บทความวิจัย

การสังเคราะห์สารประกอบเชิงซ้อนสังกะสีกับเอทิลีนไดเอมีนและกรดมาโลนิก
Synthesis of Zinc(II) complex with Ethylenediamine and Malonic acid

สิรินาฏ ชูเศษ[1] เชวง ภัควัตชัย[2] และอานอบ คันฑะชา[3*]
Sirinart Chooset[1], Chaveng Pakawatchai[2] and Anob Kantacha[3*]

บทคัดย่อ

งานวิจัยนี้ได้สังเคราะห์สารประกอบเชิงซ้อน $[Zn(mal)_2(H_2O)_2]\cdot en$ โดยใช้ $ZnCl_2$ กับ เอทิลีนไดเอมีนและกรดมาโลนิก เป็นสารตั้งต้น ในอัตราส่วน 1:2:2 ศึกษาโครงสร้างด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว และศึกษาสมบัติทางสเปกโตรสโกปีด้วยฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรโฟโตมิทรี อัลตราไวโอเลตวิสิเบิลสเปกโทรโฟโตมิทรี พบว่า สารประกอบเชิงซ้อนสังกะสี(II) มีรูปทรงทางเรขาคณิตเป็นแบบทรงเหลี่ยมแปดหน้าบิดเบี้ยวโดยอะตอมออกซิเจนทั้ง 4 อะตอม จากหมู่มาโลเนต 2 หมู่สร้างพันธะโคออดิเนตโคเวเลนซ์กับสังกะสี(II) ในตำแหน่งแกนนอน (equatorial) และอะตอมออกซิเจน 2 อะตอมของน้ำในตำแหน่งบนแกนตั้ง (axial) ผลจากสเปกตรัมอินฟราเรดพบแถบสเปกตรัมที่สำคัญดังนี้ 3438, 3193-3015, 1595, 1344-1411 และ 486 cm-1 ซึ่งเป็นช่วงการดูดกลืนรังสีอินฟราเรดของหมู่ฟังก์ชั่น NH_2, C=O, ν(C-H) และ ν(Zn-O) ตามลำดับ และพบค่าการดูดกลืนแสงของสารประกอบเชิงซ้อนนี้ที่ความยาวคลื่นสูงสุดที่ 275 nm ซึ่งเป็นแถบการดูดกลืนในลักษณะของ charge-transfer แบบ $\pi \rightarrow \pi^*$

คำสำคัญ : สารประกอบเชิงซ้อนของสังกะสี(II) คีเลต กรดมาโลนิก และเอทิลีนไดเอมีน

Abstract

The metal complex, $[Zn(mal)_2(H_2O)_2]\cdot en$ has been prepared via the reaction of Zinc(II) chloride ($ZnCl_2$), ethylenediamine (en) and malonic acid using the 1:2:2 mol ratio. The metal complex, investigated by spectroscopic and single crystal x-ray diffraction technique, supports the formation of distorted octahedral complex, with the Zn(II) ion located within two bidentates of malonato groups in the equatorial position. The Zn(II) ion has distorted octahedral coordination by four oxygen atoms of two malonato groups,

---

[1] Master's Degree Student, Department of Chemistry, Faculty of Science, Thaksin University, Songkla, 90000

[2] ผศ.ดร., ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ หาดใหญ่ 90000

[3] อ.ดร., สาขาวิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยทักษิณ สงขลา 90000

[*] Corresponding author : E-mail: k_anob@hotmail.com Tel. 083-1931922

and coordinated two oxygen atoms of the water in trans position. The IR spectra of Zn(II) complex in regions 3438, 3193-3015, 1595, 1344-1411 and 486 cm^{-1} are assigned tothe NH_2, C=O, ν(C-H) and ν(Zn-O), respectively. UV-Vis spectra indicated that the bands below 275 nm are belonged to the charge-transfer bands.

Keywords : Zinc complex, Chelate, Malonic Acid and Ethylenediamine

Introduction

Zinc is an essential component of an important number of proteins, being indispensable for its stability or catalytic function. It is present in over 300 enzymes including fundamental enzymatic systems that participate in the formation (polymerases, transferases, and ligases) or degradation (hydrolases) of proteins, nucleic acids, lipids, porphyrins and biological activities, such as anticandida antimycobacterial and antimicrobial activities. [1]

Recently, coordination compounds containing malonic acid as a ligand have been intensively studied due to their potential application as materials in molecular electronics, catalysis, biologically active compounds, molecular-based magnetic materials, etc. Malonic acid, $HOOC–CH_2–COOH$, acts as a ligand with various dentate abilities. As the coordination modes depend on the nature of the metal and on synthesis conditions, the crystal structures of malonate complexes are very diverse from ionic to three-dimensional polymers. [2] The malonate ligand occupies one or two coordination positions and neutralizes two positive charges of the metallic ion, allowing the inclusion of other ligands in the coordination sphere of the metal. An important feature of the malonic bridge is the fact that magnitude of the exchange interaction depends on the possible bridging modes that it can adopt. Therefore, the ferro or antiferromagnetic interactions may appear in malonate complexes, governed by the dimensionality of the structure.

In this paper, a novel zinc (II) complex of ethylenediamine and malonic acid was synthesized and characterized by both spectroscopic technique and single crystal x-ray diffraction method.

Materials and Method

$ZnCl_2$, ethylenediamine and malonic acid were all purchased from commercial source and used as received. IR spectra were obtained using KBr discs on Perkin-Elmer 1710 Fourier-transform IR spectrophotometer between 4000 – 400 cm^{-1}. UV-vis spectra were determined with a Shimadzu UV-1601 (200-400 nm) using aqueous solutions. Single crystal suitable for x-ray crystallographic analysis were obtained by the slow evaporation of solvent from the water solution of complex at room temperature. X-ray data for complex were collected at 293 K on a Bruker SMART APEX CCD area-detector diffractometer with graphite mono-chromated Mo Kα - radiation (K = 0.71073 Å). The data integration and reduction were processed with SAINT (Bruker, 2003) software. [3] An empirical absorption correction was applied to the collected reflections with SADABS program. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for x-ray crystallography.

The structure was solved by the direct method using SHELXS-97 program [4] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program. Figures were drawn using Mercury - 3.0 [5] and Diamond - 3.0. [6]

Experimental

Synthesis of [Zn(mal)2(H2O)2]·en

To a stirred colorless solution of $ZnCl_2$ (0.6814 g, 5 mmol) in absolute ethanol (10 ml) was added 1,2-diaminoethane (0.65 ml, 10 mmol) in absolute ethanol (5 mL) to give a colorless solution solution. Malonic acid (1.0406 g, 10 mmol) in absolute ethanol (10 mL) was added to a give colorless solution and colorless solid. The solution was then stirred at room temperature for 24 h. The solution was filtered. The solid was washed with absolute ethanol and acetone to a give colorless solid. Yield: ≈ 75%. The product was purified by crystallization from H_2O. The physical properties and analytical x-ray data are given in Table 1.

Results and Discussion

Table 1. Physical properties and analytical data of Zinc(II) complexes containing malonato and ethylenediamine ligand.

Complex	Reaction	Empirical formula	Melting point (°C)	Colour
$[Zn(mal)_2(H_2O)_2]\cdot en$	$ZnCl_2 + 2C_2H_8N_2 + 2C_3H_4O_4$	$C_8H_{16}N_2O_{10}Zn$	170	colorless crystal

The Zn(II) complex is found to be air stable and insoluble in non-polar solvent, but it is soluble in polar solvent, such as H2O and DMSO. The analytical data of the complex and some physical properties are summarized in Table 1.

IR studies

The preliminary identification of $[Zn(mal)_2(H_2O)_2]\cdot en$ complex was done from their IR spectra in Figure 1. The IR spectra of complex were show in Figure 1. The absorption as region 3438 cm^{-1} was assignable to symmetric OH stretching and a band at 1611 cm^{-1} was assigned to HOH bending vibration of coordinated water. In the IR spectroscopy of complexes, the C = O stretches at 1595 cm^{-1}, whichindicate that the malonato ligands adopt a chelating coordination mode. The complex shows bands in the 1344 -1411 and 1597-1611 cm^{-1} regions, which may be assigned to ν(C - N) and ν(C – H), respectively. Strong bands around 3193 and 3015 cm^{-1} for the complex are consistent with NH_2 stretches. An importance feature, which is the appearance of a new band of peak intensity at 486 cm^{-1}, as attributable to ν(Zn - O) which assigns to the involvement of oxygen in coordination.

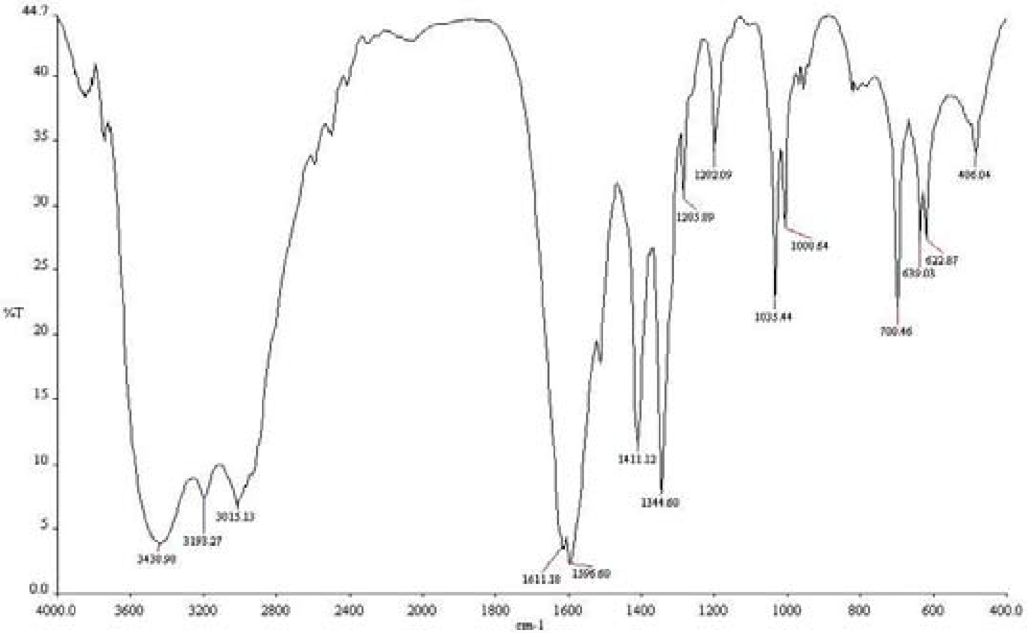

Figure 1. The IR spectrum complex of $[Zn(mal)_2(H_2O)_2]$•en

Crystal structure description of $[Zn(mal)_2(H_2O)_2]$•en

Suitable crystals of Zn(II) complex was grown by slow evaporation of aqueous solutions at room temperature.A colorless crystal size is 0.34 x 0.116 x 0.049 mm. The crystallographic data are given in Table 3. The complex crystallizes in the monoclinic and space group $P2_1/c$. The molecular structure is shown in Figure 2. The unit cell containstwo metal complexes of formula $[Zn(mal)_2(H_2O)_2]$•en and two ethylenediamine as shown in Figure 3. In the complex, the zinc(II) centre has slightly distorted octahedral geometry in which the H_2O ligands are placed trans to each other in the axial positions, with a bond angle of O(5)#1-Zn(1)-O(5) 180.00(8)o and the two malonate groups are trans to each other in the equatorial positions. The Zn(II) ion is coordinated by the four oxygen donors of malonato ligands. The bite angles of malonate ligands, O(2)-Zn(1)-O(1) and O(2)#1-Zn(1)-O(1)#1, are 88.57(5) and 88.57(4) ^{o}, respectively. It was found that the Zn(1)-O(1) and Zn(1)-O(2) bond lengths are 2.0241(12) and 2.0672(11) Å significantly, indicating that these malonate act as anions and a molecule of ethylenediamine is, however, solvated on the Zn(II) complex.

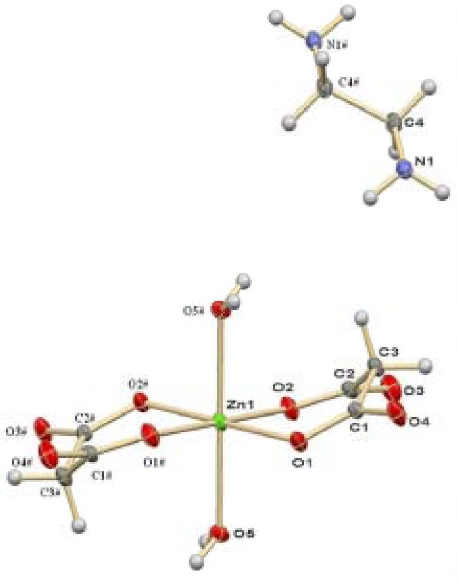

Fig 2. ORTEP view of the crystal structure of [Zn(mal)$_2$(H2O)$_2$]•en

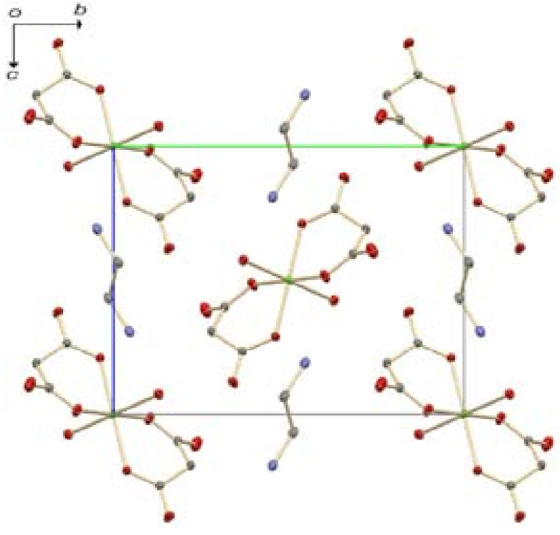

Figure 3. Unit cell diagrams of [Zn(mal)$_2$(H$_2$O)$_2$]•en. Zn(green) atoms are shown as small spheres of arbitrary radii.

A view of hydrogen bonds is present in the structure as shown in Figure 4. The bond lengths and angles for hydrogen bonding are summarized in Table 2.

Table 2. Selected hydrogen bonds for complex, $[Zn(mal)_2(H_2O)_2]$•en.

D-H...A	d(D-H) [Å]	d(H...A) [Å]	d(D...A) [Å]	<(DHA) [^{O}]
O(5)-H(5A)...O(4)#3	0.828(15)	2.055(17)	2.8319(18)	156(2)
O(5)-H(5A)...O(2)#3	0.828(15)	2.409(18)	3.1093(17)	142.8(19)
O(5)-H(5B)...O(3)#4	0.820(16)	1.893(16)	2.7066(18)	171(2)
N(1)-H(1A)...O(4)#5	0.871(16)	1.880(17)	2.737(2)	168(2)
N(1)-H(1B)...O(5)#6	0.864(17)	2.17(2)	2.890(2)	140(2)

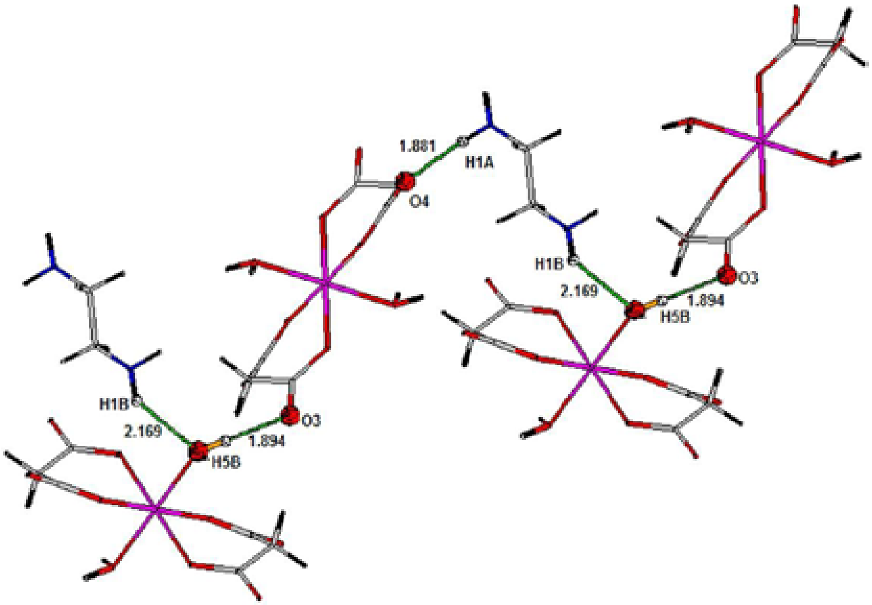

Figure 4. Hydrogen bonding of $[Zn(mal)_2(H_2O)_2]$•en

Table 3. Crystal data and structure refinement for complex

Empirical formula	$C_8H_{16}N_2O_{10}Zn$
Formula weight	365.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a	5.9086(6) Å
b	12.1325(12) Å
c	9.3459(9) Å
β	92.378(2)^O
V (Å^3)	669.39(11) Å^3
Z	2
Density (calculated)	1.814 Mg/m^3
Independent reflections	1662 [R(int) = 0.0214]
Crystal size	0.34 x 0.116 x 0.049 mm^3
Final R indices [I>2sigma(I)]	R1 = 0.0243, wR2 = 0.0674
R indices (all data)	R1 = 0.0268, wR2 = 0.0689

Electronic spectra

In Figure 5, the electronic of complex was recorded in aqueous solutions. Complex shows intense bands in the regions 275-325 nm which are assignable to $\pi \rightarrow \pi^*$ intraligand charge-transfer transition.

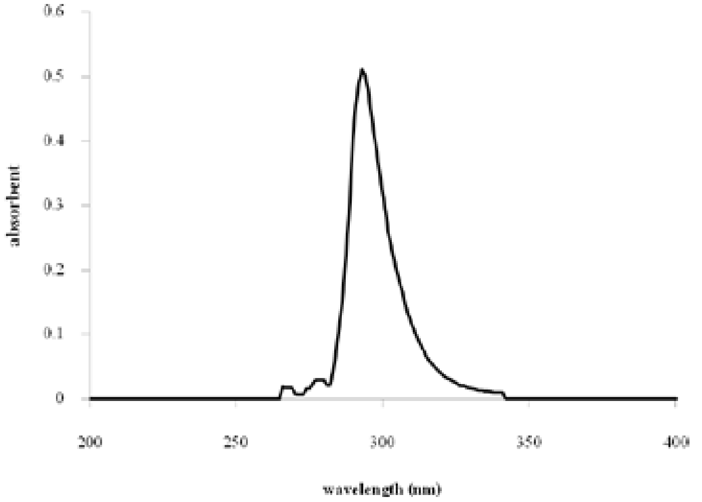

Figure 5. The visible spectrum of $[Zn(mal)_2(H_2O)_2]$•en

จากงานประชุมวิชาการระดับชาติครั้งที่ 22 ปี 2555

Conclusions

In this work, a novel $[Zn(mal)_2(H_2O)_2]$•en has been synthesized using a reaction of zinc (II) chloride, malonic acid and ethylenediamine. The structure of $[Zn(mal)_2(H_2O)_2]$•en has been confirmed by Single Crystal X-ray Diffraction (SCXRD). The Zn(II) ion has distorted octahedral coordination by four oxygen atoms of two malonato groups, and coordinated two oxygen atoms of the water in trans position as characterization from the IR, SCXRD and UV-visibletechniques.

Acknowledgement

The author is grateful to Dr. Anob Kantacha for improvement paper and also grateful to Dr. Saowanit Saithong, Department of Chemistry, Faculty of Science, Prince of Songkla University for single crystal x-ray data and this workwas supported by chemistry laboratory, Department of Chemistry, Faculty of Science, Thaksin University.

References

[1] Claudia, C.W. and Enrique, J. B. (2009). Vibrational spectra of Zn(II) complexes of the amino acids with hydrophobic residues. **Spectrochimica Acta Part A**. 72, 936–940.

[2] Filippova, I.G.(2002). Polymorphism Of Coordination Compounds With Malonic Acid. **Moldavian Journal of the Physical Sciences.** 1, 3-6.

[3] Sheldrick, G.M., SHELXL-97, SAINT and SADABS. (2003). Bruker AXS Inc., Madison, Wisconsin, USA.

[4] Sheldrick, G.M. (2008). A short history of SHELX. Acta Crystallographica Section A. 64(1), 112-122.

[5] Macrae,C.F.,Bruno,I.J.,Chisholm,J.A.,Edgington,P.R.,McCabe,P.,Pidcock,E.,Rodriguez-Monge,L.,Taylor, R., van de Streek, J. and Wood, P. A. (2008). Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures. **Journal of Applied Crystallography.** 41(2), 466-470.

[6] Brandenburg, K. and Putz, H. (2005). DIAMOND. Release 3.0c. Crystal Impact GbR, Bonn, Germany.

[7] Megha, M., Sushil, K., Savita K. and Rajeev, G. (2011). "Nickel and copper complexes with few amide-based macrocyclic and open-chain Ligands," **Inorganica Chimica Acta.** 377, 144–154.

[8] Robert, W., Andrew, D. and Philip, L. (1997). "The non-formation of Macrocyclic tetraamides by coordinated ligand reactions," **Polyhedron.** 16(20), 3261-3266.

[9] Sergey, P. G., Yaroslaw, D. L. and Philip, L. (2004). "Solution properties of the nickel(II,III) and copper (II,III) complexes of trans-dioxocyclam (trans-dioxocyclam(5,12-dioxo-1,4,8,11-tetraazacyclotetradecane) and the X-ray crystal structure of the N-rac-isomer of the nickel(II) complex," **Inorganica Chimica Acta**. 357, 1023-1030.

[10] Yaroslav, D.L., Sergei, P.G., Igor, M.M., Kent, N.D., John, D.L. and Alexander, Y.N. (1998). "New cyclamtype copper(II) complexes with amide molecular padlock: synthesis, properties and crystal structure," **Inorganic Chemica Acta.** 282(2), 142-148.

[11] Yaroslaw, D. L., Sergey, P. G., Robert W. H., Tanja E. and Philip, L. (2000). "The crystal and molecular structures ofthe nickel (II) complexes of malonamide-derived unsubstituted 14- and 13-membered tetraazamacrocycles and NMR study of the complexes in aqueous solution," **Journal of the Chemical Society**. 2023 –2029.