

Synthesis and Spectroscopic Characterization of New N-(1-(2,4-dihydroxyphenyl)ethylidene)-2-hydroxybenzohydrazide Transition Metal Ion Complexes with Ni(II), Zn(II) and Cd(II)

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Abstract

A new tetrahedral ligand *N'*-(1-(2,4-dihydroxyphenyl)ethylidene)-2-hydroxybenzohydrazide (H₂L) was synthesized by refluxing 1-(2,4-dihydroxyphenyl) ethanone with 2-hydroxybenzohydrazide. Three transition metal complexes with Cd²⁺, Ni²⁺ and Zn²⁺ were also synthesized with H₂L. Characterization of all newly synthesized compounds was achieved using elemental analyses, mass spectroscopy, magnetic susceptibility, molar conductivity, UV–VIS, IR and ¹HNMR, spectral studies. Studies indicate that the complexes are expected to exist in distorted octahedral shape and the ligand coordinates through azomethine nitrogen and two phenolic oxygens, in addition to the two water molecules.

Keywords: Ethylidene, Hydrazide, Ethanone, Complexes.

Introduction

The development of the so-called Schiff base compounds has attracted a lot of interest in the fields of coordination chemistry and material sciences^[1]. The Schiff base can accommodate different metal centers involving various coordination modes thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry^[1]. In recent years, great attentions have been paid to the Schiff bases ligands that contain N-donor bridging. Transition Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms^[1]. The use of ligands in generation of metal complexes is relatively light, they are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agent^[2, 3].

The hydrazones constitute important class medicinal compounds due to their wide variety of pharmacological and analytical applications^[2-5]. They also bestow applications in floral arena as plant growth regulators^[6, 7]. Actually salicylaldehydes are valuable for the synthesis of transition metal complexes due to their application as ion-selective electrode^[8]. Some complexes containing nitrogen and oxygen donor atoms are effective as stereospecific catalysts for oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry^[1, 9].

In this study a newly *N'*-(1-(2,4-dihydroxyphenyl)ethylidene)-2-hydroxybenzohydrazide (H₂L) Schiff base has been synthesized by condensation reaction of 1-(2,4-dihydroxyphenyl) ethanone with 2-hydroxybenzohydrazide. Cd²⁺, Ni²⁺ and Zn²⁺ metal ion complexes with ligand were also synthesized and characterized using different physicochemical techniques.

Method Experimental Work

Materials

All the chemicals and reagents were of analytical grade and were used as supplied without any further purification. The solvents used in the synthesis are absolute ethanol (99.8%, Scharlau), ethanol (95%, Hamburg), dimethylsulphoxide (Scharlau), while the metal salts used for synthesis are cadmium(II) acetate (BDH), nickel(II) acetate tetrahydrate (Fluka) and zinc(II) acetate dihydrate (Fluka).

Physical Measurements

Melting points were carried out using Gallenkamp M.F.B 6000. The infrared spectra of the prepared compounds were recorded using FT-IR-8300-Shimadzu, in the wave length range of (4000-400) cm⁻¹. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000 (Flame Atomic Absorption Spectrophotometer for the determination of (M²⁺) metal ions at certain

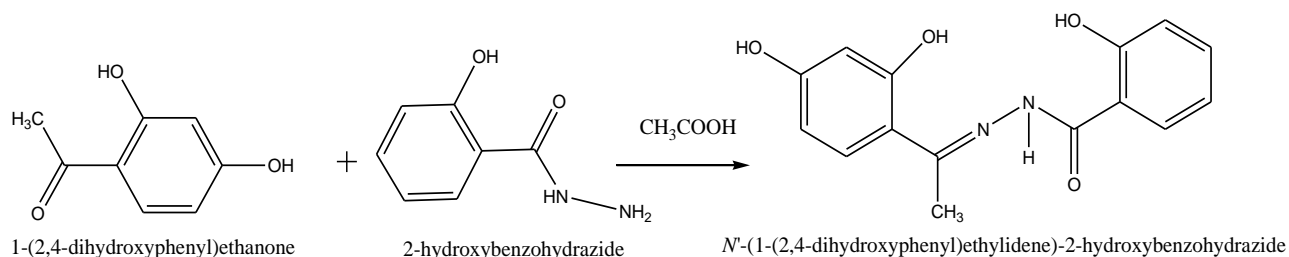
wavenumber. The measurements were carried out using (GBC-933 Flame). Carbon, hydrogen, nitrogen elemental analyses were carried out using a Leco CHNS-932 analyzer.

The electronic spectra of the prepared compounds were obtained using (UV-Vis-160A) Shimadzu Spectro-photometer, with wave-length range (200-1100 nm) using (DMSO) at (10^{-5} M). The molar conductivity measurements were carried out using Wissenschaftlich-TechnischWerk-statten 1120 Weilheim I.O.B, Drucker-Printer. The magnetic susceptibility values were obtained at room temperature using (Magnetic Susceptibility Balance), of Johnson matthey catalytic system division. Mass spectra were recorded using Shimadzu Gas Chromatography- Mass Spectrometer (GCMS-QP5050A) using direct injection (DI-MS) technique. The sample was subjected to radiofrequency waves and the resonance peaks were recorded once reorientation occurred to the nuclear spin of the sample molecules and detected by the JEOL ECA 400 MHz NMR spectrometer. Dimethylsulphoxide (DMSO) was used as a solvent and the internal standard for NMR spectra recorded was tetramethylsilane (TMS).

Preparation of *N'*-(1-(2,4-dihydroxyphenyl) ethylidene)-2-hydroxybenzohydrazide(H₂L) Ligand

The ligand was prepared by modification of a literature method [11]. The ligand *N'*-(1-(2,4-dihydroxyphenyl) ethylidene)-2-hydroxybenzohydrazide (H₂L) was prepared by the condensation reaction of 1-(2,4-dihydroxyphenyl) ethanone with 2-hydroxybenzohydrazide. An equimolar mixture in absolute ethanol (30 mL) were refluxed. A few drops of glacial acetic acid were added as catalyst. The mixture was heated under reflux for 24 h. The gained precipitate was isolated by filtration, washed with diethyl ether, recrystallized, and then dehydrated under vacuum. The yield was 70,2%. The reaction is showing below:

¹H-NMR (DMSO δ ppm): 11,02 (singlet 1H, NH), 9,83-10,61 (multiple phenolic-H), 7,38-7,82 (multiple aromatic-H), 3,02 (singlet 3H, -CH₃).



Synthesis equation of the (HPEHB) ligand.

Preparation of Metal Complexes

The complexes were prepared using a general procedure [12] in which an ethanol solution (≈ 20 ml) of each of metal salt were added to a solution of the ligand (≈ 10 ml) which dissolved in absolute ethanol. The equimolar mixture were refluxed with stirring for three hours, the resulting precipitate were filtered and washed with diethyl ether and recrystallized from hot 90% ethanol then dried under vacuum. The obtained metal complexes were crystalline, non-hygroscopic and stable at

room temperature. Table (1) shows the physical properties of the ligand and metal complexes.

Table (1)
Physical properties of the new compounds.

Molecular formula	Colour	M.P (°C)	Yield (%)	Molecular weight (g.mol ⁻¹)	Symbol	% Found(calculated)			
						C	H	N	Metal (%)
C ₁₀ H ₁₂ N ₂ O ₂	Yellow	> 300	70,2	286,10	H.L	71,79 (72,93)	8,81 (8,93)	9,79 (9,78)	-
C ₁₀ H ₁₂ CdN ₂ O ₂	Yellow	> 300	77,0	432,71	Cd(II) H.L. 2H ₂ O	42,37 (41,64)	3,81 (3,73)	6,39 (6,47)	20,26 (20,98)
C ₁₀ H ₁₂ ZnN ₂ O ₂	Yellow	> 300	78,2	380,69	Zn(II) H.L. 2H ₂ O	47,44 (47,71)	4,26 (4,18)	7,37 (7,26)	17,34 (17,90)
C ₁₀ H ₁₂ NiN ₂ O ₂	Dark brown	> 300	79,7	378,99	Ni(II) H.L. 2H ₂ O	40,33 (47,04)	4,17 (4,26)	7,26 (7,39)	14,77 (10,49)

Results and Discussion

The complexes were analyzed for carbon, hydrogen and nitrogen contents and their percentages. The analytical data for the ligand and the complexes are given in Table (1) above.

Metal and elemental analysis in Table (1) shows that the stoichiometry of the complexes was found to be 1:1 (M:L) and the experimental values of CHN and the metal contents are in a good agreement with the theoretical values.

UV-Visible Spectroscopy, Magnetic Susceptibility and Molar Conductivity Analyses

The electronic spectrum of the Schiff base exhibits band at 314 nm ascribed to the n-π* transitions. Table (2) shows the transitions

bands of the Schiff base and its metal complexes. The electronic spectra of the Cd²⁺ and Zn²⁺ complexes displays bands at 362 nm and 306 nm respectively which attribute to π-π* transitions, while the bands at 306 nm and 308 nm respectively assigned to n-π* transitions. The bands at 426 nm that appears in Ni²⁺ spectrum belong to ligand metal charge transfer (L-MCT) [17].

Conductivity measurements of complexes were carried out in 10⁻³ M dimethyl sulphoxide (DMSO) solvent. The molar conductance values are listed in the Table (2). The table reveals that the conductance values of all the metal complexes lie in the range of non-electrolytes [18]. The magnetic susceptibility measurements, Table (2), show that all the metal complexes have diamagnetic nature [19].

Table (2)
Magnetic, Conductivity and Electronic data for the Ligand and the Metal Complexes in (10⁻³ M) Using DMSO solvent.

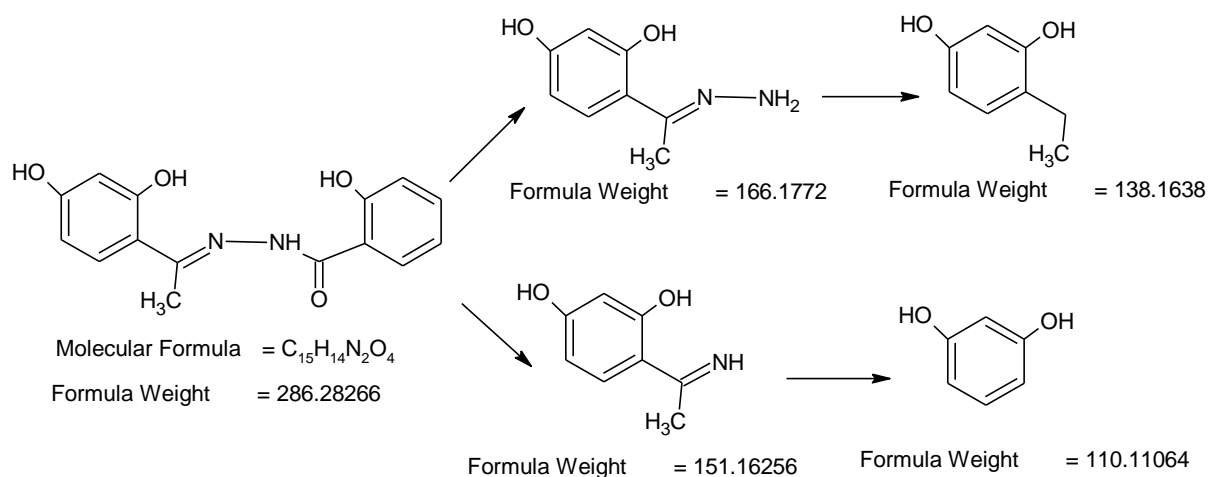
Complex	Magnetic Property μ _{eff} . (B.M.)	Conductivity μS.cm ⁻¹	λ _{max} (log ε) (nm)	Suggested structure
H.L	-	-	314 (3,42)	-
Cd(II) H.L. 2H ₂ O	Diamagnetic	2,40	306 (4,07), 362 (3,46)	Distorted O.H
Zn(II) H.L. 2H ₂ O	Diamagnetic	4,87	308 (3,80), 306 (3,94)	Distorted O.H

Ni(II) H ₂ L·2H ₂ O	Diamagnetic	λ, 92	ε ₂₂₆ (3,00), 336 (3,02), 300 (ε, 22)	Distorted O.H
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Mass Spectroscopy

The mass spectroscopic analysis was used to assist in determining the molecular formula of the ligand and to predict its structure through the examination of fragment ions. The relatively low intensities of the molecular ion peaks [M]⁺, is indicative of the ease of

fragmentation of the compound and this has reflected the number of heteroatoms present in the structure. Fig.(1) shows the mass spectrum of the ligand while the fragment ions and the mass fragmentation patterns are shown below:^[17]



Fragmentation of the Ligand.

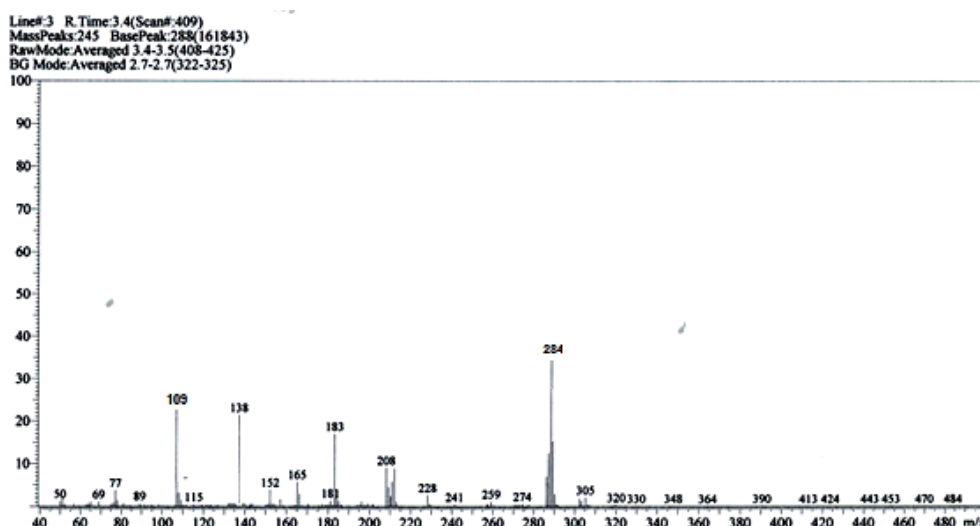


Fig.(1) Mass Spectrum of the new Schiff base.

Infrared Spectral Studies

The IR spectral data of the ligand and its metal complexes are shown in Table (3); it showed that the ligand H₂L behaves as a dinegatively tetradentate of the type N₂O₂ with

two coordinating sites (N, O). This behavior was proved by the shift of ν(C=N), ν(C=O) signals to lower frequencies (1660, 1608, 1679 cm⁻¹) respectively for (C=O) and (1604, 1612 and 1608 cm⁻¹) respectively for (C=N).

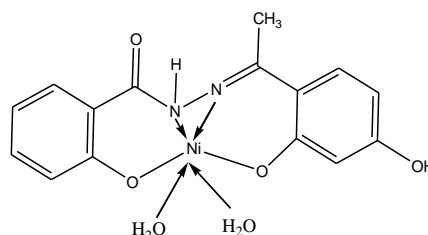
The simultaneous appearance of new bands in the $509-510\text{ cm}^{-1}$ and $423-432\text{ cm}^{-1}$ is due to (M-O) and (M-N) suggesting the coordination of the metal ions with the ligand via nitrogen and oxygen^[17,18]. $1608, 1679\text{ cm}^{-1}$ respectively for (C=O) and ($1604, 1612$ and 1608 cm^{-1} respectively for (C=N). The

simultaneous appearance of new bands in the $509-510\text{ cm}^{-1}$ and $423-432\text{ cm}^{-1}$ is due to (M-O) and (M-N) suggesting the coordination of the metal ions with the ligand via nitrogen and oxygen^[17,18].

Table (3)
Infra-Red spectral data (cm^{-1}) for ligand and metal complexes.

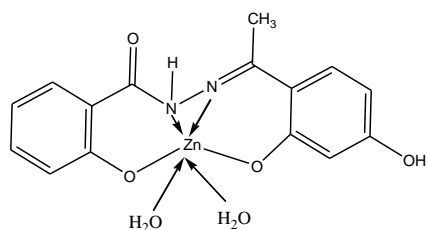
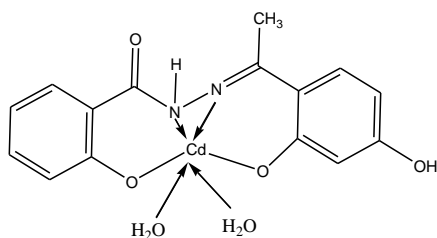
Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
H ₂ L	1617	1710	1107	-	-
Cd(II) H ₂ L.2H ₂ O	1604	1660	1128	509	432
Zn(II) H ₂ L.2H ₂ O	1612	1608	1123	510	423
Ni(II) H ₂ L.2H ₂ O	1608	1679	1118	513	428

The suggested structures of the metal complexes are shown below where the complexes shows two vicinal nitrogen atoms coordinating a metal center due to attraction of amide hydrogen by the oxygen of carbonyl group which increase the possibility of the amide nitrogen to coordinated to the central metal as was presented by Kumar *et al*, 2012^[19].



Conclusion

New Schiff base H₂L and its (M²⁺) complexes were prepared and characterized using elemental analysis. The study confirmed that the ligand was coordinated to the central metal ion as di-negatively charged coordinated ligand. Based on the data obtained, the stoichiometry and the tentative structure for the metal complexes were suggested to be in distorted octahedral.



Suggested structures of the metal complexes.

References

- [1] Gulsen, T.; Halil, B.; Hakan, D.; Cemil, O. "Synthesis, characterization, tautomerism and theoretical study of some new Schiff base derivatives"; Spectrochimica Acta; Part A 79, 1073-1083, 2011.
- [2] Naeimi, H.; Rabiei, K.; Salimi, F. "Rapid, efficient and facile synthesis and characterization of novel Schiff bases and their complexes with transition metal ions"; Dyes and Pigments. 70, 294-297, 2007.
- [3] Osowole, A.A.: Syntheses and Characterization of Some Tetradentate Schiff-Base Complexes and Their Heteroleptic Analogues"; E-Journal of Chem. 5(1), 130-135, 2008.
- [4] Deshpande, M.M.; Seema I.H.; Kulkarni, P.A. "Preparation, Physical Characterization and Antimicrobial Evaluation of Co(II), Ni(II) and Fe(III) Complexes of Heterocyclic Schiff Bases"; Int. J. Bio. & Pharma. Res., 4(6), 460-464, 2013.
- [5] Tamasi, G.; Chiasserini, L.; Savini, L.; Sega, A.; Cini, R. "Structural study of ribonucleotide reductase inhibitor hydrazones. Synthesis and X-ray diffraction analysis of a copper (II)-

- benzoylpyridine- γ -quinolinyl hydrazone complex"; J. Inorg. Biochem. 99(6). 1347-59. 2005.
- [7] Sriram, D.; Yogeewari, P.; Madhu, K. "Synthesis and in *vitro* and in *vivo* antimycobacterial activity of isonicotinoyl hydrazones"; Bioorg. Med. Chem. Lett. 10(20), 4502-5. 2005.
- [8] El-Sherif, A.A. "Synthesis, spectroscopic characterization and biological activity on newly synthesized copper(II) and nickel(II) complexes incorporating bidentate oxygen-nitrogen hydrazone ligands"; Inorg. Chim. Acta, 362(14), 4991-5000. 2009.
- [9] Mohammed, B.; Orville, G.; Willem, H.M. "Synthesis, characterization and molecular sensing behavior of $[ZnCl_2(\eta^2-N,N,O-dpkbh)](dpkbh=di-\gamma$ -pyridyl ketone benzoyl hydrazone). J. Mol. Str.1, 873(1-3), 17-28. 2008.
- [10] Al-Hazmi, G. A.; El-Asmy, A.A. "Synthesis, spectroscopy and thermal analysis of copper(II) hydrazone complexes"; J. Coord. Chem. 62(2), 337-345. 2009.
- [11] Abbaspour, A.; Esmailbeig, A.R.; Jarrahpour, A.A.; Khajeh, B.; Kia, R. "Aluminium (III)-selective electrode based on a newly synthesized tetradentate Schiff base"; Talanta. 58(2), 397-403. 2002.
- [12] Basu, A.; Das, G. "Zn (II) and Hg(II) complexes of naphthalene based thiosemicarbazone: Structure and spectroscopic studies". Inorg. Chim. Acta. 372, 394-399. 2011.
- [13] Hakan, E.; Okan, Z.; Cihan, D.; Orhan, B. "Synthesis, spectroscopic, thermal Studies, antimicrobial activities and crystal structures of Co(II), Ni(II), Cu(II) and Zn(II)-orotate complexes with γ -methylimidazole"; Polyhedron. 28(14), 3087-3093. 2009.
- [14] Al-Hassani, R.A.M.; Mhammed, S.M.; Rasheed, E.M. "Synthesis, Characterization and Biological Study of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with a New Tetradentate Schiff Base Ligand"; Iraqi National J. Chem. 43. 2011.
- [15] Gutmann, V. "The Donor-Acceptor Approach to Molecular Interaction"; Plenum Press; N.Y. (USA). pp. 25-37. 1988.
- [16] Tarafder, M.; Kasbollah, A.; Crouse, K.; Ali, M.; Yamin, M.; Fun, H.K. "Synthesis and Characterisation of Zn(II) and Cd(II) complexes of S-benzyl- β -N-(γ -pyridyl) methylenedithiocarbamate (HNNS): bioactivity of the HNNS Schiff base and its Zn(II), Cu(II) and Cd(II) complexes and the X-ray structure of the $[Zn(NNS)_2]$ complex"; Polyhedron. 20, 2363-2370. 2001.
- [17] Mitra, A.; Banerjee, T.; Roychowdhury, P.; Chaudhuri, S.; Bera, P.; Saha, N. "Synthesis and spectroscopic characterisation of cobalt (III) complexes with S-benzyl dithiocarbamate of ρ -methyl- γ -formyl pyrazole (HMPzSB): X-ray crystal structure of $[Co(MPzSB)_2]Cl$ "; Polyhedron. 16(21), 3735-3742. 1997.
- [18] Kumar, G.; Kumar, D.; Devi, S.; Johari, R.; Singh, C.P. "Synthesis, spectral characterization and antimicrobial evaluation of Schiff base Cu (II), Ni (II) and Co (II) complexes"; Eur. J. Med. Chem. 45, 3056-3062. 2010.
- [19] Boghaei, D.M.; Gharagozlou, M. "Spectral characterization of novel ternary zinc(II) complexes containing 1,10-phenanthroline and Schiff bases derived from amino acids and salicylaldehyde- ρ -sulfonates"; Spectrochim. Acta A. 67, 944-949. 2007.
- [20] Kumar, K.; Parasad, A.; Srilaltha, V., Swami, G.; Ravindranath, L. "Synthesis and Characterization of Iron Complexes of Resacetophenone Salicyloyl Hydrazone"; Chem. Bull. "POLITEHNICA" Univ. (Timisoara). 57(71), 1-8. 2012.

الخلاصة

ليكاند جديد رباعي السطوح ن²⁺-1-(2,4-ثنائي هيدروكسي فنييل) اثيليدين)-2-هايدروكسي بنزوهيدرازين (H₂L) قد تم تحضيره بتصعيد 1-(2,4-ثنائي هيدروكسي فنييل) ايثانول مع 2-هايدروكسي بنزوهيدرازيد. ثلاثة معقدات من العناصر الانتقالية من ثنائي الكادميوم، ثنائي النيكل، وثنائي الخارصين قد تم تحضيرها مع (H₂L). تشخيص جميع المركبات المحضرة قد تم انجازه باستخدام

الدراسات الطيفية لآهزة تحليل للعناصر، المطيف الكتلي،
الحساسية المغناطيسية، التوصيلية المولارية، فوق البنفسجية
- المرئية، تحت الحمراء و الرنين المغناطيسي. الدراسات
تشير الى ان المتوقع بان المعقدات تكون على شكل ثماني
السطوح المشوه وان الليكند يتناسق من خلال نيتروجين

الازوميثان واثنين اوكسجين الفينولية بالاضافة الى حزينتين
ماء.