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Rapid Microwave-Assisted Solution Phase Synthesis and Spectroscopic Characterization of Salicylidene-o-Aminophenol and Its Metal(II) Complexes

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Rapid Microwave-Assisted Solution Phase Synthesis and Spectroscopic Characterization of Salicylidene-o-Aminophenol and Its Metal(II) Complexes

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Salicylidene-o-aminophenol and its Zn(II), Cd(II) complexes are synthesized by rapid microwave-assisted solution phase method and characterized by elemental analysis, IR, ES-MS, and molar conductivity. The structure of salicylidene-o-aminophenol was also confirmed by X-ray diffraction.

Keywords salicylidene-o-aminophenol, complex, synthesis, microwave irradiation

INTRODUCTION

Schiff bases and the relevant transition metal complexes containing nitrogen and oxygen donor atoms play important role in biologic and inorganic chemistry and have been studied extensively.^[1-4] The traditional synthesis for them is often carried out by refluxing the mixture of aldehyde (or ketone) and amine for several hours.^[5,6] Its disadvantage of longer reaction time makes people to seek a more effective method. Solid-phase reaction at room temperature^[7,8] or solvent-free synthesis assisted by microwave irradiation^[9] has been successfully employed for Schiff-base formation in the condition of uniform mixing. However, the remarkable merits of simple procedure and excellent homodispersity make the solution synthesis a convenient practicing method, when the reaction time is highly shortened with the aid of microwave irradiation. As a heating method, microwave irradiation has been found to have many uses in chemistry due to its convenient, simple, rapid, and environmentally friendly characteristics.^[10] Herein, on the basis of previous reports,^[6] salicylidene-o-aminophenol and its metal(II) complexes were synthesized in methanol solution assisted by microwave irradiation in 5 min. They were characterized by elemental analysis, IR, ES-MS, and molar conductivity. The formation of salicylidene-o-aminophenol was also confirmed by X-ray diffraction.

EXPERIMENTAL

Materials and Instruments

All the starting materials and solvents were of analytical purity. Elemental analysis was determined with a Perkin-Elmer 240C instrument. Solution electrical conductivity was measured by a BSD-A numerical conductometer (Jiangsu, China) with solution concentration of $\sim 1.0 \times 10^{-3}$ mol \cdot dm⁻³ in methanol at 279 K. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. The ES mass spectral measurement of the complexes was carried out on a LCQ System (Finngann MAT, USA) using methanol as mobile phase.

Microwave irradiation experiments were carried out in HY-7001 microwave reactor at a frequency of 2.45 GHz with continuous microwave irradiation power from 0 to 700 W. The microwave reactor, which was designed by Huaihai Institute of Technology, was composed of a microwave cavity, electromagnetic stirrer, water condenser, and microcomputer-based control system.^[11]

Synthesis of Schiff Base and Its Complexes

The mixture of salicylaldehyde (5 mmol) and o-aminophenol (5 mmol) in 25 cm³ absolute methanol was placed in the microwave reactor and subjected to microwave irradiation for 5 min. Microcrystals of salicylidene-o-aminophenol (L) were obtained on the removing solvent. Orange-brown single crystals suitable for X-ray structure determination were obtained by slow evaporation of its methanol solution for about 4 days at ambient temperature.

The mixture of salicylaldehyde (5 mmol), $M(ClO_4)_2 \cdot 6H_2O$ (5 mmol), and o-aminophenol (5 mmol) in 30 cm³ absolute methanol was placed in the microwave reactor and subjected to microwave irradiation for 5 min. Microcrystals of complexes

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Compounds	Yield (%)	$\begin{array}{c} \Lambda_M\\ (\mathbf{S}.\mathbf{cm}^2.\mathbf{mol}^{-1}) \end{array}$	Empirical formula	Anal. found (Calcd.) (%)			
				С	Н	N	
L	96	—	$C_{13}H_{11}NO_2$	73.01 (73.24)	5.12 (5.16)	6.61 (6.57)	
$ZnL \cdot H_2O$	94	20	$C_{13}H_{11}NO_3Zn$	53.20 (53.24)	3.76 (3.75)	4.82 (4.78)	
CdL·4H ₂ O	95	23	$C_{13}H_{17}NO_6Cd$	39.34 (39.29)	4.22 (4.28)	3.51 (3.53)	

TABLE 1 Analytical data for the compounds

were obtained on removing solvent. Table 1 lists analytical data of the compounds.

Crystallographic Measurements

An orange-brown block single crystal of dimensions $0.14 \times 0.30 \times 0.38$ mm was mounted on a glass fiber. The crystal data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with *Mo-Ka* radiation ($\lambda = 0.71073$ Å) over the range $2.22 \le \theta \le 25.01^\circ$ with a ω scan mode. Data reductions and cell refinements were performed with Smart-CCD software. An absorption correction by using SADABS software was applied. The structures were solved by direct methods and refined by full-matrix least squares on F² using SHELXL-97.^[12] The oxygen atoms of hydroxyl groups in one molecular unit L₁ were found disordered, and the site occupancy factor of O1, O2, O1', O2' were fixed at 0.5 and refined isotropically. All H atoms were placed in calculated position. Table 2 lists relevant crystallographic data.

RESULTS AND DISCUSSION

Microwave-Assisted Synthesis

Microwave is an electromagnetic wave containing electric and magnetic field components. Microwave irradiation is known to induce some specific effects on molecular motion such as the migration of ions and dipoles, so it can cause molecularlevel heating that leads to homogeneous and quick thermal reaction.^[13] The dependence of the yield of the objective products on the microwave irradiation time, power, and the quantity of solvent CH₃OH was tested in our experiment. The result shows that the yield increases rapidly with the heating time and approaches a maximum within ca. 5 min. The quantity of solvent CH₃OH also has inference to the reaction. To a certain range, the appropriate solvent quantity increase will improve conversion rate, but the solvent's continuing rise (more then 30 mL) will no longer benefit to the reaction. So the solvent volume of 25 to 30 mL is an optimization. In the above optimum condition, microwave irradiation power was adjusted to 220 W, so that the reaction system had a moderate reflux.

Spectroscopic Characterization

Elemental analyses, IR, and ES-MS spectra of the compounds indicated that a Schiff base structure was formed. Condensation of all primary amine groups and carbonyl groups is confirmed by the lack of N-H double stretching bands in the IR region 3150–3450 cm⁻¹ and the presence of strong C=N stretching bands at 1623–1630 cm⁻¹. The mass spectra of the complexes showed that the parent peaks compare well with their formula weights. The main peak at m/z 276.3 in ZnL·H₂O is assigned to [ZnL+H]⁺, and the peak at m/z 325.6 in CdL·4H₂O is corresponding to [CdL+H]⁺. The molar conductivity of the complexes (Λ_M (CH₃OH, 289K) = 20–23 S·cm²·mol⁻¹) is attributable to non-electrolyte and molecular complex. But the coordination geometry of ZnL·H₂O and CdL·4H₂O is not very clear.

TABLE 2 Crystallographic data for salicylidene-o-aminophenol (L)

Empirical formula	C ₂₆ H ₂₂ N ₂ O ₄
Formula weight	426.46
Crystal system	Monoclinic
Space group	C2/c
a/Å	38.24(3)
b/Å	9.012(6)
c/Å	12.295(9)
$\beta/(^{\circ})$	105.909(12)
V/Å ³	4075(5)
Z	8
μ/mm^{-1}	0.095
θ range/(°)	$2.22^\circ \le \theta \le 25.01^\circ$
$D_{cal}/(g \cdot cm^{-3})$	1.390
F(000)	1792
Reflections measured/unique	10,045/3546
	$[R_{int} = 0.1547]$
Goodness of fit on F^2	1.001
R_1/wR_2	0.0883/0.1656
Largest difference peak and hole/($e \cdot \mathring{A}^{-3}$)	0.378/-0.625



FIG. 1. Crystal structure of L.

Crystal Structure of Salicylidene-o-Aminophenol (L)

The structure of salicylidene-o-aminophenol (L) was further confirmed by single-crystal X-ray diffraction. The crystal structure of L is shown in Figure 1. It consists of two different molecular units of L₁ and L₂, joined together through hydrogen bonds and intermolecular van der Waals forces, as shown in Figure 2. The two units are basically similar but somewhat different with respect to the bond lengths and bond angles. In L₁, The dihedral angle of the two aromatic rings is 1.4° and almost is coplanar. The centroid–centroid distance of the two parallel aromatic rings is 6.419 Å, indicating no interaction between them. In L₂, the dihedral angle of the two aromatic rings is 12.9° with the centroid–centroid distance of 6.431 Å.



FIG. 2. The unit cell package of L.

CONCLUSION

Salicylidene-o-aminophenol and its metal(II) complexes have been synthesized efficiently using microwave irradiation and characterized by elemental analysis, IR, ES-MS, molar conductivity, and X-ray diffraction. Compared with the conventional synthesis, microwave synthesis has many advantages such as higher efficiency, lower solvent consumption, shorter reaction time, and so on. The result shows that the chemical reactions in microwave field were influenced by several factors including microwave irradiation time, power, and solvent. Microwave-assisted synthesis method provides a simpler route to obtain Schiff base and its complexes.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center as the supplementary publication nos. CCDC 255222 for salicylidene-o-aminophenol. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

REFERENCES

- Yamada, S. Advancement in stereochemical aspects of Schiff base metal complexes. *Coord. Chem. Rev.*, 1999, 190–192, 537–555.
- Bedioui, F. Zeolite-encapsulated and clay-intercalated metal porphyrin, phthalocyanine and Schiff-base complexes as models for biomimetic oxidation catalysts: an overview. *Coord. Chem. Rev.*, **1995**, 144, 39–68.
- Wagner, M.R., and Walker, F.A. Spectroscopic study of 1:1 copper(II) complexes with Schiff base ligands derived from salicylaldehyde and lhistidine and its analogs. *Inorg. Chem.*, **1983**, 22, 3021–3028.
- Casella, L., and Gullotti., M. Coordination modes of histidine. 2. Stereochemistry of the reaction between histidine derivatives and pyridoxal analogs conformational properties of zinc(II) complexes of histidine Schiff bases. J. Am. Chem. Soc., 1981, 103, 6338–6347.
- Khalil, S.M.E., Stefan, S.L., and Bashir, K.A. Schiff base complexes derived from salicylaldehyde with amine, [NI(1,2-pn)₂Cl₂]·3H₂O and [Cu(1,2pn)₂]SO₄·2H₂O, as complex ligands. *Synth. React. Inorg. Met. Org. Chem.*, 2001, 31, 927–951.
- Mishra, A.P., Khare, M., Gautam, S.K. Synthesis, physico-chemical characterization, and antibacterial studies of some bioactive Schiff bases and their metal chelates. *Synth. React. Inorg. Met. Org. Chem.*, 2002, 32, 1485–1500.
- Li, R.Y., Bei, F.L., Ma, W.X., Yang, X.J., Xu, X.Y., Lu, L.D., and Wang, X. One step synthesis of N-salicylidene-4-aminoantipyrine by solid phase reaction at room temperature. *Chin. J. Org. Chem.*, 2003, 23, 846–849.
- Li, R.Y., Bei, F.L., Yang, X.J., Xu, X.Y., Lu, L.D., and Wang. X. Solid phase synthesis, characterization and crystal structure of N-(4hydroxyphenylmethylene)-1-naphthylamine. *Chin. J. Appl. Chem.*, 2003, 20, 911–913.
- Yang, H., Sun, W.H., Li, Z., and Wang, L. Solvent-free syntheses of salicylaldimines assisted by microwave irradiation. *Synth. Comm.*, 2002, 32, 2395–2402.
- Strauss, C.R., and Trainor, R.W. Invited review developments in microwaveassisted organic chemistry. *Aust. J. Chem.*, 1995, 48, 1665–1692.
- Gong, C.L., and Ji, Y.G. The design of microcomputer based control system for microwave heating reaction still. *Process Automation Instrumentation*, (China). 2002, 23, 45–47.
- Sheldrick G.M., SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.
- 13. Saskia. A.G. Microwave chemistry. Chem. Soc. Rev., 1997, 26, 233-238.