

Synthesis, Crystal Structure, Chromatographic Separation, and Thermogravimetric Investigation of a ONNO Type Asymmetric Schiff Base and Its Trinuclear Complexes¹

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Received November 22, 2013

Abstract—1,3-Propanediamine was put to react with 2-hydroxybenzaldehyde and 2-hydroxyacetophenone sequentially in aprotic medium. The crystalline product was examined by high performance liquid chromatography. The composition was 66% asymmetric Schiff base *N*(2-hydroxybenzylidene)-*N'*(2-hydroxyacetophenone)-1,3-propanediamine (SALLACH₂) and 33% bis-*N,N'*(2-hydroxyacetophenylidene)-1,3-propanediamine (LACH₂). As the crystals were uniform and of appropriate size, the molecular model of the material was revealed by X-ray diffraction. It was seen that two molecules of SALLACH₂ and one molecule of LACH₂ formed the mixed crystals. The substance was separated to its components and the asymmetric Schiff base was purified with a silica column. The substance was characterized with elemental analysis, FT-IR, MS, ¹H NMR, and ¹³C NMR. In addition, six tri-nuclear complex with the nuclear structure of Ni^{II}–Ni^{II}–Ni^{II}, Ni^{II}–Cu^{II}–Ni^{II}, Ni^{II}–Mn^{II}–Ni^{II} were prepared from this Schiff base and stoichiometry was determined by elemental analysis, FT-IR and thermogravimetry. Finally, the molecular structures of two complexes were brought to light by XRD which highlights the asymmetry of the ligand more clearly.

DOI: 10.1134/S1070328414080089

INTRODUCTION

The Schiff bases that were made up of diamines and aldehydes have been in the literature of coordination chemistry since 1930s [1–6]. The mentioned Schiff bases have symmetric structures established by single type aldehyde components. Among those, bis-*N,N'*(2-hydroxyphenylidene)-1,2-diaminoethane and bis-*N,N'*(2-hydroxyphenylidene)-1,3-propanediamine (LH₂) hold an important place as tetradentate ONNO type ligands. Especially, LH₂ and its derivatives, that form poly-nuclear complexes with interesting structures, are often noticed [7–13].

On the other hand, studies involving asymmetric Schiff bases prepared from diamines are not too much seen. The studies on the asymmetrical ONNO type Schiff bases have increased in recent years in literature [14–20]. In these studies, Schiff bases are prepared from symmetrical diamine and different two aldehyde compounds or an asymmetrical diamine and an aldehyde compound.

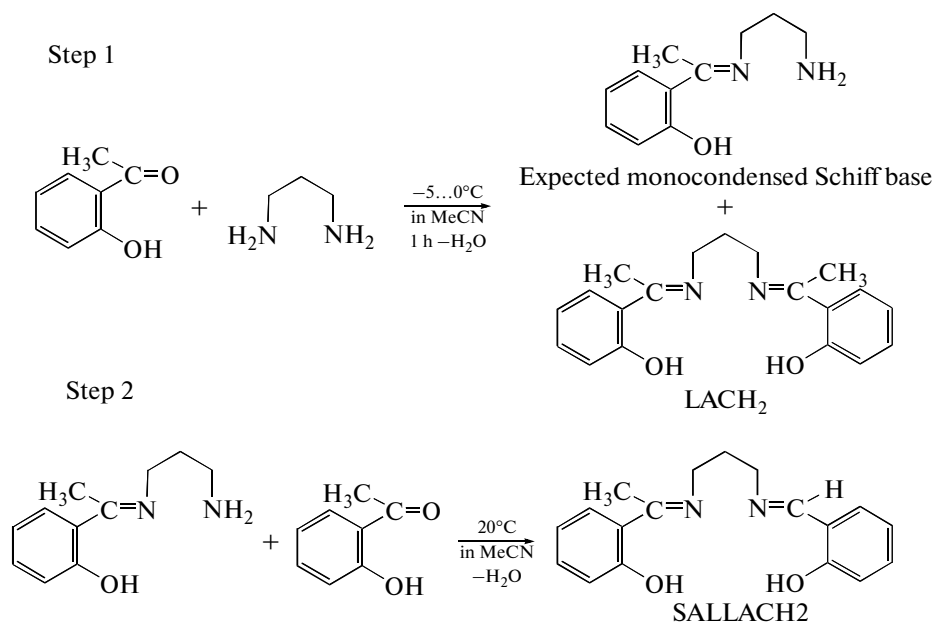
Generally, the template synthesis method was employed in the preparation of these complexes and

without preferably preparing the asymmetric Schiff base, the aldehyde and amine components were put to react in the presence of the metal ion of interest.

The first complex that involves an asymmetric Schiff base was reported in 1973 [21]. However, despite the fact that the name “asymmetric Schiff base” and the idea beyond it have been long known, there has not been any report on the synthesis and characterization of such a substance. This study has been designed to fill this gap.

The Schiff base made up of 1,3-propanediamine and 2-hydroxybenzaldehyde has a tendency to form polynuclear complexes of bis-*N,N'*(2-hydroxyphenylidene)-1,3-propanediamine (LACH₂). Despite the resemblance, a poly-nuclear complex involving bis-*N,N'*(2-hydroxyacetophenylidene)-1,3-propanediamine was absent in the literature. In this context, an asymmetric Schiff base of 1,3-propanediamine with one amino group condensed with 2-hydroxybenzaldehyde and the other amino group with 2-hydroxyacetophenone (SALLACH₂) was designed. Sketch for preparation of asymmetrical Schiff base SALLACH₂:

¹ The article is published in the original.



To this end, the molar equivalent carbonyl component was put to react with one mole of amine in aprotic medium and under cold conditions. After a certain time, the other aldehyde component was added to the mixture. It was clear that the obtained product was going to be a mixture. Therefore, every solid substance obtained by this method was analyzed by high performance liquid chromatography (HPLC). Because that the mixture contained symmetric Schiff bases, they were also prepared accordingly to be used as HPLC standards. It is very likely that the symmetric Schiff bases are thermodynamically more stable than their asymmetric counterparts since during the synthesis when two of the carbonyl components were added jointly onto the amine component, asymmetric Schiff base formation was not observed. On the other hand, if metal ions are present in the environment, there are studies attesting the asymmetric Schiff base complex formation [15–18].

In this study the asymmetric Schiff base of 1,3-propanediamine with one amino group condensed with 2-hydroxybenzaldehyde and the other amino group with 2-hydroxyacetophenone was successfully synthesized and isolated SALLACH₂. The product was a crystalline solid. It was analyzed by X-ray diffraction methods and the molecular structure was determined. Later on, the mixture was purified by column chromatography and the asymmetric Schiff base was isolated. The elemental analysis and characterization study were done by means of FT-IR, ¹H NMR, ¹³C NMR, MS and DSC. The abbreviation SALLACH₂ will be used for the isolated Schiff base from now on.

The transformation of the isolated Schiff base to its symmetric counterparts by hydrolyzation in amphiprotic solvents was observed. In addition, six trinuclear

complexes were prepared from asymmetrical Schiff base. The complex structure also contains acetate (AcO⁻) or nitrite (NO₂⁻) anions as μ bridges [22]. The formulas of the complexes are given below.

If NiSALLAC is described as the complex between Ni²⁺ ion and SALLACH₂ Schiff base, formulas of six trinuclear complexes are as follows: {(NiSALLAC)Ni(AcO)₂(DMF)₂} (I); {(NiSALLAC)₂Cu(AcO)₂(DMF)₂} (II); {(NiSALLAC)₂Mn(AcO)₂(DMF)₂} (III); {(NiSALLAC)₂Ni(NO₂)₂(DMF)₂} (IV); {(NiSALLAC)₂Cu(NO₂)₂(DMF)₂} (V); {(NiSALLAC)₂Mn(NO₂)₂(DMF)₂} (VI).

EXPERIMENTAL

Materials and apparatus. Used reagents were of Merck or Fluka brands and they were used without further purification. In this study, Shimadzu Infinity FTIR-Spectrometer equipped with three reflectional ATR unit was used for IR spectra. The C, H, and N analyses were performed on Elementar Vario Micro Cube instrument. Metal analyses were recorded on GBC Avanta PM Model atomic absorption spectrometer using FAAS mode. Complex (2–3 mg) was dissolved in 1 mL HNO₃ (63%) with heating, diluted to 100 mL and given to nebulizer of atomic absorption spectroscopy (AAS) for metal analysis. The mass spectra were obtained by Shimadzu, 2010 plus with direct inlet (DI) unit with an electron impact ionizer. DI temperature was varied between 40–140°C and ionization was done with electrons with 70 eV energy. The NMR spectra were recorded on the Bruker Ultrashield 300 MHz NMR spectrometer. DMSO-d₆ solution was

the solvent. The thermogravimetric analyses were performed by Shimadzu DTG-60H. In thermogravimetric analyses, temperature was varied between 30–600°C. These analyses were performed at 10°C/min rate and under N₂ atmosphere in Pt pans. Calibration of the instrument was done with metallic In, Pb or Zn.

Synthesis of *N*(2-hydroxybenzylidene)-*N'*(2-hydroxyacetophenone)-1,3-propanediamine (SALLACH₂). The asymmetric Schiff base was prepared in MeCN that was dehydrated by CaH₂. 1,3-Diaminopropane (3.7 g, 0.05 mol) was dissolved in 50 mL MeCN and the temperature was decreased to –10°C in a salt-ice bath. 2-Hydroxyacetophenone (6.80 g, 0.05 mol) was added with constantly stirring for 5 min. This solution was kept in ice-water mixture for half an hour and the temperature was kept under 1°C. After the duration, salicylaldehyde (2-hydroxybenzaldehyde) (6.10 g, 0.05 mol) was added to the solution and again the solution was kept in ice-water mixture for half an hour, stirring. After that, this solution was kept in the deep freeze at –20°C for 12 h. A yellow crystalline substance was obtained and filtered by vacuum. The filtrate was rinsed with MeCN and Et₂O and air-dried. The yield was 72–75%, m.p. = 88–89°C.

This crystalline substance was chromatographically investigated. In chromatographic studies, the concentration of the asymmetric Schiff base within the mixture was determined by using symmetric Schiff bases (LH₂ and LACH₂) as HPLC standards. The mobile phase was selected as 85% MeCN : 15% H₂O in which the resolution was at its maximum. The chromatograms obtained by using 100 ppm stock LH₂, LACH₂ and SALLACH₂ can be seen in Fig. 1.

A silica column (Merck silica gel 60, 40–63 μm) with 50 cm height and 2.0 cm diameter was used to separate the mixture. 50% EtAcO : 50% *n*-C₆H₁₄ was selected as the most suitable solvent for separation. It was observed that LACH₂ moved rapidly within this solvent. In addition, the ratio of the *R_f* value of LACH₂ and *R_f* value of SALLACH₂ was approximately two. Both substances being yellow, their locations in the column were noted easily and the eluates were collected. The compounds were obtained separately by evaporating the solvent. SALLACH₂ was recrystallized in a little volume of MeCN and its purity was checked by HPLC.

C₁₈H₂₀N₂O₂ (SALLACH₂)

anal. calcd., %: C, 72.94; H, 6.80; N, 9.44.

Found, %: C, 73.34; H, 6.55; N, 9.86.

IR (ν, cm⁻¹): 3010–3023 ν(C–H_{Ar}), 2941–2854 ν(C–H_{Aliph}), 1631–1624 ν(C=N), 1610 ν(C=C_{ring}), 1278–1159 ν(C–O_{Phenol}), 752 δ(C–H_{Ar}). λ_{max} = 242 nm, ε = 8164 dm³ mol⁻¹ cm⁻¹ in DMSO. ¹H NMR (CH₃SOCH₃-d₆; δ, ppm): 16.55 s., 13.47 s., 8.58 s.,

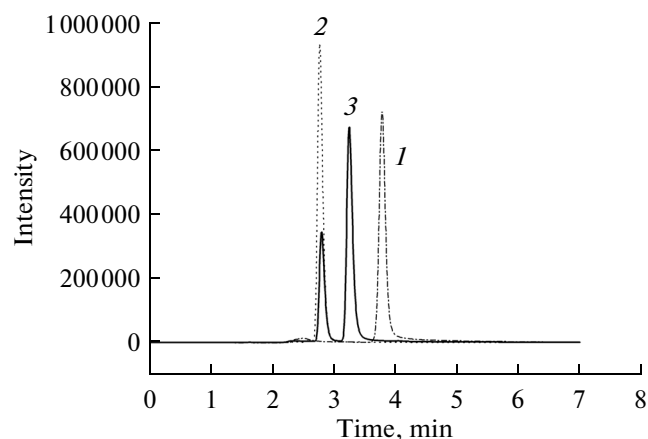


Fig. 1. Obtained chromatograms for the mixture of Schiff bases: symmetric LH₂, symmetric LACH₂ and 2SALLACH₂ · LACH₂ with 85% MeCN : 15% H₂O mobile phase: LH₂ (1), LACH₂ (2), 2SALLACH₂ · LACH₂ (3).

7.62 d., 7.45 d., 7.31 p., 6.88 t., 6.77 t., 3.73 t., 3.66 t. 2.40 s., 2.06 p.; ¹³C NMR (CH₃SOCH₃-d₆; δ, ppm): 167.70, 164.32, 161.13, 132.86, 132.74, 132.09, 129.21, 119.31, 119.11, 118.97, 118.95, 118.62, 117.13, 117.08, 116.91, 56.46, 46, 33, 14.80. The yield was 36–40%, m.p. = 92–93°C.

All complexes were prepared by template synthesis. The reaction of the Schiff base (SALLACH₂) and Ni(II) salt was carried out in one step in DMF and in the presence of AcO⁻ or NO₂⁻ ions.

Synthesis of complexes containing acetate. 0.296 g (0.001 mol) SALLACH₂ was dissolved in 40.0 mL DMF by heating. The temperature was raised up to 95 to 110°C. To this solution, added were the solution of 0.237 g (0.001 mol) NiCl₂ · 6H₂O salt in 10 mL MeOH : DMF (50/50, v/v) and the solution of 0.0005 mol related Ni(II), Cu(II) or Mn(II) acetate in 10 mL MeOH : DMF (50/50, v/v), 0.250 g Ni(AcO)₂ · 4H₂O for **I**, 0.201 g Cu(AcO)₂ · H₂O for **II** and 0.246 g Mn(AcO)₂ · 4H₂O for **III**. The final mixture was allowed left to stand for 4–5 days. The formed crystalline complex was separated by vacuum filtration and air dried.

{(NiSALLAC)₂Ni(AcO)₂(DMF)₂} (**I**)

anal. calcd., %: C, 53.65; H, 5.87; N, 8.15; Ni, 17.10.

Found, %: C, 53.04; H, 5.7; N, 7.57; Ni, 18.35.

IR (ν, cm⁻¹): 3022–3049 ν(C–H_{Ar}), 2920–2848 ν(C–H_{Aliph}), 1651 ν(C=O_{DMF}), 1633 ν(C=O_{Acetate}), 1604 ν(C=N), 1583 ν(C=C_{ring}), 1193 ν(C–O_{Phenol}), 752 δ(C–H_{Ar}). λ_{max} = 348 nm, ε = 16457 dm³ mol⁻¹ cm⁻¹ in DMSO.

Thermoanalytical data (TG): between 157 and 185°C (DMF lost) theoretical mass loss 14.17%; found 14.02 ± 0.95%.

$\{(NiSALLAC)_2Cu(AcO)_2(DMF)_2\}$ (II)

anal. C, 53.40; H, 5.84; N, 8.12; Ni, 11.34; Cu, 6.14. calcd., %:

Found, %: C, 53.91; H, 6.12; N, 7.91; Ni, 11.38; Cu, 6.42.

IR (ν , cm^{-1}): 3012–3053 $\nu(C-H_{Ar})$, 2929–2847 $\nu(C-H_{Aliph})$, 1645 $\nu(C=O_{DMF})$, 1636 $\nu(C=O_{Acetate})$, 1612 $\nu(C=N)$, 1612 $\nu(C=C_{ring})$, 1193 $\nu(C-O_{Phenol})$, 756 $\delta(C-H_{Ar})$. $\lambda_{max} = 281$ nm, $\epsilon = 102628$ dm^3 mol^{-1} cm^{-1} in DMSO.

TG: between 143 and 177°C (DMF lost) theoretical mass loss 14.11%; found 13.53 ± 0.63%.

$\{(NiSALLAC)_2Mn(AcO)_2(DMF)_2\}$ (III)

anal. C, 53.84; H, 5.89; N, 8.18; Ni, 11.44; Mn, 5.36. calcd., %:

Found, %: C, 54.37; H, 6.26; N, 7.98; Ni, 11.74; Mn, 5.48.

IR (ν , cm^{-1}): 3019–3050 $\nu(C-H_{Ar})$, 2934–2848 $\nu(C-H_{Aliph})$, 1649 $\nu(C=O_{DMF})$, 1635 $\nu(C=O_{Acetate})$, 1608 $\nu(C=N)$, 1581 $\nu(C=C_{ring})$, 1198 $\nu(C-O_{Phenol})$, 757 $\delta(C-H_{Ar})$. $\lambda_{max} = 350$ nm, $\epsilon = 15004$ dm^3 mol^{-1} cm^{-1} in DMSO.

TG: between 143 and 177°C (DMF lost) theoretical mass loss 14.2 %; found 13.96 ± 1.1%.

Synthesis of complexes containing nitrite. 0.296 g (0.001 mol) SALLACH₂ was dissolved in 40.0 mL DMF by heating. The temperature was raised up to 95 to 110°C. To this solution, added were the solution of 0.237 g (0.001 mol) NiCl₂ · 6H₂O salt in 10 mL MeOH : DMF (50/50, v/v) and the solution of 0.005 mole related metal salt in 10 mL hot DMF, 0.238 g NiCl₂ · 6H₂O for complex **IV**, 0.170 g CuCl₂ · 2H₂O for **V** and 0.198 g MnCl₂ · 4H₂O for **VI** and the solution of 0.198 g (0.003 mol) NaNO₂ salt in 10 mL hot MeOH. The final solution was allowed to stand for 5 to 6 days. The formed green crystalline complex was separated by vacuum filtration and air dried.

$\{(NiSALLAC)_2Ni(NO_2)_2(DMF)_2\}$ (IV)

anal. calcd., %: C, 50.30; H, 5.03; N, 11.17; Ni, 17.56.

Found, %: C, 49.38; H, 5.3; N, 10.62; Ni, 18.26.

IR (ν , cm^{-1}): 3012–3055 $\nu(C-H_{Ar})$, 2930–2854 $\nu(C-H_{Aliph})$, 1652 $\nu(C=O_{DMF})$, 1638 $\nu(C=O_{Acetate})$, 1595 $\nu(C=N)$, 1573 $\nu(C=C_{ring})$, 1313 $\nu(N=O)$, 1195 $\nu(C-O_{Phenol})$, 751 $\delta(C-H_{Ar})$. $\lambda_{max} = 351$ nm, $\epsilon = 12207$ dm^3 mol^{-1} cm^{-1} in DMSO.

TG: between 197 and 253°C (DMF lost) theoretical mass loss 14.56%; found 15.17 ± 1.33%.

$\{(NiSALLAC)_2Cu(NO_2)_2(DMF)_2\}$ (V)

anal. C, 50.06; H, 5.00; N, 11.11; Ni, 11.65; Cu, 6.31. calcd., %:

Found, %: C, 49.87; H, 5.21; N, 10.77; Ni, 12.05; Cu, 6.65.

IR (ν , cm^{-1}): 3013–3051 $\nu(C-H_{Ar})$, 2932–2846 $\nu(C-H_{Aliph})$, 1652 $\nu(C=O_{DMF})$, 1636 $\nu(C=O_{Acetate})$, 1598 $\nu(C=N)$, 1580 $\nu(C=C_{ring})$, 1315 $\nu(N=O)$, 1195 $\nu(C-O_{Phenol})$, 752 $\delta(C-H_{Ar})$. $\lambda_{max} = 286$ nm, $\epsilon = 96824$ dm^3 mol^{-1} cm^{-1} in DMSO.

TG: between 191 and 258°C (DMF lost) theoretical mass loss 14.49%; found 15.24 ± 0.85%.

$\{(NiSALLAC)_2Mn(NO_2)_2(DMF)_2\}$ (VI)

anal. C, 50.49; H, 5.04; N, 11.21; Ni, 11.75; Mn, 5.50. calcd., %:

Found, %: C, 49.55; H, 4.64; N, 10.98; Ni, 12.41; Mn, 5.32.

IR (ν , cm^{-1}): 3013–3055 $\nu(C-H_{Ar})$, 2932–2846 $\nu(C-H_{Aliph})$, 1651 $\nu(C=O_{DMF})$, 1635 $\nu(C=O_{Acetate})$, 1596 $\nu(C=N)$, 1578 $\nu(C=C_{ring})$, 1314 $\nu(N=O)$, 1198 $\nu(C-O_{Phenol})$, 753 $\delta(C-H_{Ar})$. $\lambda_{max} = 351$ nm, $\epsilon = 14855$ dm^3 mol^{-1} cm^{-1} in DMSO.

TG: between 201 and 261°C (DMF lost) theoretical mass loss 14.61%; found 16.44 ± 0.92%.

X-ray crystallography. A single crystals of 2SALLACH₂ · LACH₂ and complexes **IV** and **V** were analyzed on an Oxford Diffraction Xcalibur Single Crystal X-ray Diffractometer with a sapphire CCD detector using MoK α radiation ($\lambda = 0.71073$ Å) operating in $\omega/2\theta$ scan mode. The unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in $2.89^\circ \leq \theta \leq 26.37^\circ$ range for 2SALLACH₂ · LACH₂, $2.81^\circ \leq \theta \leq 26.36^\circ$ for **IV** and $2.73^\circ - 27.80^\circ$ for **V**. The data of 2SALLACH₂ · LACH₂ were collected at 293(2) K and the data of the complexes **IV** and **V** were collected at 105(2) K. The empirical absorption corrections were applied by the semi-empirical method via the CrysAlis CCD software [23]. Models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [24]. The structures of 2SALLACH₂ · LACH₂ and complexes **IV** and **V** were solved by direct methods using the SHELXS-97 software implemented in the WinGX package [25].

Crystallographic data of 2SALLACH₂ · LACH₂, **IV** and **V** are shown in Table 1. The selected bond lengths and angles are listed in Table 2. Supplementary material for structures 2SALLACH₂ · LACH₂ and complexes **IV**, **V** has been deposited with the Cambridge Crystallographic Data Centre (nos. 892463, 892464,

Table 1. Crystallographic and experimental data of 2SALLACH₂ · LACH₂, {(NiSALLAC)₂Ni(NO₂)₂(DMF)₂} (IV) and {(NiSALLAC)₂Cu(NO₂)₂(DMF)₂} (V)

Parameter	Value		
	2SALLACH ₂ · LACH ₂	IV	V
<i>M</i>	887.06	1007.86	1003.03
<i>T</i> , K	293	105	293
Crystal size, mm	0.5 × 0.4 × 0.1	0.32 × 0.26 × 0.14	0.40 × 0.30 × 0.04
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	6.7527(2)	10.5019(5)	10.5206(5)
<i>b</i> , Å	19.9830(10)	20.1010(9)	20.1224(9)
<i>c</i> , Å	20.0070(10)	10.2154(4)	10.2866(5)
α , deg	65.555(5)	90.00	90.00
β , deg	82.542(4)	90.324(5)	91.389(5)
γ , deg	86.702(3)	90.00	90.00
<i>V</i> , Å ³	2436.91(19)	2156.42(16)	2177.03(18)
<i>Z</i>	2	2	2
ρ , g cm ⁻³	1.209	1.552	1.530
μ , mm ⁻¹	0.08	1.421	1.351
<i>T</i> _{min} – <i>T</i> _{max}	0.9613–0.9921	0.6592–0.8259	0.6140–0.9479
<i>F</i> (000)	944	1046	1044
θ Range, degs	2.89–26.37	2.81–26.36	2.73–27.80
Index ranges	–8 ≤ <i>h</i> ≤ 8, –24 ≤ <i>k</i> ≤ 24, –24 ≤ <i>l</i> ≤ 25	–13 ≤ <i>h</i> ≤ 12, –25 ≤ <i>k</i> ≤ 17, 12 ≤ <i>l</i> ≤ 12	–8 ≤ <i>h</i> ≤ 13, –17 ≤ <i>k</i> ≤ 25, –12 ≤ <i>l</i> ≤ 12
Reflections collected	17270	9318	9332
Reflections unique	9810	4406	4434
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0803, 0.1999	0.0605, 0.1525	0.0540, 0.1347
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1418, 0.2333	0.0968, 0.1737	0.0861, 0.1547
Data/restraints/parameters	9810/6/633	4406/0/289	4434/0/286
GOOF of <i>F</i> ²	1.048	1.048	1.043
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$, e Å ⁻³	0.498/–0.221	0.104/–0.585	0.683/–0.415

and 936676, respectively; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

All spectral data supports the isolation of SALLACH₂ asymmetric Schiff base. Unfortunately, this asymmetric Schiff base could not be obtained as single crystal. It was re-crystallized in various solvents but none of them yielded suitable crystals for X-ray analysis. Only the mixed crystal of 2SALLACH₂ · LACH₂ has been obtained as a single crystal. It was observed that the two asymmetric Schiff base molecules and one symmetric Schiff base molecule have been crystallized together. The crystals of 2SALLACH₂ · LACH₂ compound/mix-

ture were investigated by X-ray diffraction. The pluton drawing of the molecular model obtained in the light of the X-ray diffraction study is shown in Fig. 2.

In Fig. 2, three Schiff base molecules are shown separately. The first model illustrates the asymmetric structure of the Schiff base containing C(1)–C(18) carbons, SALLACH₂. One each of methyl groups in the molecules of the Schiff bases containing C(19)–C(36) carbons and C(38)–C(56) carbons are highlighted with dashed lines. These dashed lines are connected to C(29) and C(44) of the imine groups. The probabilities of presence of a methyl group in these molecules have been calculated to be 64 and 36%, respectively.

Table 2. The selected bond lengths (Å) and angles (deg) for 2SALLACH₂ · LACH₂ and complexes IV, V

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
2SALLACH₂ · LACH₂			
C(7)–N(1)	1.265(4)	C(29)–N(4)	1.282(5)
C(7)–H(7)	0.9300	C(29)–C(36 <i>B</i>)	1.512(8)
C(8)–N(1)	1.450(4)	C(44)–C(56 <i>B</i>)	1.454(15)
C(11)–N(2)	1.290(4)	C(45)–N(5)	1.452(4)
C(11)–C(18)	1.503(4)	C(44)–N(5)	1.276(4)
C(10)–N(2)	1.456(4)	C(47)–N(6)	1.455(4)
C(25)–N(3)	1.284(4)	C(48)–C(56 <i>A</i>)	1.486(5)
C(26)–N(3)	1.456(4)	C(48)–N(6)	1.294(4)
IV			
N(1)–Ni(1)	2.006(4)	Ni(1)–Ni(2)	2.9789(5)
N(2)–O(5)	1.203(5)	Ni(2)–O(1)	2.034(3)
N(2)–O(4)	1.285(5)	Ni(2)–O(1)	2.034(3)
N(2)–Ni(1)	2.135(4)	Ni(2)–O(3)	2.047(3)
N(3)–Ni(1)	2.017(4)	Ni(2)–O(3)	2.047(3)
Ni(1)–O(3)	2.001(3)	Ni(2)–O(4)	2.099(3)
Ni(1)–O(1)	2.017(3)	Ni(2)–O(4)	2.099(3)
Ni(1)–O(2)	2.165(3)	Ni(2)–Ni(1)	2.9789(5)
V			
N(1)–Ni(1)	2.024(5)	Ni(1)–Cu(1)	2.9858(6)
N(2)–Ni(1)	2.016(5)	Cu(1)–O(2)	2.039(3)
N(3)–O(4)	1.227(6)	Cu(1)–O(1)	2.040(3)
N(3)–O(3)	1.287(6)	Cu(1)–O(3)	2.102(3)
N(3)–Ni(1)	2.152(5)	Cu(1)–Ni(1)	2.9858(6)
O(1)–Ni(1)	1.997(4)	C(7)–N(1)	1.267(8)
O(1)–Cu(1)	2.040(3)	C(7)–C(21)	1.536(9)
O(2)–Ni(1)	2.021(3)	C(11)–N(2)	1.270(8)
O(2)–Cu(1)	2.039(3)	C(11)–C(12)	1.452(8)
O(3)–Cu(1)	2.102(3)	C(11)–H(11)	0.9500
O(5)–Ni(1)	2.162(4)	C(7)–C(21)	1.536(9)
2SALLACH₂ · LACH₂			
Angle	ω, deg	Angle	ω, deg
N(1)C(7)C(6)	121.7(3)	N(4)C(29)C(30)	118.0(4)
N(1)C(7)H(7)	119.1	N(4)C(29)C(36 <i>B</i>)	121.2(4)
C(6)C(7)H(7)	119.1	C(30)C(29)C(36 <i>B</i>)	120.7(4)
N(2)C(11)C(12)	117.6(3)	N(5)C(44)C(56 <i>B</i>)	122.9(6)
N(2)C(11)C(18)	121.5(3)	N(5)C(44)C(43)	119.1(3)
C(12)C(11)C(18)	120.9(3)	C(56 <i>B</i>)C(44)C(43)	116.6(6)
N(3)C(25)C(24)	117.4(3)	N(6)C(48)C(49)	117.1(3)
N(3)C(25)C(36 <i>A</i>)	122.6(3)	N(6)C(48)C(56 <i>A</i>)	121.8(3)
C(24)C(25)C(36 <i>A</i>)	120.0(3)	C(49)C(48)C(56 <i>A</i>)	121.1(3)

Table 2. (Contd.)

Angle	ω , deg	Angle	ω , deg
IV			
O(3)Ni(1)N(1)	171.75(14)	N(2)Ni(1)O(2)	169.10(15)
O(3)Ni(1)N(3)	89.65(16)	O(1)Ni(2)O(4)	84.06(12)
N(1)Ni(1)N(3)	98.44(18)	O(3)Ni(2)O(4)	84.29(12)
O(3)Ni(1)O(1)	81.63(11)	O(1)Ni(2)O(4)	84.06(12)
N(1)Ni(1)O(1)	90.28(14)	O(3)Ni(2)O(4)	84.29(12)
N(3)Ni(1)O(1)	171.28(16)	C(1)O(1)Ni(1)	125.0(3)
O(3)Ni(1)N(2)	83.63(15)	C(1)O(1)Ni(2)	138.9(3)
N(1)Ni(1)N(2)	96.89(17)	Ni(1)O(1)Ni(2)	94.67(12)
N(3)Ni(1)N(2)	97.13(16)	C(19)O(2)Ni(1)	115.2(3)
O(1)Ni(1)N(2)	81.57(14)	C(17)O(3)Ni(1)	123.0(3)
O(3)Ni(1)O(2)	91.17(14)	C(17)O(3)Ni(2)	139.3(3)
N(1)Ni(1)O(2)	86.89(17)	Ni(1)O(3)Ni(2)	94.75(12)
N(3)Ni(1)O(2)	92.40(15)	N(2)O(4)Ni(2)	112.0(3)
O(1)Ni(1)O(2)	88.21(13)		
V			
O(1)Ni(1)N(2)	171.05(17)	O(2)Ni(1)O(5)	88.16(14)
O(1)Ni(1)O(2)	81.70(13)	N(1)Ni(1)O(5)	93.32(17)
N(2)Ni(1)O(2)	89.46(17)	N(3)Ni(1)O(5)	168.26(16)
O(1)Ni(1)N(1)	89.70(18)	O(2)Cu(1)O(3)	83.79(14)
N(2)Ni(1)N(1)	99.2(2)	O(1)Cu(1)O(3)	83.89(14)
O(2)Ni(1)N(1)	171.32(18)	O(2)Cu(1)O(3)	83.79(14)
O(1)Ni(1)N(3)	83.03(16)	O(1)Cu(1)O(3)	83.89(14)
N(2)Ni(1)N(3)	97.0(2)	N(1)C(7)C(6)	123.2(5)
O(2)Ni(1)N(3)	80.73(16)	N(1)C(7)C(21)	120.7(6)
N(1)Ni(1)N(3)	97.10(18)	C(7)N(1)Ni(1)	124.2(4)
O(1)Ni(1)O(5)	91.68(15)	C(11)N(2)Ni(1)	123.2(4)
N(2)Ni(1)O(5)	86.58(19)	C(10)N(2)Ni(1)	119.2(4)

Similarly, the probability of C(36*B*) carbon is 36% and therefore a hydrogen atom is bonded to C(25) in 64% of the time. In this case, the third model containing C(38)–C(56) is the symmetric LACH₂. The probabilities of C(56*A*) and C(56*B*) are 80 and 20%, respectively. This means that hydrogen is bonded to C(44) 20% of the time. On the other hand, the probability of hydrogen being bonded to C(48) is 80% which points that within these probabilities, the second model is the symmetric LACH₂.

In every case, two of the Schiff bases are asymmetric where the other one is symmetric in the crystal network. The HPLC result shows 67 : 33 asymmetric-symmetric Schiff base ratios. This supports the results of the X-ray diffraction stoichiometrically.

The bond lengths given in the Table 2 indicate the asymmetry, i.e. C(7)–N(1) imine bond length is 1.265 Å and the lengths of the other imine bonds are in the range 1.276 and 1.294 Å, being a little bit higher

than the first one. In Fig. 2 only the location of H(7) atom has been marked. In this imine bond the distance of C=N is the shortest. The hydrogen has been placed geometrically. For this reason, it would not be just to use the length C(7)–H(7) for comparison. However, if methyl is bonded to the imine bond, the distance of C–C rises up, to around 1.5 Å. The given bond angles were selected from the imine bond environment, therefore all are around 120°.

In Figs. 3 and 4, mass and ¹H NMR spectra of SALLACH₂ are shown, respectively. In the mass spectrum, *m/z* = 296 is the molecular peak. The molecular peaks of the symmetric Schiff bases (*m/z* = 282 and 310) were not detected in the spectrum of SALLACH₂. On the other hand, the base peak is *m/z* = 148. Other peaks belong to the fragments with *m/z* ratios 175, 162, 134, 120, 107, 91 and 77. The formation of these fragments from SALLACH₂ is given below:

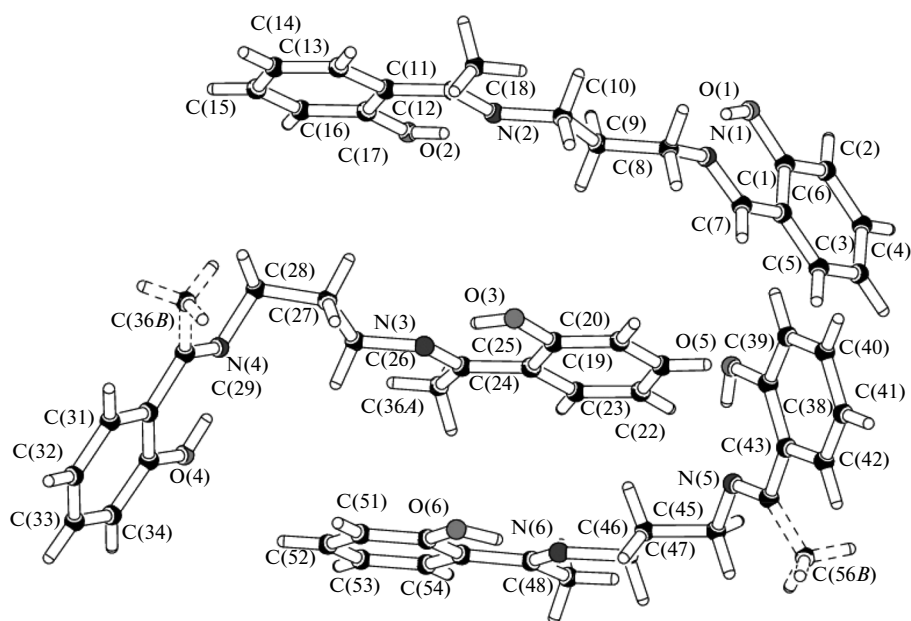


Fig. 2. The molecular model of the mixed crystal $2\text{SALLACH}_2 \cdot \text{LACH}_2$.

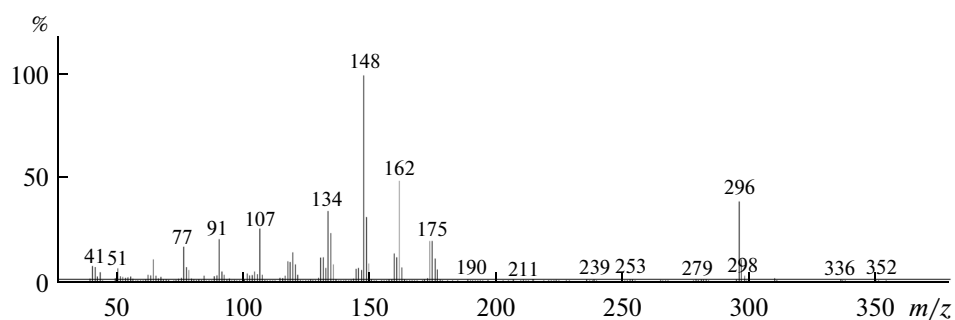


Fig. 3. The mass spectrum of SALLACH_2 obtained by Inlet prob, 2.024 s in the ion chromatogram ($T = 153^\circ\text{C}$).

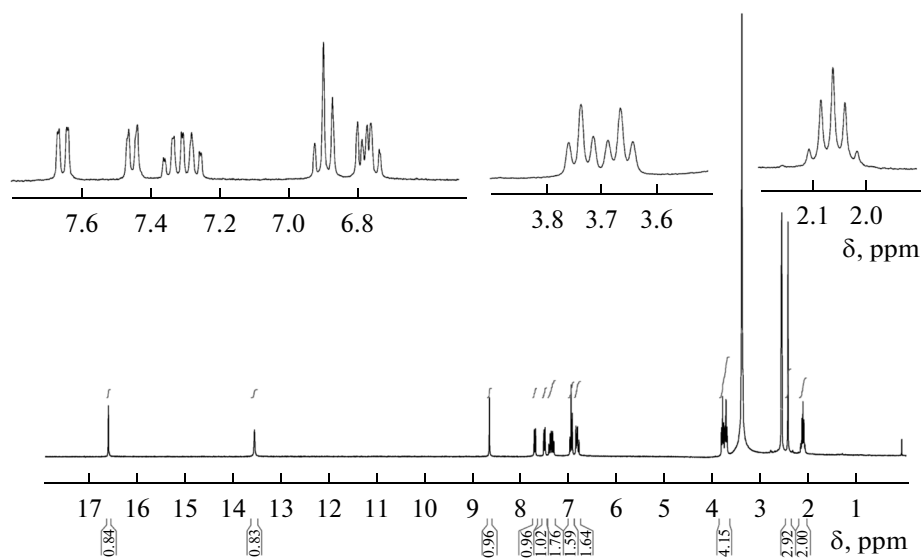
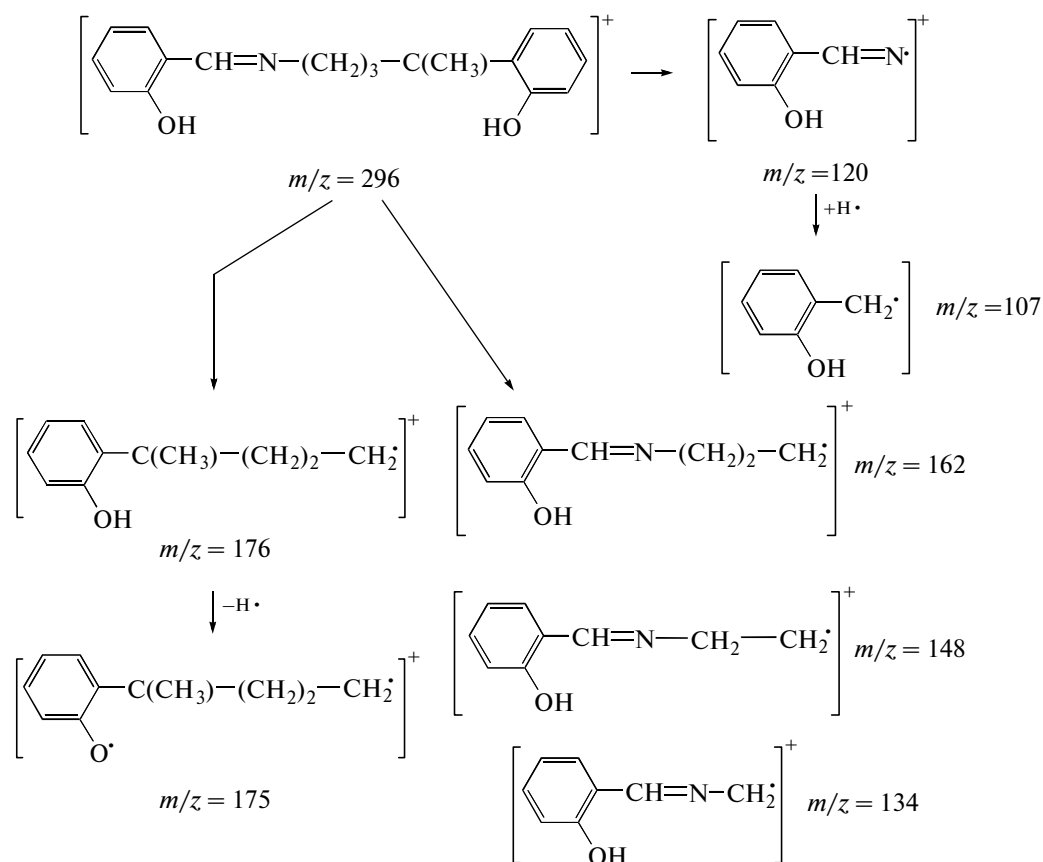


Fig. 4. ^1H NMR spectrum of refined and recrystallized SALLACH_2 .



Two different imine groups are detected in the ^1H NMR spectrum of SALLACH₂. The singlet at 8.58 ppm in Fig. 4 belongs to the iminic proton close to salicylaldehyde. The signal of the methyl group bonded to the other imine is seen at 2.40 ppm, again as a singlet. The asymmetry in the molecule is responsible for the difference of the signals of two phenolic protons, one of which at 16.55 and the other one at 13.47 ppm.

A similar case is observable for the trimethylene bridge between the imine groups. The asymmetry makes $-\text{CH}_2-$ protons different. While the methylene protons close to 2-hydroxybenzaldehyde gave triplet at 3.66 ppm, the methylene protons at the other side gave a clear triplet at 3.73 ppm. The protons of the centering methylene are affected considerably less by the asymmetry. These protons have been noticed as a pentet at 2.06 ppm. In the case of a significant asymmetry, the signal from these protons should be expected as a multiplet because that the protons of the neighboring CH_2 groups are not conjugates. Although not expected, this case can be explained. The asymmetry by the methyl group bonded to the imine group affected the neighboring methylene protons but the impressed 0.13 ppm difference was not powerful enough to be effective over the central methylene protons which force a 4 + 1 spin splitting resulting a pentet. At this point the noticeable thing is the 3 ppm difference between two

phenolic protons. Such difference cannot be explained by the electronegativity of a methyl group. It is likely that this difference emerged from the hydrogen bond between the nitrogen atom of the imine group and the phenolic hydroxide. The spectral effect of the hydrogen bonding in such Schiff bases have been long known since 1961 [26–28]. Therefore, the explanation should be just. The strong hydrogen bond vigorously affected the spectral features of the molecule. Especially in the IR spectra, hydrogen bonding hides the $\nu(\text{O}-\text{H})$ stretching or forces a shift to 1000 cm^{-1} lower-energy levels. A great number of studies have been reported on spectral effects of $\text{O}-\text{H}\cdots\text{N}=\text{C}$ hydrogen bonds [26–28]. At the same time, this hydrogen bond is one of the shortest hydrogen bonds known [29]. For this reason, although the methyl group in the imine bond is not very effective on the chemical shift, it can affect the $\text{O}-\text{H}\cdots\text{N}=\text{C}$ hydrogen bond quite significantly which creates the variation between the δ values of two phenolic protons.

^{13}C NMR spectrum also supports the findings, the signals of 18 different carbon atoms were noticed. On the other hand, in the FT-IR spectrum of SALLACH₂, two different $\nu(\text{C}=\text{N})$ stretching vibrations were detected. One of these was observed at 1631 cm^{-1} and the other one was at 1610 cm^{-1} .

Table 3. Thermoanalytical data of complexes I–VI

Complex	First thermal reaction (DMF lost)			Second thermal reaction (decomposition)	
	temperature interval, °C	theoretical mass loss, %	found mass loss, %	temperature interval, °C	found mass loss, %
I	157–185	14.17	14.02 ± 0.95	325–380	19.40 ± 2.56
II	123–158	14.11	13.53 ± 0.63	343–395	22.43 ± 3.34
III	154–187	14.23	13.96 ± 1.18	350–402	19.36 ± 3.86
IV	197–253	14.56	15.17 ± 1.33	380–490	23.45 ± 3.55
V	191–255	14.49	15.24 ± 0.85	375–465	21.65 ± 2.86
VI	201–261	14.61	16.44 ± 0.92	390–481	22.48 ± 1.97

$\nu(\text{C}=\text{N})$ Stretching of LACH_2 was observed at 1608 cm^{-1} while LH_2 's $\nu(\text{C}=\text{N})$ stretching was observed at 1629 cm^{-1} . The vibration which has been observed around 1610 cm^{-1} most probably belonged to $\nu(\text{C}=\text{N})$ stretching of the group close to the acetophenone side. This vibration must have interfered with the $\nu(\text{C}=\text{C})$ stretching of LH_2 ; because $\nu(\text{C}=\text{N})$ stretching of LH_2 has been found to be a sharp peak but in the spectrum of SALLACH_2 the peak at 1610 cm^{-1} is even stronger. $\nu(\text{C}=\text{N})$ Stretching of LACH_2 and $\nu(\text{C}=\text{C})$ stretching of LH_2 are approximately at the same energy (1608 and 1610 cm^{-1}) and both contributes the same energy in the case of SALLACH_2 . Because of this, the peak at 1610 cm^{-1} has been strengthened. With the zoom feature of the instrument the area of $1500\text{--}1700\text{ cm}^{-1}$ was examined and the presence of a shoulder shape around $1607\text{--}1608\text{ cm}^{-1}$ can be seen.

After these spectral examinations it was made sure that the asymmetric Schiff base was isolated and its complexes were studied for further evidence. The symmetric LH_2 has been known since 1946 and dozens of complexes of it have been prepared [30]. A complex having mononuclear square planar structure has been prepared with this Schiff base [31]. Later on dinuclear and trinuclear complexes have been prepared by using these mononuclear complexes [7–12]. However, there has not been any data in the literature on mononuclear and polynuclear complexes of LACH_2 . Despite the effort, unfortunately, we could not isolate mononuclear Ni(II) complex of SALLACH_2 . However, several trinuclear complexes of SALLACH_2 have been prepared in DMF by template synthesis method according to the literature. Acetate, nitrite and nitrate salts coordinated with mononuclear NiL complex with μ bridges using phenolic oxygens and trinuclear complexes were formed. Acetate, nitrite and nitrate anions of the metals joined in trinuclear complexes via μ bridge [7, 8, 11]. In this study, 6 trinuclear complexes were prepared with SALLACH_2 and acetate or nitrites of Ni(II) , Cu(II) and Mn(II) metals. These complexes characterized by IR, TG and AAS methods. Literature data, FT-IR spectra, TG and atomic absorption studies

revealed that the nuclear structure of these complexes was in the form of $\text{Ni}^{\text{II}}\text{--Ni}^{\text{II}}\text{--Ni}^{\text{II}}$, $\text{Ni}^{\text{II}}\text{--Cu}^{\text{II}}\text{--Ni}^{\text{II}}$ and $\text{Ni}^{\text{II}}\text{--Mn}^{\text{II}}\text{--Ni}^{\text{II}}$.

TG study was used for determination of the stoichiometry and characterization of complexes. In thermal decomposition of the complexes, the first group leaved from the structure is coordinated DMF. Theoretical and found mass loss is compatible and this proves that stoichiometry of the complexes (Table 3).

At first thermal reaction for complexes containing nitrite, regular mass loss corresponds to the mass of DMF at between $200\text{--}260^\circ\text{C}$ and for complexes containing acetate at between $120\text{--}180^\circ\text{C}$ (Table 3). The second thermal reaction of complexes containing nitrite is exothermic at between $400\text{--}480^\circ\text{C}$ and of complexes containing acetate at between $330\text{--}400^\circ\text{C}$. Second thermal reaction is probably decomposition of the residue. There is a research about thermal decomposition of trinuclear complexes of LH_2 in literature [32]. In this study, the second thermal reaction has been reported as endothermic and the first thermal reaction has been reported at lower temperature. However, in our study, second thermal reaction of prepared complexes using with SALLACH_2 is exothermic.

In addition, NiL mononuclear complex can be prepared with LH_2 and Ni(II) [31]. Trinuclear complexes can be prepared with symmetrical Schiff base and NiL in two steps however in this study, it was not possible two step preparation because NiSALLAC could not be prepared. In this study, complexes were prepared with template method as described in experimental section.

Judging by this point, NiSALLAC complex could not be considered as stable. After leaving coordinated DMF, the remaining units are NiSALLAC and metal acetate or nitrite. Octahedral coordination of terminal Ni^{2+} ions are distorted and Ni^{2+} ions are five-member coordination sphere [33]. Remaining portion can be stable up to a certain temperature according to coordinative strength of acetate or nitrite and after this certain temperature begin to decomposition. However, if NiSALLAC is unstable, decomposition will probably exothermic.

Suitable crystals of $\{(\text{NiSALLAC})_2\text{Ni}(\text{NO}_2)_2(\text{DMF})_2\}$ (**IV**) and $\{(\text{NiSALLAC})_2\text{Cu}(\text{NO}_2)_2(\text{DMF})_2\}$ (**V**) complexes were obtained and structures of these complexes were determined by XRD. In Fig. 5, the molecular models drawn by Pluton are shown. Terminal Ni atoms are located inside the octahedral coordination sphere among N_3O_3 donor atoms. Two out of three nitrogen donors are nitrogen atoms of SALLAC^{2-} anion and the other one is the nitrogen atom of the nitrite ion. Similarly two out of three oxygen donors are the phenolic oxygens of SALLAC^{2-} anion and the other one is of a DMF molecule. These donors have formed a facial octahedron. Central Cu and Ni atoms also have an O_6 coordination sphere. Central Cu^{2+} and Ni^{2+} ions are located between four phenolic oxygens of two SALLAC^{2-} anions and one oxygen of the nitrite groups. The phenolic oxygens and nitrite ions coordinate both terminal and central ions via a μ -bridge. The values given in Table 2 indicate that the octahedrons are not ideal. The largest angles of complex **V** around Ni^{2+} ion are $\text{N}(2)\text{N}(1)\text{O}(1)$ 171.05° , $\text{N}(1)\text{Ni}(1)\text{O}(2)$ 171.32° and $\text{N}(3)\text{N}(1)\text{O}(5)$ 168.26° . On the other hand, the longest bonds around Ni^{2+} ion are $\text{Ni}-\text{N}(5)$ 2.162 and $\text{Ni}-\text{O}(5)$ 2.152 Å.

Although the $\text{N}(3)\text{Ni}(1)\text{O}(5)$ angle is equal to 168.26° , the bond lengths indicate that the apical position of the octahedron is around $\text{N}(3)\text{Ni}(1)\text{O}(5)$. Whereas the largest angles of terminal Ni^{2+} ions of complex **IV** are $\text{N}(2)\text{Ni}(1)\text{O}(2)$ 169.10° , $\text{N}(1)\text{Ni}(1)\text{O}(3)$ 171.75° , $\text{N}(3)\text{Ni}(1)\text{O}(1)$ 171.28° and the longest bonds around terminal Ni^{2+} ions are $\text{Ni}-\text{N}(2)$ 2.135 and $\text{Ni}-\text{O}(2)$ 2.165 Å. The $\text{N}(2)-\text{Ni}-\text{O}(1)$ direction can be called as apical axis of this complex. However, considering the general terms, the distortion of the octahedron can be said to be low. For the distortions around central Cu^{2+} and Ni^{2+} ions, a clear cut statement would not be just because some of the bond angles have been calculated as 180.0° due to the symmetry. It was not possible to take the ^1H NMR and ^{13}C NMR spectra of the complex, because the complex hardly dissolves in DMF. But as it was referred in the experimental part, the results from FT-IR, elemental and TG analysis were found to be in good agreement. The mass of the DMF molecules coordinating the terminal Ni^{2+} ions were found to be $15.24 \pm 0.85\%$ and 15.17 ± 1.33 in average. It is quite close to the theoretically expected result being 14.50 and 14.56%, respectively. In the FT-IR spectrum of the complex, $\nu(\text{C}=\text{N})$ stretching vibrations were observed at 1598 cm^{-1} . So the energy of these vibrations shifted approximately 33 cm^{-1} in comparison with the ligand alone which was the expected outcome [34, 35]. The data in Table 2 indicate no significant change in bond lengths of the ligand in case of complex formation.

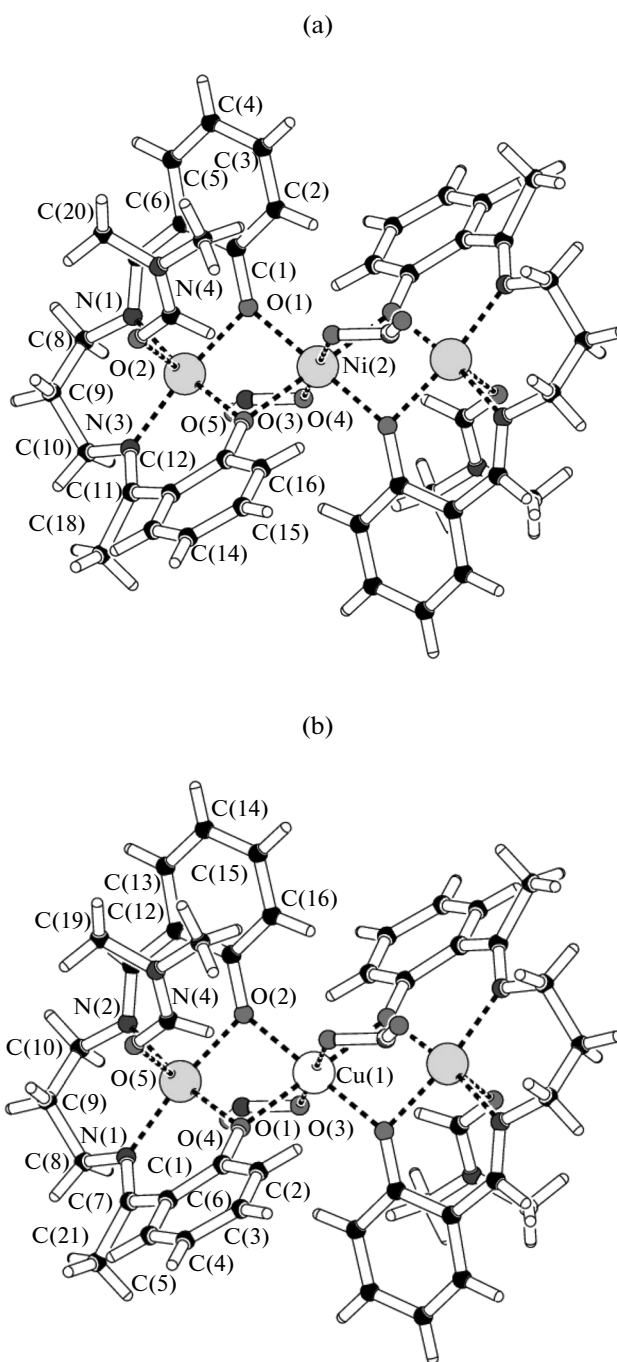


Fig. 5. PLUTON drawings of complexes **IV** (a) and **V** (b).

ACKNOWLEDGMENTS

Financial support of this work by the University of Ankara Scientific Research Fund (contract no. 12B4240003) and Ahi Evran University Scientific Research Fund (contract no. 4001.12.014) are gratefully acknowledged. We are indebted to and thank Prof. Dr. Wolfgang Donner for providing laboratory facilities at TU Darmstadt.

REFERENCES

- Peiffer, P., Breith, E., Lübbe, E., and Tsumaki, T., *Annal. Chim.*, 1933, vol. 502, p. 84.
- Martell, A.E. and Calvin, M., *Die Chemie der Metallchelate-Verbindungen*, Weinheim: Verlag Chemie, 1958, p. 199.
- Kato, M., Jonassen, H.B., and Fanning, J.C., *Chem. Rev.*, 1964, vol. 64, p. 99.
- Kato, M. and Muto, Y., *Coord. Chem. Rev.*, 1988, vol. 92, p. 45.
- Metalobos, J.S., Deibe, A.M.G., Fondo, M., et al., *Inorg. Chem. Commun.*, 2004, vol. 7, p. 311.
- Bhowmik, P., Drew, M.G.B., and Chattopadhyay, S., *Inorg. Chim. Acta*, 2011, vol. 366, p. 62.
- Fukuhara, C., Tsuneyoshi, K., Matsumoto, N., et al., *Dalton Trans.*, 1990, p. 3473.
- Uhlenbrock, S., Wegner, R., and Krebs, B., *Dalton Trans.*, 1996, p. 3731.
- You, Z.L., Zhu, H.L., and Liu, W.S., *Z. Anorg. Allg. Chem.*, 2004, vol. 630, p. 1617.
- Song, Y., Gomez, P., Roubeau, O., et al., *Inorg. Chim. Acta*, 2005, vol. 358, p. 109.
- Regliski, J., Taylor, M.K., and Kennedy, A.R., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 736.
- Yu, T., Zhang, K., Zhao, Y., et al., *Inorg. Chem. Commun.*, 2007, vol. 10, p. 401.
- Mustapha, A., Busche, C., Reglinski, J., and Kennedy, A.R., *Polyhedron*, 2011, vol. 30, p. 1530.
- Munde, A.S., Jagdale, A.N., Jadhav, S.M., and Chondhekar, T.K., *J. Serbian Chem. Soc.*, 2010, vol. 75, p. 349.
- Nejo, A.A., Kolawole, G.A., and Nejo, A.O., *J. Coord. Chem.*, 2010, vol. 63, p. 4398.
- Asadi, M. and Asadi, Z., *J. Coord. Chem.*, 2008, vol. 61, p. 640.
- Tang, B., Sun, X.P., Liu, G.L., and Li, H., *J. Mol. Struct.*, 2010, vol. 984, p. 111.
- Shebl, M., Khalil, S.M.E., Ahmed, S.A., and Medinen, H.A.A., *J. Mol. Struct.*, 2010, vol. 980, p. 39.
- Kolawole, G.A. and Osowole, A.A., *J. Coord. Chem.*, 2009, vol. 62, p. 1437.
- Ghosh, M., Fleck, M., Mahanti, B., et al., *J. Coord. Chem.*, 2012, vol. 65, p. 3884.
- Fee, W.W., Pulsford, J.D., and Vowles, P.D., *Aust. J. Chem.*, 1973, vol. 26, p. 1459.
- Atakol, O., Boca, R., Ercan, I., et al., *Chem. Phys. Lett.*, 2006, vol. 423, p. 192.
- Oxford Diffraction CrysAlis CCD and CrysAlis RED*, Version 1.170.14, Oxfordshire (England): Oxford Diffraction, 2002.
- Sheldrick, G.M., *SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
- Farrugia, L.J., *J. Appl. Cryst.*, 1999, vol. 32, p. 837.
- Freedmann, H.H., *J. Am. Chem. Soc.*, 1961, vol. 83, p. 2900.
- Golubev, N.S., Smirnov, S.N., Tolstoy, P.M., et al., *J. Mol. Struct.*, 2007, vol. 844, p. 319.
- Užarević, K., Rubčić, M., Stilinović, V., et al., *J. Mol. Struct.*, 2010, vol. 984, p. 232.
- Steiner, T., *Angew. Chem. Int. Ed.*, 2002, vol. 41, p. 48.
- Bailes, R.H. and Calvin, M., *J. Am. Chem. Soc.*, 1947, vol. 69, p. 1886.
- Drew, M.G.B., Prasad, R.N., and Sharma, R.P., *Acta Crystallogr., C*, 1985, vol. 41, p. 1755.
- Durmuş, S., Ergun, U., Jaud, J.C., et al., *J. Therm. Anal. Cal.*, 2006, vol. 86, p. 337.
- Atakol, O., Nazır, H., Arıct, C., et al., *Inorg. Chim. Acta*, vol. 342, p. 295.
- You, Z.L., Zhu, H.L., and Liu, W.S., *Z. Anorg. Allg. Chem.*, 2004, vol. 630, p. 1617.
- Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley-Interscience Publication, 1997.