

**SYNTHESES AND CHARACTERIZATION OF BIS-[5-((4-ALKOXYPHENYL-AZO)-N-(n-ALKYL-SALICYLALDIMINATO)]NICKEL(II) COMPLEXES****Ali Akbar Khandar,<sup>a\*</sup> Zolfaghar Rezvani,<sup>b</sup> Kamelia Nejati,<sup>c</sup> Alexander I. Yanovsky,<sup>d</sup> Jesus M. Martinez<sup>e</sup>**<sup>a</sup> Department of Inorganic Chemistry, Faculty of Chemistry, Tabriz University, Tabriz, Iran<sup>b</sup> Department of Chemistry, Faculty of Science, Tarbiat Moallem University of Azarbaydjan P. O. Box 51745-406, Tabriz, Iran<sup>c</sup> Payam Noor University –Tabriz Center, Department of Chemistry, Hakim Nezami street, Tabriz, Iran<sup>d</sup> Institute of Organoelement Compounds, Russian Academy of Science, 28 Vavilov St., Moscow 117813, Russia<sup>e</sup> Department of Chemistry, Faculty of Science, Valladolid University, 47005, Valladolid, Spain

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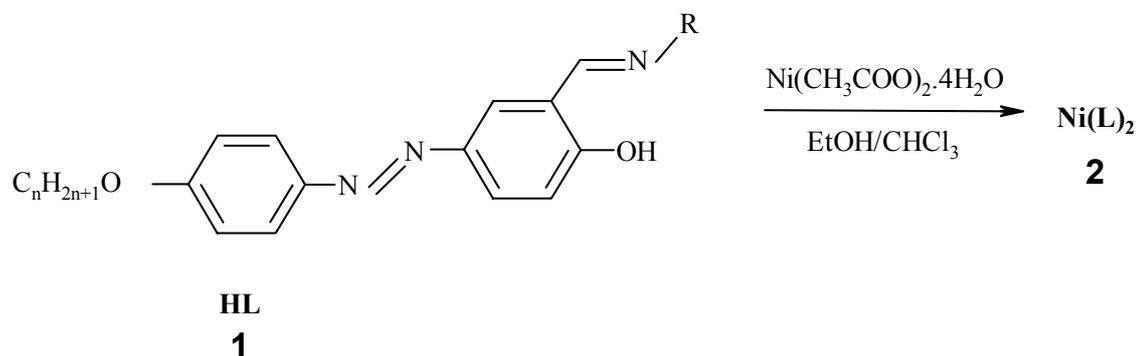
**Abstract**

A homologue series of Bis[5-((4-alkoxyphenyl)azo)-N-(n-alkyl-salicylaldiminato)]-nickel(II) complexes (alkyl = *n*-pentyl, *n*-dodecyl, alkoxy = O<sup>n</sup>C<sub>n</sub>H<sub>2n+1</sub>; n = 3–7) have been synthesized and characterized by elemental analyses and IR spectroscopy. The structure of bis[5-((4-propyloxyphenyl)azo)-N-(*n*-pentyl-salicylaldiminato)]Ni(II) has been studied by single-crystal x-ray diffraction. This complex crystallizes in triclinic system, space group P  $\bar{1}$  (No. 2), a = 9.609(3) Å, b = 12.271(4) Å, c = 17.929(10) Å,  $\alpha$  = 96.93(2)°,  $\beta$  = 103.99(2)°,  $\gamma$  = 101.67(2)°, and Z = 2. The refinement converges with R = 0.0643 and R<sub>w</sub> = 0.1411 for 7476 reflections [ $I > 2\sigma(I)$ ]. The ligand has an approximately trans-planar configuration around nickel. The coordination square is slightly distorted tetrahedrally. The angles N–Ni–N and O–Ni–O are 171.99° and 170.43°, respectively. Thermal behaviors of these complexes have been studied by using the polarizing microscope.

**Introduction**

Transition metal Schiff base complexes have been studied in great detail for their biological importance, various crystallographic features and their enzymatic reactions.<sup>1,2</sup> In the last two decades, salicylaldimine-based ligands have been widely used in the preparation of transition metal complexes with liquid crystalline character.<sup>3–7</sup> We recently reported the syntheses and liquid crystalline properties of copper (II) complex homologues based on azo-linked salicylaldimine.<sup>8</sup>

We report herein the syntheses of new Ni(II) bis(chelates), **2**, based on salicylaldimine, **1**, (see scheme). We also report the crystal structure of bis[5-((4-propyloxyphenyl)azo)-N-(*n*-pentyl-salicylaldiminato)]Ni(II) determined by single-crystal X-ray diffraction.



$n=3-7$ ;  $R=C_5H_{11}$ ,  $C_{12}H_{25}$

### Scheme

The title complexes were investigated in an attempt to synthesize new mesomorphic compounds containing a transition metal, but these complexes do not show any mesomorphic state.

## Experimental

### Reagents

All reagents and solvents were used as supplied by Merck.

### Physical measurements

Elemental (CHN) analyses were made on a Perkin-Elmer automatic equipment model 240B. IR spectra were recorded on IR-408 Shimadzu 568. Microscopic studies were carried out using Leitz Orthoplan-Pol polarizing microscope equipped with a Linkam THMSG 600 heating and cooling stage.  $^1\text{H}$ NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker AC-80, 80 MHz NMR spectrometer. All chemical shifts are reported in  $\delta$  units downfield from  $\text{Me}_4\text{Si}$ .

### X-ray crystallography

Crystals of bis[5-((4-propyloxyphenyl)azo)-*N-n*-pentylsalicylaldiminato]Ni(II) suitable for X-ray crystallography were grown by evaporation from chloroform/ethanol (2:1) solution at room temperature. Diffraction data were collected on a Siemens P3/PC diffractometer (four-circle geometry) at 158(2) K. Intensity data were obtained using

Mo  $K_{\alpha}$  radiation (0.7107 Å) monochromatized from a graphite and the  $\omega$ -2 $\theta$  scan mode was used to a maximum 2 $\theta$  value of 50.1°. The data were reduced and the structure was solved by direct method using the program SHELXTL plus version 5 refined by full matrix least-square method. In subsequent refinement, the function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $F_o$  and  $F_c$  are the observed and calculated structure factors amplitudes. The agreement indices  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum (|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  were used to evaluate the results. Atomic scattering factors were taken from the international tables for X-ray crystallography. Hydrogen atoms were introduced at theoretical positions with C-H distances of 0.95 Å for the aromatic H atoms, 0.99 Å for methylene and 0.98 Å for methyl groups. Crystallographic data for complex are given in Table 1.

### Materials

All homologue materials were prepared in the similar manner. For convenience we have substituted the terms aldehyde for 5-((4-alkoxyphenyl)-azo)-salicylaldehyde, ligand for homologues of 5-((4-alkoxyphenyl) azo)-*N-n*-alkylsalicylaldimine and complex for bis[5-((4-alkoxyphenyl)azo)-*N-n*-alkyl-salicylaldiminato]Nickel(II) complexes.

**Table 1** Crystallographic data for Ni complex

Empirical formula	C <sub>42</sub> H <sub>52</sub> N <sub>6</sub> NiO <sub>4</sub>
Formula weight	763.61
Temperature	158(2) K
Space group	P $\bar{1}$
Unit cell dimensions	a=9.609(3) Å, $\alpha$ =96.93(2)° b=12.271(4) Å, $\beta$ =103.99(2)° c=17.929(10) Å, $\gamma$ =101.67(2)°
Volume, Z	1976.8(10) Å <sup>3</sup> , 2
Density (calculated)	1.283 Mg/m <sup>3</sup>
Absorption coefficient	0.540 mm <sup>-1</sup>
F(000)	812
Crystal size	0.2×0.2×0.4 mm
$\theta$ range for data collection	1.19 to 25.05°
Limiting indices	-11 ≤ h ≤ 11, -14 ≤ k, -21 ≤ l ≤ 20
Reflections collected	7476
Independent reflections	7071 (R <sub>int</sub> = 0.0301)
Data/restraints/parameters	6963/0/487
Goodness-of-fit on F <sup>2</sup>	1.113
Final R indices [I > 2σ(I)]	0.0643
R <sub>w</sub>	0.1411
Largest diff. peak and hole	0.890 and -0.582 e Å <sup>-3</sup>

### Aldehyde

Aldehyde homologues were obtained as described elsewhere.<sup>9</sup>

### Ligand homologues

Equimolar amounts of related alkyl amine and aldehyde were condensed by refluxing in absolute ethanol. The obtained yellow solution was left at room temperature. Yellow micro-crystals were formed, filtered off and recrystallized from ethanol/chloroform.

Yield: 70-90%. MS  $m/z$  [fragment, intensity%] for  $n=3$ ,  $R=C_5H_{11}$  ( $C_{21}H_{27}N_3O_2$ ): Found 354.3 [M+1, 8], 353.3 [M, 31]. Calc. 353.2; for  $n=5$ ,  $R=C_5H_{11}$  ( $C_{23}H_{31}N_3O_2$ ): Found 382 [M+1, 33], 381.6 [M, 57]. Calc. 381.2; for  $n=5$ ,  $R=C_{12}H_{25}$  ( $C_{30}H_{46}N_3O_2$ ): Found 480.6 [M+1, 47], 479.6 [M, 57], Calc. 479.9; for  $n=7$ ,  $R=C_{12}H_{25}$  ( $C_{32}H_{50}N_3O_2$ ): Found 508.8 [M+1, 73], 507.8 [M, 100], Calc. 508.3.  $^1H$ NMR for  $n=3$ ,  $R=C_5H_{11}$ :  $\delta$  14.19 (br. s, 1H, OH), 8.30 (s, 1H, CH=N), 7.73-7.89 (4H, aromatic), 6.86-7.02 (3H, aromatic), 3.97 (t;  $J=6.5$  Hz, 2H, =N-CH<sub>2</sub>), 3.57 (t;  $J=6.5$  Hz, 2H, -O-CH<sub>2</sub>), 0.8-1.8 (18H, alkyl chains). The same spectra are observed for all ligand homologues.

### Complex homologues

A 0.5 mmol sample of a ligand was dissolved in 50 ml EtOH/CHCl<sub>3</sub> (1:1, v/v). To this was added an ethanolic solution of 0.26 mmol nickel acetate tetrahydrate and the mixture was refluxed for 2 h. The obtained green solution was left at room temperature and green needle crystals were collected by filtration, washed with ethanol and then recrystallized from EtOH/CHCl<sub>3</sub> (3:1, v/v). Yield 75-85%.

### Analyses Found( Calc.):

$n=3$ ,  $R=C_5H_{11}$  ( $C_{42}H_{52}NiN_6O_4$ ), C 65.7(66.06), H 6.75(6.82), N 10.7(11.01).

$n=5$ ,  $R=C_5H_{11}$  ( $C_{46}H_{60}NiN_6O_4$ ), C 67.8(67.42), H 7.2(7.33), N 9.9(10.26).

$n=4$ ,  $R=C_{12}H_{25}$  ( $C_{58}H_{84}NiN_6O_4$ ), C 70.0(70.54), H 8.5(8.51), N 8.2(8.51).

$n=6$ ,  $R=C_{12}H_{25}$  ( $C_{62}H_{92}NiN_6O_4$ ), C 72.2(72.61), H 8.6(8.98), N 7.8(8.19).

## Results and discussion

### Syntheses

Ligands and complexes were obtained in good yield and purity. Ligand homologues were characterized by MS, IR and  $^1\text{H}$ NMR spectroscopy and complex homologues were characterized by elemental analyses and IR spectroscopy.

Melting points of ligands and complex homologues are given in Table 2 and 5, respectively. Melting points of nickel(II) complexes regularly decrease with increasing of  $n$  and  $R$ , whereas there are no similar correlations in the ligand homologues.

**Table 2** Melting points ( $^{\circ}\text{C}$ ) of ligand homologues

$R^a$	$n^a$				
	3	4	5	6	7
$^n\text{C}_5\text{H}_{11}$	63-64	64-65	67-68	66-67	67-68
$^n\text{C}_{12}\text{H}_{25}$	71-72	68-70	72-75	79-81	71-72

<sup>a</sup>: See scheme

Some selected IR data for new compounds are shown in Table 3. The same IR spectra are observed for all of the ligand homologues. For the IR spectra of nickel complexes,  $\nu_{\text{C}=\text{N}}$  shifted to lower wave numbers by  $15\text{ cm}^{-1}$  and  $\nu_{\text{C}=\text{O}}$  to greater wave numbers by  $12\text{ cm}^{-1}$  upon coordination<sup>10,11</sup> in comparison to the free ligands. On the other hand the disappearance of OH bands of free ligands in Ni complex homologues indicate that OH group has deprotonated and coordinated to Ni(II) ion as  $-\text{O}^-$ . These observations, elemental analyses results, and x-ray structure show that the ligand coordinated to nickel(II) via N, O in 2:1 ratio.

**Table 3** Some selected IR data for compounds<sup>a</sup>

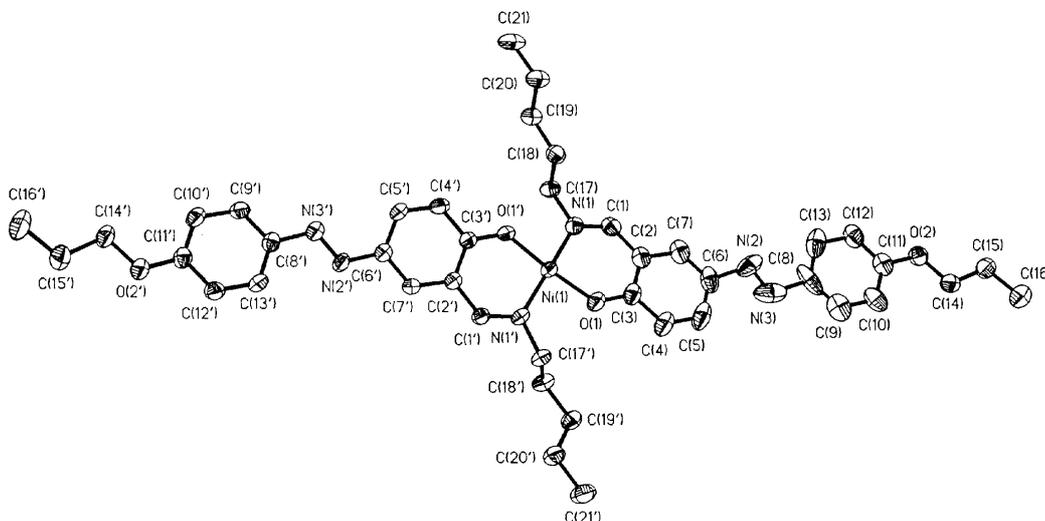
	Compound	
	HL	$\text{NiL}_2$
OH	3450(m) <sup>b</sup>	-
C-H(aromatic)	3050(w) <sup>b</sup>	3050(m)
C-H(aliphatic)	2950(s) <sup>b</sup> , 2850(s)	2750, 2850, 2900(s)
C=N	1623(s)	1608(s)
C=C	1600(s)	1605(s)
N=N	1505(s)	1505(s)
C-O(etheric)	1245(s)	1245(s)
C-O(phenolic)	1107(m)	1119(s)

<sup>a</sup> IR in KBr disk( $\text{cm}^{-1}$ ) <sup>b</sup> s–strong, m–medium, w–weak

*Crystal structure of bis[5-((4-n-propyloxyphenyl)azo)-N-(n-pentyl-salicylaldiminato)] Nickel(II)*

The crystal structure and unit cell diagram of the complex are illustrated in figure 1 and figure 2 respectively. The selected bond lengths and angles are given in Table 4. It can be seen from figure 1 that the ligands have an approximately trans-planar configuration around Ni central ion. The two chelate rings, [Ni(1) O(1) N(1) C(1) C(2) C(3)] and [Ni(1) O(1') N(1') C(1') C(2') C(3')], are accurately planar with maximum deviation of 0.02 and 0.05 Å from their mean planes respectively. The tilted angle between these two rings is 13.2°.

The Ni-N (1.920 Å) and Ni-O (1.833 Å) distances are similar to the corresponding values (1.92 and 1.84 Å) in trans planar bis-(*N*-isopropyl-3-methylsalicylideneiminato)<sup>12</sup>- and bis-(*N*-ethylsalicylideneiminato)-nickel(II),<sup>13</sup> the mean values (1.91 and 1.83) in bis-(*N*-methylsalicylideneiminato)-nickel(II),<sup>14</sup> and values (1.905 and 1.844 Å) in bis-(*N*-allylsalicylideneiminato)-nickel(II).<sup>15</sup> These differences are not significant.



**Figure 1.** Crystal structure of nickel complex

*Thermal properties*

Thermal properties of the Ni complex homologues were studied by using polarizing microscope equipped with heating and cooling stage. None of the complexes exhibited

liquid crystalline properties on heating, and clearly melted into an isotropic liquid as seen optically. The complex  $n=7$ ,  $R=C_{12}H_{25}$  (see scheme), shows crystalline polymorphism. This complex melts to the isotropic liquid on the first heating at 110 °C and then on cooling, crystallizes in two different forms. In the second heating, each crystalline form melts to isotropic liquid at 110 °C and 115 °C respectively. The other complexes melt to isotropic liquid at first heating and crystallize in virgin crystalline form at cooling and then melt to isotropic liquid at second heating. Thermal data for complexes are given in Table 5.

**Table 4** Selected bond lengths (Å) and angles (°) for Ni complex

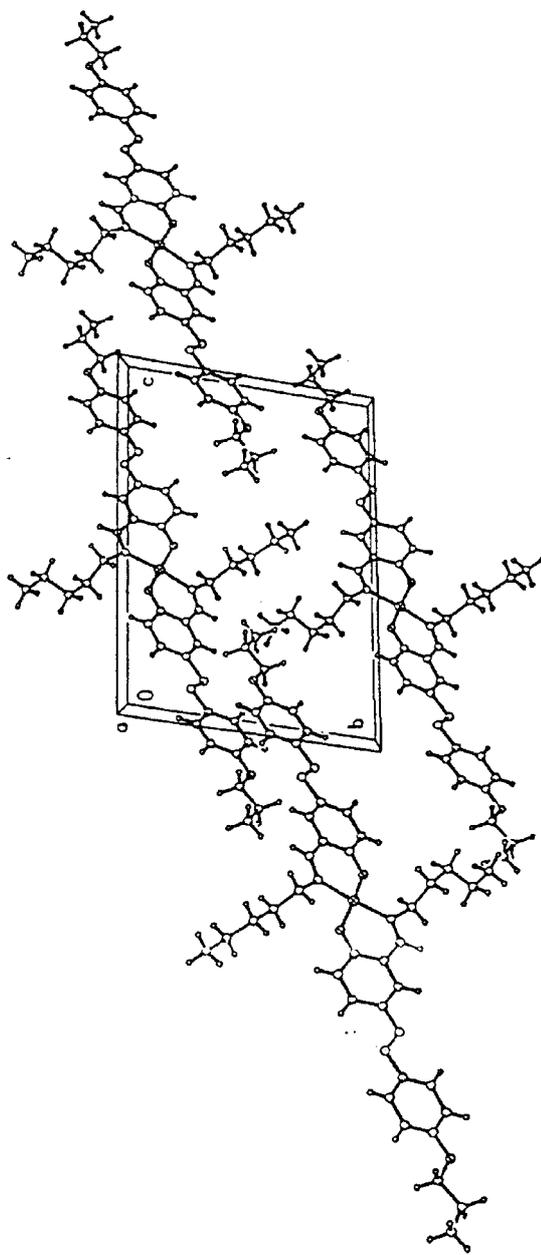
Ni(1)-O(1)	1.831(3)	Ni(1)-O(1')	1.835(3)
Ni(1)-N(1)	1.918(3)	Ni(1)-N(1')	1.923(3)
C(1)-N(1)	1.280(5)	C(1')-N(1')	1.294(5)
C(3)-O(1)	1.309(5)	C(3')-O(1')	1.298(5)
N(1)-Ni(1)-N(1')	171.99(14)	N(1)-Ni(1)-O(1')	87.34(13)
O(1)-Ni(1)-O(1')	170.43(14)	O(1')-Ni(1)-N(1')	93.21(12)
O(1)-Ni(1)-N(1')	93.21(14)	N(1')-Ni(1)-O(1)	87.57(13)

**Table 5** Thermal data for Nickel complexes

n	Transition <sup>a</sup>		Temperature(° C) <sup>b</sup>	
	R= <sup>n</sup> C <sub>5</sub> H <sub>11</sub>	R= <sup>n</sup> C <sub>12</sub> H <sub>25</sub>	R= <sup>n</sup> C <sub>5</sub> H <sub>11</sub>	R= <sup>n</sup> C <sub>12</sub> H <sub>25</sub>
3	C <sup>c</sup> ----I <sup>d</sup>	C----I	200	130
4	C----I	C----I	173	130
5	C----I	C----I	169	126
6	C----I	C----I	164	122
7	C----I	C+C' <sup>e</sup> ----I+ C'	154	110
		I+ C'----I		115

a: Observed in microscope , b: Second heating cycle

c, e: Crystal , d: Isotropic



**Figure 2.** Unit cell of bis-[5-((4-*n*-propoxyphenoxy)azo)-*N*-(*n*-pentylsalicylaldiminato)]nickel(II)-

### Supplementary data

Supplementary crystallographic data are available from the CCDC, 12 , Union Road, Cambridge, CB2 1EZ, UK on request, quoting the deposition number CCDC 141264.

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### References

1. Bindlish, J. M.; Bhatia, S. C.; Jain, P. C. *Indian J. Chem.* **1975**, *13*, 81–82.
2. Kashyap, J. R. P.; Bindlish, J. M.; Jain, P. C. *Indian J. Chem.* **1973**, *11*, 388–389.
3. Giroud A. M.; Maitlis P. M. *Angew. Chem. Int. Ed. Eng.* **1991**, *30*, 375–402.
4. Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215–274.
5. Hudson, S. A.; Maitlis P. M. *Chem. Rev.* **1993**, *93*, 861–885.
6. Bruce, D. W.; *J. Chem. Soc. Dalton Trans.* **1993**, 2983–583.
7. Seraano, J. L., editor. *Metallomesogens, synthses, properties and applications*. Weinhiem, VCH.1996.
8. Khandar, A. A.; Rezvani, Z. *Polyhedron* **1998**, *18*, 129–133.
9. Khandar, A. A.; Rezvani, Z. *Iran. J. Chem. & Chem. Eng.* **1999**, *18*, 19–23.
10. Saxena A. K.; Raj, P. *Synth. React. Inorg. Meta-Org. Chem.* **1990**, *20*, 199–208.
11. Zhou, X. X.; Song, Q. B.; Ma, Y. X. *Synth. React. Inorg. Meta-Org. Chem.* **1991**, *21*, 1407–1416.
12. Braun, R. L.; Ligafelter, E. C., *Acta Crystallogr.* **1966**, *21*, 546–553.
13. Shkol'nokova, L. M.; Knyazeva, A. N.; Voflikova, V. A., *J. Struct. Chem. (Engl. Trans.)* **1967**, *8*, 77–82.
14. Frasson, E.; Panattoni, C.; Sacconi, L., *J. Phys. Chem.* **1959**, *63*, 1908–1911.
15. Bhatia, S. C.; Bindlish, J. M.; Agya, R. C.; Prem, C. J., *J. Chem. Soc., Dalton Trans.* **1981**, 1773–1779.

### Povzetek

Sintetizirali smo homologno vrsto bis[5-((4-alkoksifenil)azo)-*N*-(*n*-alkil-salicilaldiminato)]-nikel(II) kompleksov (alkil= *n*-pentil, *n*-dodecil, alkoksi=O<sup>n</sup>C<sub>n</sub>H<sub>2n+1</sub>; n=3-7). Strukture smo potrdili z elementnimi analizami in IR spektroskopijo. Strukturo bis[5-((4-propyloksifenil)azo)-*N*-(*n*-pentil-salicilaldiminato)]Ni(II) smo potrdili z rentgensko difrakcijsko analizo. Ta kompleks kristalizira v triklnskem sistemu, prostorska skupina P  $\bar{1}$  (No. 2), a=9.609(3) Å, b=12.271(4) Å, c=17.929(10) Å,  $\alpha$ =96.93(2)°,  $\beta$ =103.99(2)°,  $\gamma$ =101.67(2)° in Z=2. Študirali smo tudi termične lastnosti kompleksov z uporabo polarizacijskega mikroskopa.