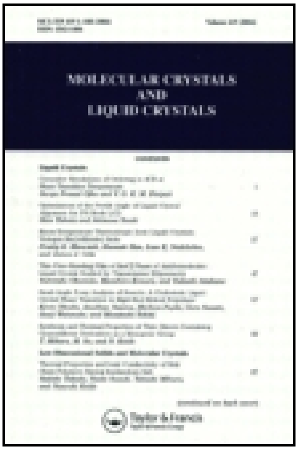

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Di(5-substituted-salicylidene)ethylene diaminato-Complexes (Part II). Mesomorphic Properties of Di(5-alkylsalicylidene)ethylene diaminato Nickel(II) and Copper(II) Complexes and an X-Ray Structure Determination of Di(5-hexyloxy salicylidene)ethylenediaminato Nickel(II)

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(*Received April 5, 1990*)

Di(5-alkylsalicylidene)ethylenediaminato nickel(II) and copper(II) complexes have been synthesized and investigated. They show similar behaviour to the corresponding alkyloxy-substituted complexes—wide mesophase ranges and calamitic smectic phases. The thermal stability of the nickel(II) complexes is higher than that of the copper(II) complexes.

The title compound crystallizes with one water molecule per formula unit (water—diethyl ether interface) and $Z = 4$ in space group $P2_1/c$. X-ray crystal structure analysis shows that the molecular skeleton with the exception of the ethylene bridge is essentially planar and adopts a maximum stretched form. The crystal packing is characterized by a herringbone arrangement of columns of centrosymmetrical pairs of molecules.

Keywords: nickel(II) complexes, copper(II) complexes, salicylaldiminato complexes, metallo-mesogens, smectic A complexes

INTRODUCTION

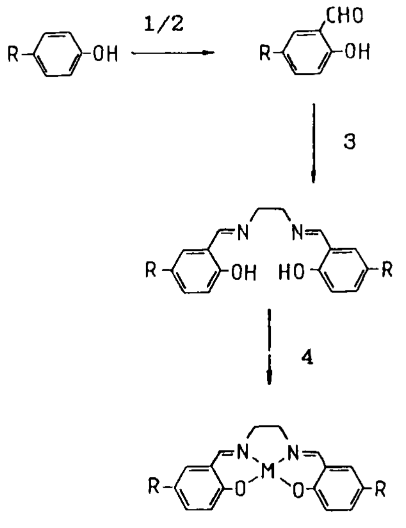
We recently reported[1] the synthesis and investigation of di(5-alkyloxysalicylidene)ethylenediaminato-complexes which exhibit a calamitic A phase. Metal complexes derived from salicylaldimines have been widely studied[2] and because of their ease of preparation it is not surprising that many groups use complexes of this type to obtain liquid crystalline compounds incorporating transition metals.[3–6]

Although the field of metal-containing mesogenic compounds is steadily growing, there is still a lack of substances suitable for detailed physico-chemical investigations. Chemical stability, low melting temperatures and high mesophase stability are some of the desired properties.

In continuation of our work on salicylaldiminato-complexes we have synthesized a number of di(5-alkylsalicylidene)ethylenediaminato-complexes. We have also determined the crystal structure of the alkyloxy-substituted nickel(II) complex (VIc) by X-ray diffraction.

EXPERIMENTAL

The synthesis of the ligands (III) and chelates (IV, V) was carried out according to the procedure used for the corresponding alkyloxy-substituted complexes.[1] (Figure 1). Elemental analytical data for the nickel and copper complexes are given in Tables I and II.
^{1}H NMR†
($CDCl_3$)TMS: for example, for compounds (II), (III), (IV) with R = C_6H_{13}



(II)

(III)

(IV) : R = C_nH_{2n+1}
M = Ni
(V) : R = C_nH_{2n+1}
M = Cu
(VI) : R = OC_nH_{2n+1}
M = Ni
(VII): R = OC_nH_{2n+1}
M = Cu

1 $SnCl_4/Bu_3N$
2 HCHO
3 $H_2NCH_2CH_2NH_2$
4 $NiCl_2 \cdot 6H_2O$

FIGURE 1 Reaction scheme.

---

† ^{1}H NMR performed on a Bruker Spectrometer WP 200, AC 80.

TABLE I

Elemental analyses of Di(5-alkylsalicylidene)ethylenediaminato nickel(II) complexes

	n	Molecular Formula	Elemental Analysis* (Calc.) (%) C	H	N
IVa	5	$C_{26}H_{34}N_2O_2Ni$	66.93(67.11)	7.18(7.36)	6.14(6.02)
IVb	6	$C_{28}H_{38}N_2O_2Ni$	68.02(68.16)	7.82(7.76)	5.56(5.67)
IVc	8	$C_{32}H_{46}N_2O_2Ni$	69.76(69.94)	8.11(8.43)	5.20(5.09)
IVd	9	$C_{34}H_{50}N_2O_2Ni$	70.43(70.70)	8.51(8.72)	4.71(4.85)
IVe	10	$C_{36}H_{54}N_2O_2Ni$	71.65(71.41)	9.19(8.99)	4.67(4.62)

*Elemental analysis performed on Elemental Analyser Mod. 1102 (Fa. Carlo Erba, Milano)

(II) : 2.6(t, 2H, CH_2) 6.8 – 7.2(m, 3H, C_6H_3) 9.8(s, 1H, CHO) 10.6(s, 1H, OH).
(III) : 2.5(t, 4H, $2CH_2$) 3.9(s, 4H, N—CH_2—CH_2—N) 6.8(s, 2H, 2CH=N) 6.9 – 7.3(m, 6H, $2C_6H_3$) 8.3(s, 2H, 2OH).
(IV) : 2.5(t, 4H, $2CH_2$) 3.4(s, 4H, N—CH_2—CH_2—N) 6.7(s, 2H, 2CH=N) 6.9 – 7.3(m, 6H, $2C_6H_3$).

RESULTS AND DISCUSSION

The nickel(II) and copper(II) chelates (IV), (V) were examined by optical microscopy and DSC with the results shown in Tables III and IV.

The alkyl-substituted complexes exhibit a calamitic smectic A phase. Decomposition occurs increasingly on heating towards the clearing temperature, but the nickel chelates are much more stable than the copper chelates. In the case of the copper compounds (V) and (VII), the decomposition starts rapidly at the transition

TABLE II

Elemental analyses of Di(5-alkylsalicylidene)ethylenediaminato copper(II) complexes

	n	Molecular Formula	Elemental Analysis (Calc.) (%) C	H	N
Va	5	$C_{26}H_{34}N_2O_2Cu$	66.24(66.42)	7.18(7.29)	6.01(5.96)
Vb	6	$C_{28}H_{38}N_2O_2Cu$	67.48(67.53)	7.61(7.69)	5.59(5.62)
Vc	8	$C_{32}H_{46}N_2O_2Cu$	69.11(69.33)	8.22(8.36)	4.91(5.05)
Vd	9	$C_{34}H_{50}N_2O_2Cu$	69.89(70.12)	8.49(8.65)	4.65(4.81)
Ve	10	$C_{36}H_{54}N_2O_2Cu$	70.69(70.83)	8.78(8.91)	4.51(4.59)

TABLE III

Transition temperatures (°C) for the nickel complexes (IV)

	n	K		S_1		S_2		S_A		I
IVa	5	.	134	_		.	284	.	298	.
IVb	6	.	84	.	118	.	245	.	310	.
IVc	8	.	86	_		.	230	.	308	.
IVd	9	.	66	.	91	.	204	.	287	.
IVe	10	.	71	.	112	.	208	.	286	.

K = crystal; S = smectic; I = isotropic

to the S_A phase. The reason for this could be that the salicylaldiminato copper(II) complexes are dependent on stabilization by strong axial interactions[7] and with the transition to the S_A phase, the molecules lose the possibility of such stabilization.

The smectic phases lying below the smectic A phase are difficult to characterize. From optical observations, an S_H or S_G phase is thought to be present, but a definite identification of the phase types must await the results of X-ray investigations.

The results obtained with the compounds (IV) and the publication by Shaffer and Sheth[4] lead us to conclude that we misinterpreted[1] the K/S_X-transitions as solid/solid transitions in the case of the alkyloxy copper(II)- and nickel(II)-compounds (VI), (VII). Realizing this and consequent upon further DSC investigations (e.g. Figures 2 and 3) we have arrived at the results shown in Tables V and VI.

The fact that the alkyloxy-substituted salicylaldiminato-complexes of Shaffer and Sheth[4] exhibit extremely low clearing temperatures could be a consequence of the synthetic route they used. Traces of monoalkylated complex may lead to a drastic decrease in the transition temperatures of the chelates.

Some copper(II) complexes exhibit unusual double melting behaviour.[8,9] The DSC-investigations of our copper complexes (V) and (VII) turned out to be very

TABLE IV

Transition temperatures (°C) for the copper complexes (V)

	n	K		S_1		S_2		S_A		I
Va	5	.		_		.	263	.	283	.
Vb	6	.		_		.	252	.	282	.
Vc	8	.		_		.	235	.	280	.
Vd	9	.		_		.	225	.	271	.
Ve	10	.		_		.	215	.	260	.

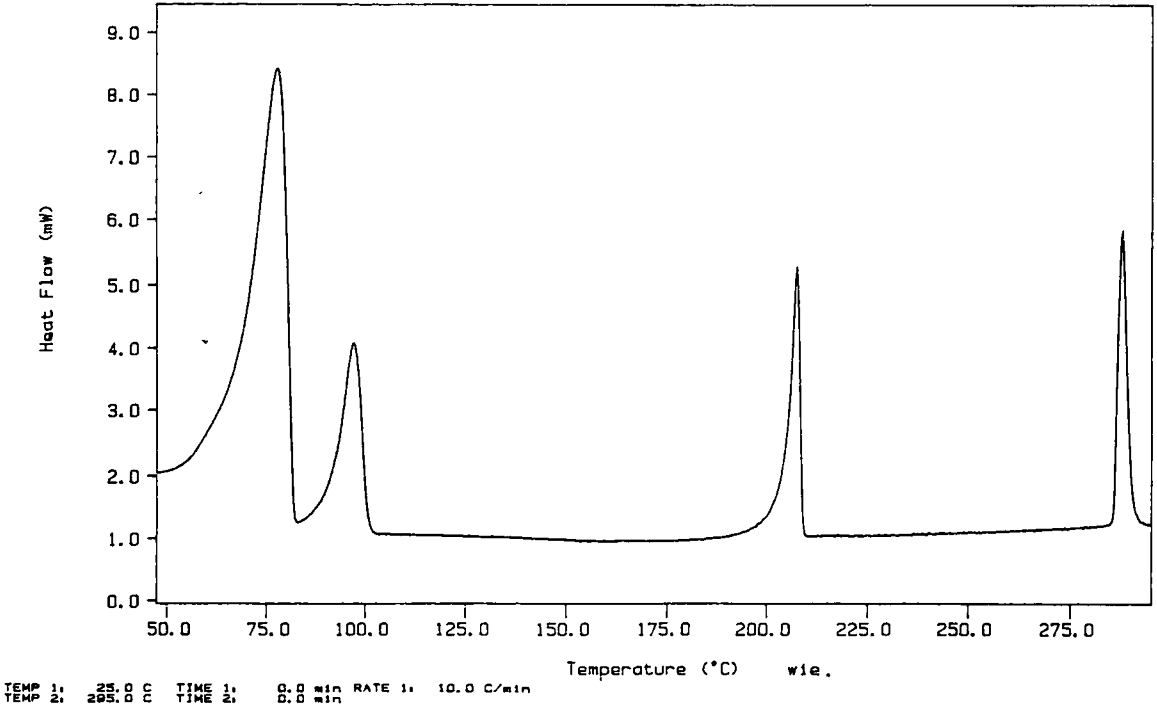


FIGURE 2 Differential scanning calorimetry thermogram for IVd
(10°C/min) 1. 66.5°C – 47.39 kJ/mol
2. 91.4°C – 11.127 kJ/mol
3. 204.4°C – 9.195 kJ/mol
4. 286.1°C – 7.188 kJ/mol.

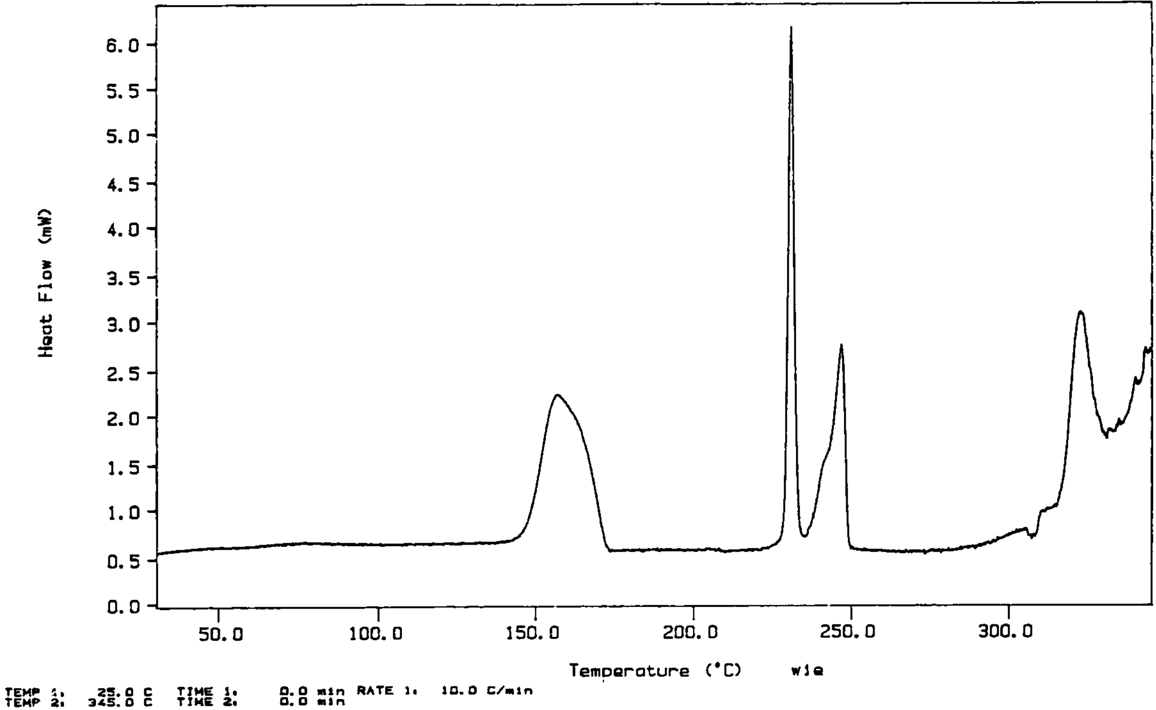


FIGURE 3 Differential scanning calorimetry thermogram for VIb
(10°C/min) 1. 148.5°C – 13.152 kJ/mol
2. 229.1°C – 5.975 kJ/mol
3. 241.9°C – 6.273 kJ/mol
4. 317.8°C – 6.887 kJ/mol.

TABLE V

Transition temperatures (°C) for the nickel complexes (VI)

	n	K		S_1		S_2		S_A		I
VIa	4	.	73	_		.	260	.	295	.
VIb	5	.	148	.	229	.	241	.	317	.
VIc	6	.		_		.	214	.	299	.
VId	7	.	76	.	109	.	192	.	296	.
VIe	8	.	61	_		.	186	.	300	.

complicated because of the onset of decomposition after entering the S_A phase. However, we did find that these compounds occur as metastable forms after purification (recrystallization from ethyl acetate). An exothermic conversion then occurs shortly before reaching the S_A phase and this indicates a crystallization process, i.e., the transition to the thermodynamically stable form. Cooling down the sample from the S_A phase reveals that there is another smectic phase (S_2) below the S_A phase; this can be supercooled to room temperature. Microscopical observations confirmed these results. It is evident that there are still many problems to solve, especially if this behaviour is to be related to the unusual double melting behaviour[8,9] mentioned earlier. Therefore we only give values for the phase transitions that we have established with certainty.

X-RAY STRUCTURE DETERMINATION

Experimental

Numerous attempts to grow crystals of (VIc) from organic solvents or solvent mixtures failed. Finally, optically clear red crystals suitable for X-ray investigations

TABLE VI

Transition temperatures (°C) for the copper complexes (VII)

	n	K		S_1		S_2		S_A		I
VIIa	4	.		_		.	265	.	272	.
VIIb	5	.		_		.	252	.	268	.
VIIc	6	.		_		.	267	.	282	.
VIId	7	.		_		.	257	.	270	.
VIIe	8	.		_		.	248	.	273	.

were grown at a water-diethyl ether interface. Under these conditions the compound crystallizes with one water molecule per complex molecule. A crystal with dimensions 0.30 × 0.27 × 0.10 mm was mounted on a Syntex $P2_1$ diffractometer giving the parameters of a monoclinic unit cell, space group $P2_1/c$, by a least squares treatment of the setting angles for 14 reflections with $20° \leq 2\theta \leq 30°$ for graphite monochromatized CuKα radiation (cf. Table VII). 3450 unique reflection intensities were measured for $2\theta \leq 115°$ and h, k, l between $0, 0, \bar{15}$ and 15, 13, 15 in $\theta/2\theta$ scan (bisecting mode) at room temperature. The intensities of the two check reflections $30\bar{2}$ and $1\bar{3}\bar{1}$ were measured after every 100 reflections and varied at the most by ±2.7 and ±3.6%, respectively. 2741 (= 79.5%) of the reflections had intensities $I \geq 1.96\ \sigma(I)$ and were considered observed. Lorentz and polarisation corrections were applied during data reduction, whereas absorption and extinction effects were neglected.

The structure was solved by Patterson methods using the program SHELXS86[10] and completed and refined by full-matrix least-squares calculations in SHELX76.[11] After several cycles of refinement with isotropic displacement parameters for the non-hydrogen atoms, an empirical absorption correction with minimum and maximum coefficients of 0.833 and 1.310, respectively, was applied using the program DIFABS.[12] The non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms at C_{sp^2} atoms were located by a difference Fourier synthesis and kept fixed during the further refinement; the other H-atom positions were geometrically calculated. During the last cycles of refinement, weights $w = 1/\sigma^2(F_o)$ were used and three reflections with big $F_o - F_c$ differences, probably extinction influenced, were excluded. 8.3 reflections per parameter were available, the maximum shift/σ value in the last cycle was 0.208. The final R value amounts to 0.065 ($R_w = 0.060$); maximum and minimum peak heights in a difference Fourier map are 0.34 and -0.36 e Å^{-3}, respectively.

All calculations were done on an IBM compatible PC of Poznan University.

TABLE VII

Crystal data for (VIc)

$C_{28}H_{38}N_2NiO_4.H_2O$	M.Wt. = 543.3
Monoclinic	Space group $P2_1/c$
a = 14.620 (2) Å	Z = 4
b = 12.789 (2) Å	$F(000)$ = 1160
c = 14.590 (3) Å	μ(CuKα) = 13.1 cm^{-1}
β = 91.62 (2) °	D_m* = 1.31 g cm^{-3}
V = 2726.9 (8) Å^3	D_c = 1.323 g cm^{-3}

*Flotation in aqueous KI solution

The non-hydrogen atomic positional and equivalent isotropic displacement parameters are given in Table VIII.

Results and Discussion

The molecular structure of the compound including the crystal-water oxygen atom is illustrated in an ORTEP plot[13] in Figure 4, and selected geometric bond parameters are summarized in Table IX.

Bond lengths and angles are in good agreement with expected values. Those of the central core of the complex closely resemble those found for the unsubstituted di(salicylidene)ethylenediaminato nickel(II) complex[14] (A) and are also compa-

TABLE VIII

Final fractional coordinates and isotropic equivalents of anisotropic displacement parameters (Å^2) for non-hydrogen atoms of VIc (esd's in parentheses)

$U_{eq} = 1/3\Sigma_i\Sigma_j a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	x	y	z	U_{eq}
Ni1	0.05517(6)	0.04377(6)	0.22706(5)	0.0396(3)
N1	0.0253(3)	−0.0467(3)	0.3207(3)	0.041(2)
N2	−0.0583(3)	0.0127(3)	0.1770(3)	0.041(2)
O1	0.1656(2)	0.0828(3)	0.2816(2)	0.047(1)
O2	0.0885(2)	0.1297(3)	0.1315(2)	0.043(1)
O3	0.3032(3)	−0.0105(3)	0.6295(2)	0.063(2)
O4	−0.1056(2)	0.2561(3)	−0.1801(2)	0.052(1)
C1	0.6798(5)	−0.0853(6)	0.9758(5)	0.098(3)
C2	0.6491(4)	−0.0269(5)	0.8888(5)	0.074(3)
C3	0.5516(4)	−0.0507(5)	0.8612(4)	0.065(3)
C4	0.5172(4)	0.0049(5)	0.7750(4)	0.062(2)
C5	0.4188(4)	−0.0215(5)	0.7483(4)	0.066(3)
C6	0.3922(4)	0.0277(5)	0.6575(4)	0.060(3)
C7	0.2701(4)	0.0168(4)	0.5429(4)	0.048(2)
C8	0.1902(4)	−0.0294(4)	0.5128(4)	0.047(2)
C9	0.1522(4)	−0.0084(4)	0.4258(4)	0.041(2)
C10	0.1967(4)	0.0615(4)	0.3650(3)	0.042(2)
C11	0.2774(4)	0.1085(4)	0.3989(4)	0.047(2)
C12	0.3142(4)	0.0890(4)	0.4845(4)	0.049(2)
C13	0.0684(4)	−0.0609(4)	0.3983(4)	0.046(2)
C14	−0.0564(4)	−0.1123(4)	0.2999(4)	0.045(2)
C15	−0.4549(5)	0.2406(6)	−0.5608(4)	0.079(3)
C16	−0.4281(5)	0.1979(5)	−0.4657(4)	0.057(2)
C17	−0.3410(4)	0.2496(4)	−0.4279(4)	0.051(2)
C18	−0.3126(4)	0.2081(4)	−0.3329(4)	0.047(2)
C19	−0.2235(4)	0.2576(4)	−0.2961(4)	0.048(2)
C20	−0.1938(4)	0.2114(4)	−0.2054(3)	0.050(2)
C21	−0.0626(4)	0.2173(4)	−0.1022(3)	0.041(2)
C22	−0.1001(4)	0.1466(4)	−0.0423(3)	0.042(2)
C23	−0.0496(4)	0.1147(4)	0.0378(3)	0.037(2)
C24	0.0391(4)	0.1530(4)	0.0570(3)	0.039(2)
C25	0.0759(4)	0.2228(4)	−0.0071(3)	0.041(2)
C26	0.0260(4)	0.2538(4)	−0.0843(4)	0.044(2)
C27	−0.0936(4)	0.0445(4)	0.1001(4)	0.043(2)
C28	−0.1186(4)	−0.0502(5)	0.2364(4)	0.051(2)
O1′	0.2562(4)	0.2592(4)	0.2017(4)	0.114(3)

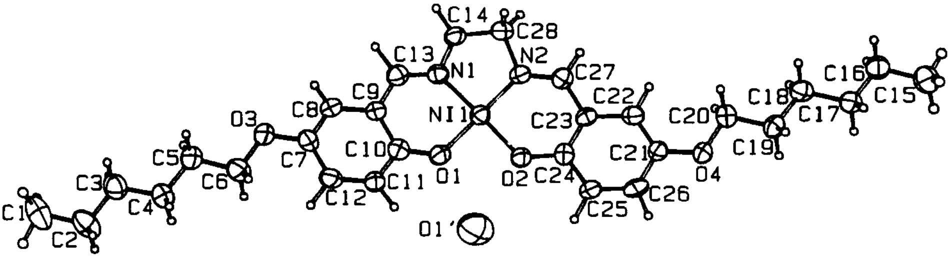


FIGURE 4 ORTEP plot[13] of the molecule of VIc with atom labels including the crystal-water oxygen atom. (Thermal ellipsoids at the 50% probability level, circles for H atoms have arbitrary size.)

TABLE IX

Selected bond distances (Å) and angles (°) for VIc (esd's in parentheses)

Ni1 - N1	1.852(4)	Ni1 - N2	1.838(4)
Ni1 - O1	1.849(3)	Ni1 - O2	1.851(3)
N1 - C13	1.292(7)	N2 - C27	1.287(7)
N1 - C14	1.485(7)	N2 - C28	1.490(7)
O1 - C10	1.315(6)	O2 - C24	1.322(6)
O3 - C6	1.438(7)	O4 - C20	1.449(7)
O3 - C7	1.385(7)	O3 - C21	1.376(6)
C7 - C8	1.371(8)	C21 - C22	1.382(7)
C8 - C9	1.397(7)	C22 - C23	1.423(7)
C9 - C10	1.429(7)	C23 - C24	1.407(7)
C10 - C11	1.402(8)	C24 - C25	1.411(7)
C11 - C12	1.368(8)	C25 - C26	1.384(7)
C12 - C7	1.423(8)	C26 - C21	1.394(8)
C9 - C13	1.444(7)	C23 - C27	1.442(7)
C14 - C28	1.506(7)		
N1 - Ni1 - N2	86.0(2)	O1 - Ni1 - O2	85.3(2)
N1 - Ni1 - O1	94.2(2)	N2 - Ni1 - O2	94.7(2)
Ni1 - N1 - C13	127.9(4)	Ni1 - N2 - C27	127.9(4)
Ni1 - N1 - C14	114.0(3)	Ni1 - N2 - C28	115.3(3)
Ni1 - O1 - C10	128.0(4)	Ni1 - O2 - C24	127.1(4)
C6 - O3 - C7	117.6(4)	C20 - O4 - C21	116.8(4)
O3 - C7 - C8	117.2(5)	O4 - C21 - C22	125.4(5)
O3 - C7 - C12	124.0(5)	O4 - C21 - C26	115.8(5)
C8 - C7 - C12	118.9(5)	C22 - C21 - C26	118.9(5)
C7 - C8 - C9	121.5(5)	C21 - C22 - C23	120.1(5)
C8 - C9 - C10	120.5(5)	C22 - C23 - C24	121.2(5)
C8 - C9 - C13	118.4(5)	C22 - C23 - C27	117.8(5)
C10 - C9 - C13	121.1(5)	C24 - C23 - C27	121.1(5)
C9 - C10 - C11	116.2(5)	C23 - C24 - C25	117.1(5)
C9 - C10 - O1	123.6(5)	C23 - C24 - O2	124.4(4)
C11 - C10 - O1	120.2(5)	C25 - C24 - O2	118.5(5)
C10 - C11 - C12	123.3(5)	C24 - C25 - C26	121.2(5)
C11 - C12 - C7	119.5(5)	C25 - C26 - C21	121.5(5)
C9 - C13 - N1	124.5(5)	C23 - C27 - N2	124.8(5)
N1 - C14 - C28	107.2(4)	N2 - C28 - C14	106.6(4)

rable to those for similar four-coordinated nickel(II) complexes compiled by Drew, Prasad and Sharma.[15] Mean values for bond lengths and angles of the alkyl chains are 1.520(12) Å and 112.3(1.3)°; the average C_{sp^2} − H bond length amounts to 1.05(9) Å.

The geometry of the quadridentate ligand leads to the *cis* form of the molecular core.The Ni atom has a square planar coordination with an average 0.053(3) Å deviation of the donor atoms from the mean plane through Ni1, N1, N2, O1, O2 towards a tetrahedral coordination as in the nickel(II) complex with 2, 2'-hydroxy-*N*, *N'*-ethylenedinaphthalene-1-methanimine[16] (B) (mean deviation 0.036(3) Å) and in contrast to *N*, *N'*-trimethylenedisalicylideneaminato nickel(II), [15] where the mirror symmetry of the molecules does not allow a tetrahedral but only a fold-like distortion of the square.

One of the six-membered rings at Ni (Ni1, N2, O2, C23, C24, C27) is exactly planar and the other one is slightly folded about the line N1 . . . O1: the plane containing Ni1, N1 and O1 and the least squares plane through N1, O1, C9, C10 and C13 (maximum deviation from this plane 0.019(5) Å for C13) make an angle of 6.7°. A similar distortion has been found for the unsubstituted complex (A) with one planar ring and one ring folded by about 9°. The five-membered ring (Ni1, N1, C14, C28, N2) has a twist conformation with deviations of C14 and C28 from the plane of the other three atoms of 0.306(5) and −0.194(6) Å, respectively, the ethylene bridge being in a gauche form with a torsion angle N1 − C14 − C28 − N2 of 34.2(5)°. Both phenyl rings are exactly planar. The alkyloxy chains adopt the all-*trans* conformation and are oriented with respect to the central molecular core in such a way that the molecule as a whole has a maximum stretched form. Thus, the banana shape of the central part is largely compensated.

The crystal-water oxygen atom is situated near the coordination plane of Ni1 (distance 0.650(5) Å). It has a relatively close contact of 2.879(6) Å to O1 (sum of corresponding van der Waals radii = 3.02 Å[17]) and an approximately van der Waals distance to O2 (3.108(6) Å). The O1 . . . O1' distance suggests a hydrogen bond, but there is no clear evidence for it since the positions of the H atoms of the water molecule are unknown.

The mutual orientation of the different molecular moieties may be clearly seen from Figure 5, showing a centrosymmetrical pair of molecules in a projection approximately perpendicular to that in Figure 4. The non-H skeleton, except for the ethylene bridge, is essentially planar with a slight double-S bed of this plane. The largest interplanar angles are those calculated for the least-squares planes of

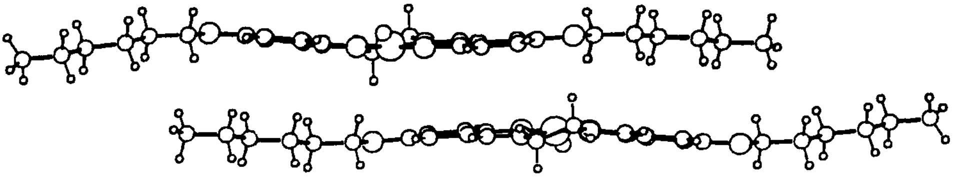


FIGURE 5 PLUTO plot[18] of a centrosymmetrical pair of molecules VIc in a projection along the line N1 . . . O1.

TABLE X

Intermolecular distances of non-hydrogen atoms of VIc (in Å) shorter than the sum of the corresponding van der Waals radii + 0.2 Å

a) between the two molecules of a centrosymmetrical pair			
Ni1 . . . C20	3.860(6)	C23 . . . C23	3.468(7)
Ni1 . . . C21	3.806(5)	C23 . . . C27	3.580(7)
Ni1 . . . C22	3.705(5)	C23 . . . C23	3.516(7)
b) other contacts (symmetry relation x, $0.5 - y$, $0.5 + z$)			
C10 . . . C26	3.530(8)	C19 . . . C27	3.531(7)

phenyl ring I (C7 . . . C12) and alkyloxy chain I (C1 . . . O3), 12.6°, and phenyl ring I and phenyl ring II (C21 . . . C26), 11.4°.

There is no intermolecular non-hydrogen atom contact shorter than the sum of the corresponding van der Waals radii within the crystal structure presented here. Most of the shortest intermolecular distances have been found between the atoms of a centrosymmetrical pair of molecules drawn in Figure 5 (cf. Table X). Such a pair of molecules is reminiscent of the complex dimers in A and B. However, the Ni atoms of adjacent centrosymmetrical molecules in these compounds lie almost exactly above one another with rather short distances of 3.21(1) Å and 3.2244(4) Å for A and B, respectively, suggesting a Ni . . . Ni interaction. In the case of the compound under investigation, the two Ni atoms in the pair are separated by 6.867(1) Å. The shortest Ni . . . Ni distance in the structure is 6.633(1) Å (symmetry

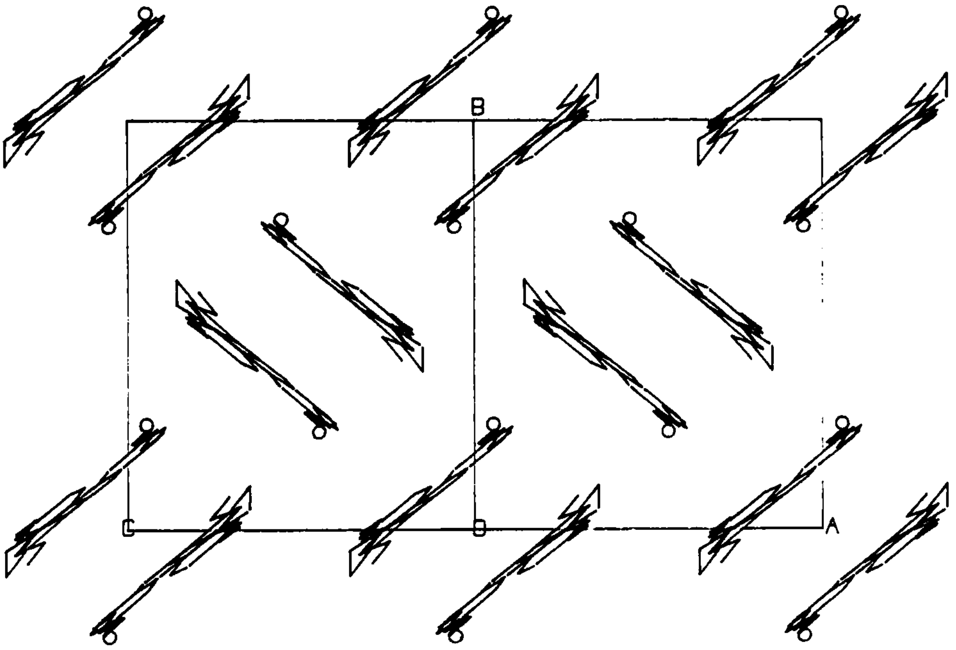


FIGURE 6 PLUTO drawing of the molecular packing of VIc in a projection along [101] (H atoms omitted for clarity, crystal-water oxygen atoms drawn as circles).

relation $-x, 0.5 + y, 0.5 - z$). Thus, Ni . . . Ni interactions do not play any role in the crystal packing. The closest approach of the two centrosymmetric molecules is realized in the region of phenyl ring II and the adjacent six-membered ring at Ni1 (cf. Table X).

The packing of the pairs of molecules is illustrated in Figures 6 and 7. They are arranged in a kind of double herringbone fashion (Figure 6). By viewing the structure in a direction perpendicular to that of Figure 6, the pattern of Figure 7 is generated: pairs of molecules connected by appropriate inversion centres form infinite columns, which are related by the action of the *c*-glide planes of the space group. The two kinds of columns drawn in Figure 7 are stacked alternately on top of each other in the [110] direction.

The crystal-water molecules are situated in a kind of channel parallel to [001] as can be seen in Figure 8.

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The X-ray investigations were performed at the Department of Crystallography of the Poznan University and supported by the project CPBP 01.12 10.3.

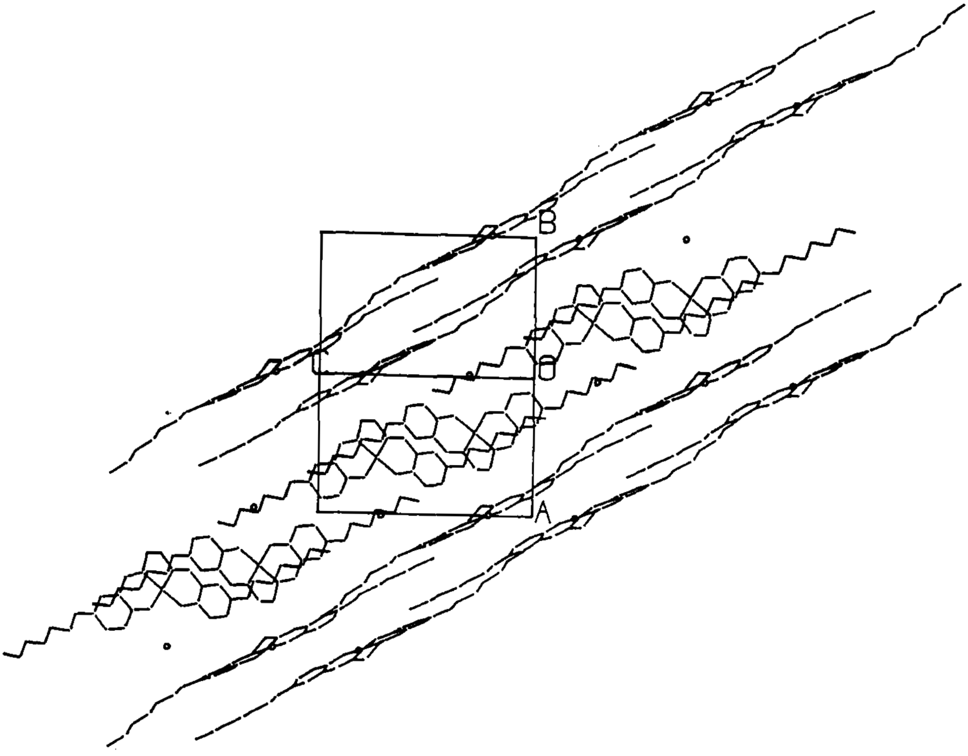

FIGURE 7 PLUTO projection along [110] for a part of the crystal structure of VIc (cf. text; without H atoms, O1′ as circle).

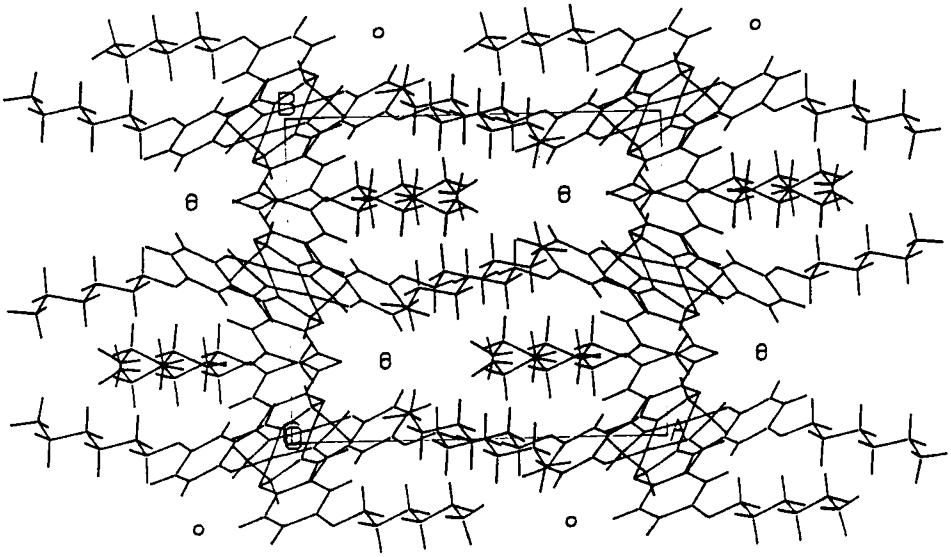

FIGURE 8 PLUTO plot of the crystal structure of VIc in a projection along [001]. (Crystal-water oxygen atoms drawn as circles.)

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