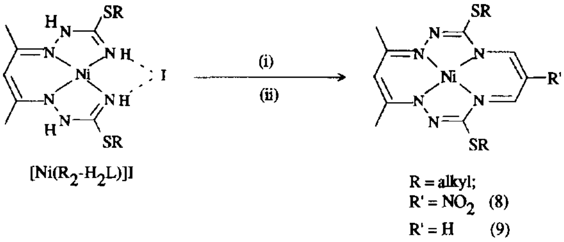
We now report the X-ray diffraction data of the n-C_3H_7 derivative of **8** and the C_2H_5 derivative of **9**.

EXPERIMENTAL

Starting complexes $[Ni(R_2\text{-}H_2L)]I$, where $R = n\text{-}C_3H_7$, C_2H_5, the sodium salt of malonic aldehyde monohydrate and 1,1,3,3-tetraethoxypropane were prepared according to reported procedures.[14,15]

Synthesis of 8

A mixture of $[Ni(R_2\text{-}H_2L)]I$, where $R = n\text{-}C_3H_7$ (0.51 g, 1.0 mmol) and the sodium salt of malonic aldehyde monohydrate (0.31 g, 2.0 mmol) in methanol (50 cm^3) was heated under reflux for 4 h. After cooling to room temperature the product was isolated by filtration, then washed with methanol and ether. Yield: 0.08 g (18%).



Scheme 2. (i) Sodium salt of malonic aldehyde monohydrate, MeOH, 60°C, 4–5 h; (ii) 1,1,3,3-tetraethoxypropane, dmf/H_2O (3 : 1), 100°C, 10–12 h.

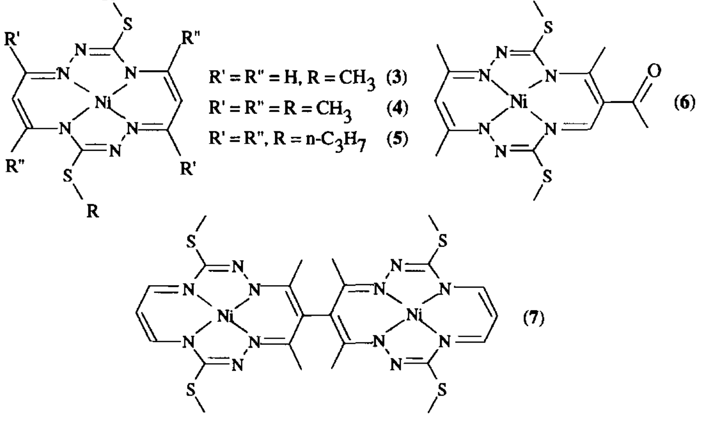
Synthesis of 9

A mixture of $[Ni(R_2\text{-}H_2L)]I$, where $R = C_2H_5$ (2.42 g, 5.0 mmol) and tetraethoxypropane (2.20 g, 10.0 mmol) in dimethylformamide (dmf)–water 3 : 1 (100 cm^3) was heated to 100°C for 11 h. The solvent was evaporated to dryness under reduced pressure. The residue was then dissolved in chloroform and the product precipitated by addition of hexane. The crude product was purified by column chromatography on silica, using a mixture of chloroform–hexane (1 : 5) as eluent. Yield: 0.26 g (13%).

Single crystals suitable for the X-ray diffraction study were obtained by slow evaporation of chloroform–hexane (1 : 1) solutions of **8** and **9** at room temperature.

Crystal structure determination

Crystal data, data collection and parameters of **8** and **9** are given in Table 1. Data collection for both compounds was performed on a RED-4 diffractometer, equipped with a graphite monochromator and Mo K_α radiation by the ω-scanning



Scheme 1.

Table 1. Crystal data, data collection and parameters of **8** and **9**

	8	**9**
Formula	$C_{16}H_{23}NiN_7O_2S_2$	$C_{14}H_{20}NiN_6S_2$
M_r	468.2	395.2
Crystal system	monoclinic	triclinic
Space group	C1 2/c1 (N15)	$P\bar{1}$ (N2)
a (Å)	22.346(4)	18.327(3)
b (Å)	12.029(2)	10.799(3)
c (Å)	7.457(4)	4.507(2)
α (°)	90.00	85.95(3)
β (°)	76.74(2)	81.06(2)
γ (°)	90.00	96.84(1)
V (Å^3)	1951(2)	871.3(9)
Z	4	2
T (°C)	20	20
D_{calc} (g cm^{-3})	1.468	1.506
μ (cm^{-1})	12.21	13.49
R, R_w	0.0567, 0.0588	0.0394, 0.0423
$(\Delta\rho)_{max}$ (eÅ^{-3})	0.73	0.52
$(\Delta/\sigma)_{max}$	0.5	0.3

Table 2. Interatomic distances and angles of **8** and **9**

8			
Interatomic distances (Å)			
Ni—N1	1.828(6)	C8—C9	1.28(1)
Ni—N3	1.841(6)	N3—C2	1.32(1)
N1—N2	1.419(9)	C2—C3	1.411(8)
N2—C1	1.30(1)	C3—N4	1.42(1)
C1—N3	1.401(9)	N4—O	1.246(8)
C1—S	1.754(8)	N1—C4	1.31(1)
S—C7	1.83(1)	C4—C5	1.405(9)
C7—C8	1.49(1)	C4—C6	1.500(10)
Bond angles (°)			
N1—Ni—N3	84.5(3)	Ni—N3—C2	127.3(5)
Ni—N1—N2	115.1(5)	N3—C2—C3	121.5(6)
N1—N2—C1	110.6(1)	C2—C3—N4	116.8(6)
N2—C1—S	120.6(6)	C3—N4—O	118.8(6)
C1—S—C7	113.0(7)	Ni—N1—C4	128.3(5)
S—C7—C8	113.0(7)	N1—C4—C5	120.8(7)
C7—C8—C9	125.8(10)	N1—C4—C6	121.0(7)
Ni—N3—C1	111.4(4)	C5—C4—C6	118.1(7)
9			
Interatomic distances (Å)			
Ni—N1	1.825(3)	N4—C4	1.333(6)
Ni—N3	1.839(4)	N4—C5	1.408(5)
Ni—N4	1.845(3)	N5—C5	1.313(6)
Ni—N6	1.834(4)	N5—N6	1.407(5)
S1—C1	1.759(5)	N6—C6	1.349(6)
S1—C11	1.800(6)	C2—C3	1.393(7)
S2—C5	1.749(4)	C3—C4	1.382(7)
S2—C9	1.817(5)	C6—C7	1.391(6)
N1—N2	1.403(5)	C6—C66	1.516(7)
N1—C8	1.353(6)	C7—C8	1.408(6)
N2—C1	1.305(6)	C8—C88	1.489(6)
N3—C1	1.402(6)	C9—C10	1.515(7)
N3—C2	1.340(6)	C11—C12	1.529(8)
Bond angles (°)			
N1—Ni—N3	83.8(2)	N5—N6—C6	116.6(3)
N1—Ni—N6	96.0(2)	S1—C1—N2	121.0(3)
N3—Ni—N4	95.8(2)	S1—C1—N3	120.4(3)
N4—Ni—N6	84.2(2)	N2—C1—N3	118.5(4)
C1—S1—C11	101.2(2)	N3—C2—C3	123.5(4)
C5—S2—C9	100.8(2)	C2—C3—C4	124.5(4)
Ni—N1—N2	116.5(3)	N4—C4—C3	123.8(4)
Ni—N1—C8	127.5(3)	S2—C5—N4	120.6(3)
N2—N1—C8	115.9(3)	S2—C5—N5	120.7(3)
N1—N2—C1	109.6(4)	N4—C5—N5	118.6(4)
Ni—N3—C1	111.4(3)	N6—C6—C7	121.4(4)
Ni—N3—C2	126.0(3)	N6—C6—C66	118.4(4)
C1—N3—C2	122.5(4)	C7—C6—C66	120.0(4)
Ni—N4—C4	126.1(3)	C6—C7—C8	126.9(4)
Ni—N4—C5	111.0(3)	N1—C8—C7	120.7(4)
C4—N4—C5	122.6(4)	N1—C8—C88	118.9(4)
C5—N5—N6	109.9(3)	C7—C8—C88	120.2(4)
Ni—N6—N5	116.1(3)	S2—C9—C10	108.2(3)
Ni—N6—C6	127.2(3)	S1—C11—C12	109.9(4)

method with a constant speed 8° min^{-1} within the range of angles $2 \leqslant \theta \leqslant 25°$. The unit cell parameters were refined on the basis of 12 reflections of the $h00$, $0k0$ and $00l$ type within the range $6 \leqslant \theta \leqslant 9°$ in the case of **8** and on the basis of 16 reflections within the range $5 \leqslant \theta \leqslant 10°$ in the case of **9**. The crystal stability and measuring track were checked hourly using a set of standard reflections. The intensity change did not exceed 2 and 1% for **8** and **9**, respectively. In the case of **8** and **9**, 823 and 1929 reflections, respectively, with $I \geqslant 3\sigma(I)$ were measured. The structures were solved by the Patterson method using an XTLSM program.[16] The refinement was performed by standard least-squares techniques in anisotropic approximation for non-hydrogen atoms and isotropic for hydrogen atoms using a weighting scheme $\omega = 1/[\sigma^2(F)+0.0050F^2]$. The H-atoms were located from a differential Fourier synthesis.

Thermal parameters, atom coordinates, and a listing of observed and calculated structure factors have been deposited with the Editor, from whom copies are available on request.

RESULTS AND DISCUSSION

The molecular structures of **8** (R = n-C_3H_7) and **9** (R = C_2H_5) are presented in Figs 1 and 2, respectively. Interatomic distances and angles are sum-

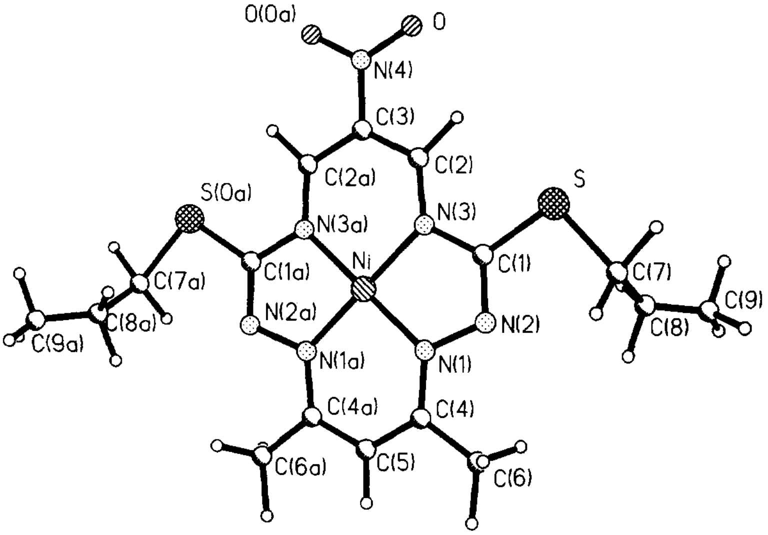


Fig. 1. Molecular structure of **8**, showing the atom-numbering scheme.

marized in Tables 2 and 3. In both compounds square planar coordination of the nickel ion by 14-membered doubly charged hexaazamacrocycle is revealed. As in the case of **6**, for complexes **8** and **9** a *cis*-arrangement of S-alkylisothiosemicarbazide moieties relative to the nickel ion is characteristic, which is in accordance with the chemical prehistory of both complexes. Note a similar arrangement of S—CH_2- (first link of the alkyl chain) bonds in **8** and **9**. These bonds lie in the *cis*-position relative to the double N═C bond of the isothiosemicarbazide moiety in both structures. We have already men-

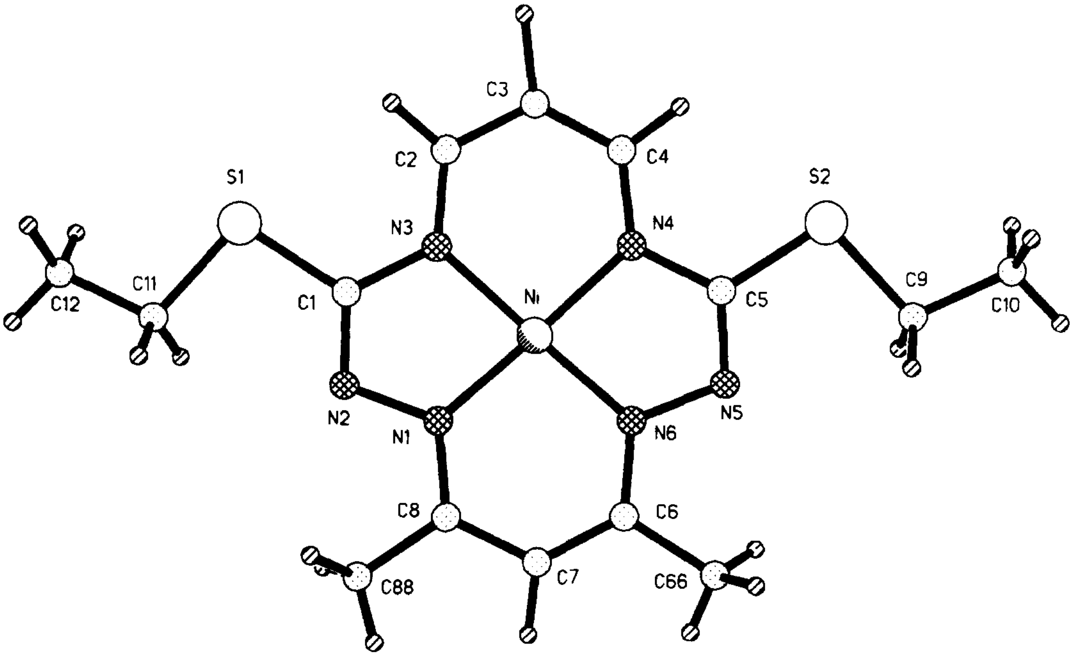


Fig. 2. Molecular structure of **9**, show the atom-numbering scheme.

Table 3. Interatomic distances for compounds 3–9

Compound	Ni—N_{hydr}	Ni—N_{thioam}	Bond lengths		C—N	C—S	Ref.
			N—N	N—C			
3	1.827[a]	1.829[a]	1.404[a]	1.296[a]	1.386[a]	1.749[a]	14
	1.818[b]	1.826[b]	1.408[b]	1.298[b]	1.395[b]	1.743[b]	
4	1.835	1.882	1.400	1.299	1.403	1.773	11
5	1.807	1.825	1.340	1.302	1.368	1.720	10
	1.815	1.819	1.326	1.294	1.393	1.700	
6	1.826	1.872	1.392	1.289	1.427	1.773	9
	1.827	1.839	1.406	1.286	1.416	1.750	
7	1.79	1.82	1.43	1.28	1.41	1.74	13
	1.79	1.82	1.43	1.27	1.42	1.74	
	1.78	1.82	1.45	1.28	1.43	1.73	
	1.79	1.80	1.44	1.26	1.44	1.74	
8	1.828	1.841	1.419	1.300	1.401	1.754	This work
9	1.825	1.839	1.403	1.305	1.402	1.759	This work
	1.834	1.845	1.407	1.313	1.408	1.749	

[a] Molecule A.
[b] Molecule B.

tioned[17] that the orientation of the substituents at the sulphur atom depends on packing conditions and the presence of S···S interactions.

It is noteworthy that complex **8** possesses a C_2 symmetry axis. This lies in the plane of the macrocycle and passes through Ni, C5, C3 and N4 atoms (Fig. 1). In this case only half of molecule **8** is crystallographically independent. The distance Ni—N_{hydr} is equal to 1.828(6) in **8**, and 1.825(3), 1.834(4) Å in **9**. This bond is shorter in both compounds when compared with Ni—$N_{thioamide}$ [1.841(6) for **8** and 1.839(4), 1.845(3) Å for **9**]. Selected geometrical parameters of some nickel(II) complexes of 14-membered hexaazamacrocycles based on S-alkylisothiosemicarbazides are summarized in Table 3. The tendency of shortening the distance Ni—N_{hydr} relative to Ni—$N_{thioamide}$ is observed in all cases.

Upon coordination of a tetradentate ligand with the nickel ion four metallorings are formed: two six-membered NiN_2C_3 and two five-membered NiN_3C. The five-membered metallocycles are practically planar in both structures. The bond distribution in the isothiosemicarbazide fragment of **8** and **9** is similar to that for **6** (see Table 2). In the case of **8** the N—N bond length is equal to 1.419, N═C 1.300, C—N 1.401 Å and in **9** the corresponding average parameters amount to 1.405, 1.309 and 1.405 Å. It should be noted that these bond distances are not significantly different from those found in other related structures (see Table 2). In the thioether fragments in **8** the C—S distances are 1.754(8) and 1.83(1) Å. The corresponding mean parameters in **9** are 1.754 and 1.809 Å. The angles at the S atom are close to 100–101°. The propyl substituent in **8** and the ethyl one in **9** come out from the plane of the five-membered metallocycles.

It should be noted that the six-membered chelate rings are essentially planar. The distribution of bonds in them (Table 2) indicates extensive delocalization over the chelate ring. The NO_2 group in **8** is coplanar with the corresponding metallocycle and is involved in a common delocalization of π-electrons. It should be noted that the plane of the NO_2 group forms an angle of 3.2° with the organic portion of the six-membered metallo ring of $[Fe\{(n\text{-}C_3H_7)_2Q\}(NO)]$,[18] where $H_3(n\text{-}C_3H_7)_2Q$ = nitromalondialdehyde bis(S-propylisothiosemicarbazone).

The query concerning packing square planar complexes has a special significance. In general Ni···Ni, Ni—L or π–π interactions between planar high conjugate molecules are possible. A large number of Ni, Pd or Pt complexes with π-conjugated ligands form one-dimensional stacked structures.[19–22] These metal complexes often stack with a separation distance around 3.4 Å, which is considered as the optimal distance for π–π interactions.[23] This distance is far too long for direct overlap of d_z^2 orbitals of the metal atoms.

The packing diagrams of **8** and **9** are shown in Figs 3 and 4. In both structures the packing of molecular complexes **8** and **9** takes place according

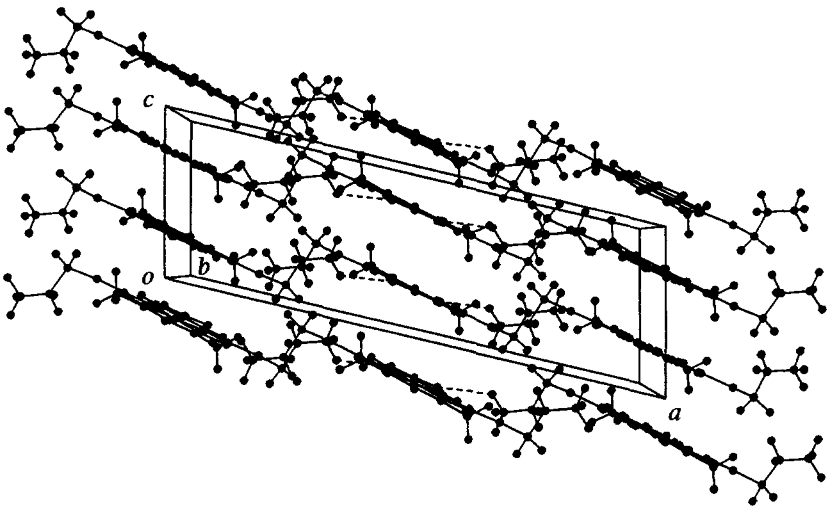


Fig. 3. Perspective view of the packing in the unit cell of **8**.

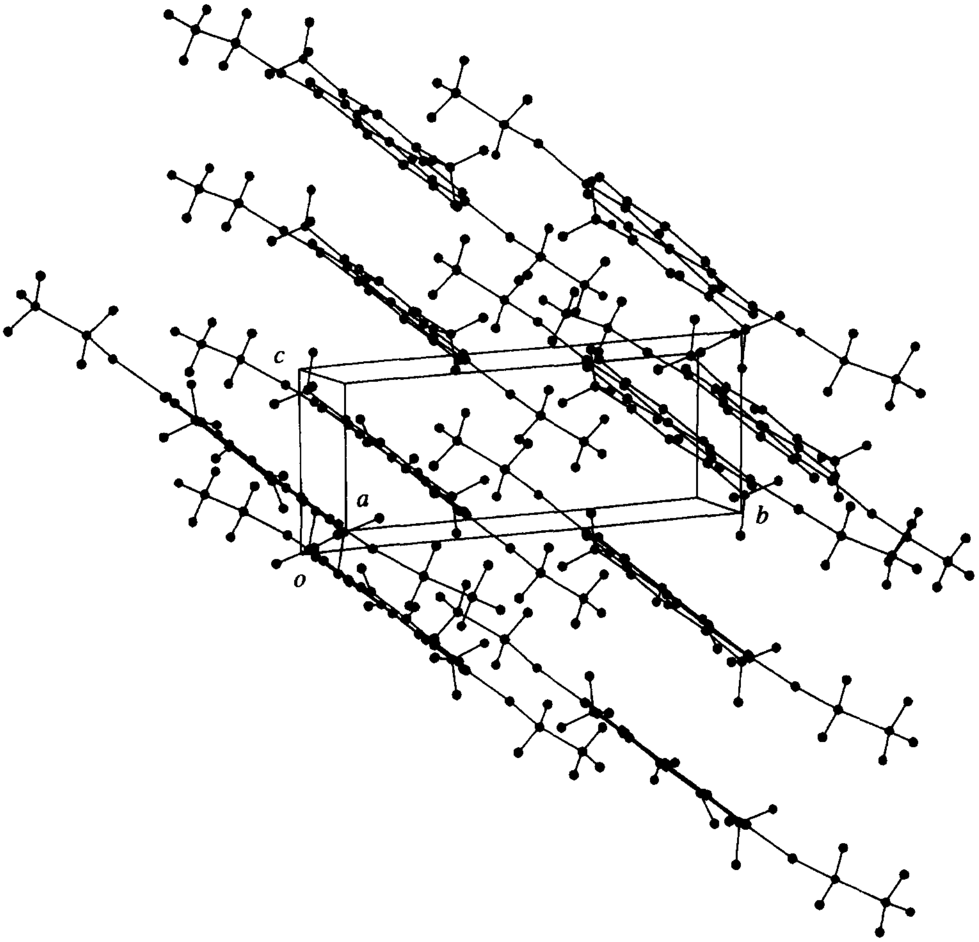


Fig. 4. Perspective view of the packing in the unit cell of **9**.

to the scheme shown in Fig. 5(a). The interplanar separations are equal to 3.37 and 3.49 Å in **8** and **9**, respectively. The shortest Ni—N distances between atoms belonging to different molecules in the stack are as follows: for **8**, Ni—N3 (symmetry code $-x$, $1-y$, $1-z$) is equal to 3.918 Å (two bonds according to C_2 symmetry) and for **9**, Ni—N1 ($x, y, z-1$) 3.713 and Ni—N4 ($x, y, z+1$) 3.695 Å. The shortest Ni···Ni contacts are 4.951 Å for **8** and 4.507 Å for **9**.

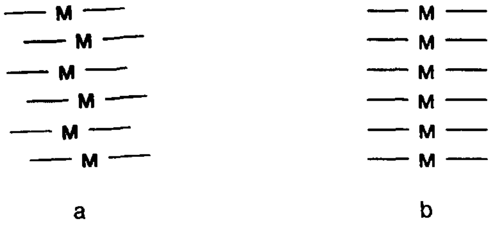


Fig. 5. Spatial arrangement of the one-dimensional stack in **8** and **9** (a) and **4** (b).

It should be noted that in the case of **4** another spatial arrangement of the one-dimensional stack shown in Fig. 5(b) has been revealed.[11]

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