

Succinate Bridged Polymeric Complexes of Copper (II) and Zinc (II) Acetylacetonate

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Authors' contributions

This work was carried out by author LM. Author AM performed the work to fill in the gaps. The paper is written by the author AM. Both authors read and approved the final manuscript.

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ABSTRACT

Cu(II) and Zn(II) salts were treated with 2,4-pentanedione to synthesize copper (II) acetylacetonate and zinc (II) acetylacetonate. These complexes were subsequently cross linked with succinate to produce corresponding bridged dimers. The UV- visible spectrum of the complex showed absorption maximum at around 660nm, while the infrared spectra exhibited the absorption bands at 1419 cm^{-1} and 1429 cm^{-1} for the Cu(II) and Zn(II) complexes, respectively.

Keywords: Acetylacetone; copper; zinc; succinic acid.

1. INTRODUCTION

Metal clusters are also known as polynuclear compounds and coordination polymers. These compounds are of interest due to their applications as bioactive molecules and as single molecule magnets. To be specific, the coordination polymers are used as electrical conductors and in catalysis; they are also useful in the area of molecular electronics, medicine and as sensors [1]. Inorganic chemist faces difficulty with these compounds due to difficulty in their characterization, despite the molecules' wide application [2].

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Recently many research groups have been designing new methods for the preparation of these compounds. Their strategy is to employ the rigid ligands with strong affinity for specific bonding modes and to use the metal ions with preferred coordination geometries. This approach has been successful in producing a series of intriguing metal–organic clusters [3]. The structures of these clusters are moderately predictable. The coordination geometry of the metal ion as well as the coordinating site and the flexibility of the pre-organized ligand donor are also known. The coordination modes of any polydentate ligand increase if ligands that form five- or six membered ring are avoided. This resulted in the formation of many stable and serendipitous structures [2]. The family of organic ligands used, many at times in combination with terminal aromatic N-donors for the construction of metal-organic clusters and coordination polymers consist of various types of dicarboxylates which are capable of bridging metal ion at different distances [1].

A typical ligand normally used as bridging agent is 2, 2'-bipyrimidine (bpm). This ligand has been used successfully in numerous transition metal complexes to bridge metal ions and to function as a channel for energy and electron transfer [4,5]. Baker et al [6] synthesized 2, 2'-bipyrimidine adducts of the β -diketonate complexes of lanthanides metal ion. In these dinuclear species each lanthanide was eight coordinate and bound to six oxygen atoms from β -diketonate and two nitrogen atoms from the bridging bpm ligand. Since the IR and UV visible spectra of these complexes were dominated by ligand absorptions in both the solid and solution state, they suggested that the spectra resemble those of the monomeric lanthanide species [6].

A mixed ligand (Fig. 1) and dimeric Cu^{II} complex $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]\text{L} \cdot 12.5\text{H}_2\text{O}$ ($\text{H}_2\text{L}=\text{succinic acid}$) containing bridging succinate moiety and also non-coordinated succinate dianion was prepared from polymeric $\text{Cu}(\text{II})$ succinate by nucleophilic reaction with o-phenanthroline (phen) followed by depolymerization [7].

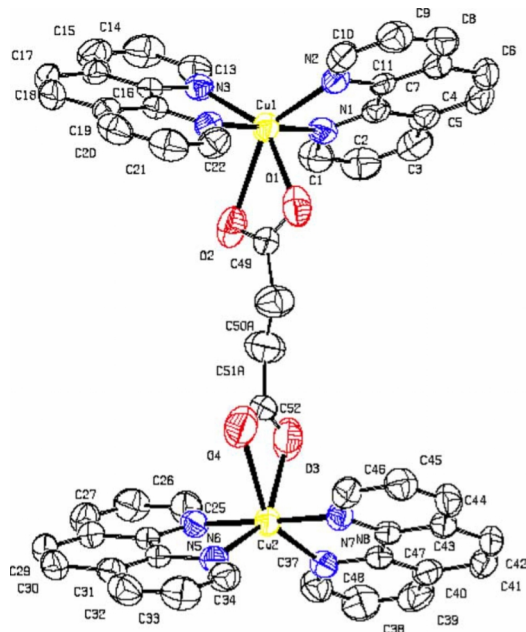


Fig. 1. X-ray crystal structure showing succinic acid used as bridging ligand [7]

A ligand blend reaction system consisting of succinamate $\text{OOC-CH}_2\text{-CH}_2\text{-CONH}_2$ and various aromatic $\text{N,N}'$ -donors as mean of dinuclear and polymeric copper(II) compounds was reported by Chadjistamatis et al. [8], where several reaction schemes were employed. The novel cationic coordination polymers obtained from their reactions consist of alternating $[\text{Cu}_2(\text{Hsucm})_2(\text{dmpby})_2]^{2+}$ and $[\text{Cu}_2(\text{Hsucm})_3(\text{dmpby})_2]^+$ dinuclear units.

Herein, we report the synthesis of polynuclear β -diketonate complexes linked through succinate as bridging agent.

2. MATERIALS AND METHODS

2.1 Materials

All reagents and chemicals purchased from Aldrich sigma were of analytical/spectroscopic grade and used without further purification. Melting points were measured using a digital melting point apparatus 1A 9000. The IR spectra were recorded on FT-IR -8400 Fourier transform infrared. UV-Vis Spectra were recorded using Uv-vis T-60u Spectrophotometer, PG instrument Ltd.

2.2 Synthesis of $[(\text{Cu}^{\text{II}}(\text{acac})_2)_2(\text{suc})]$

To an ethanol (50 mL) solution of β -diketone (0.001mol) were added three drops of ethanolic solution of NaOH. Copper (II) chloride (0.8524mol) was then added to the mixture which immediately yielded precipitate. Succinic acid (0.59mol) was added to the precipitate and the suspension was refluxed for 1 hour. The resultant blue precipitate was cooled washed twice with 10 mL ethanol and dried in a desiccator for 3 days. The yield was 74%. Calculated for $\text{Cu}_2\text{C}_{24}\text{H}_{28}\text{O}_{12}$: C,45.35; H, 4.44; O, 30.21; Found: C, 45.21; H, 4.53; O, 30.33.

2.3 Synthesis of $[(\text{Zn}^{\text{II}}(\text{acac})_2)_2(\text{suc})]$

To an ethanol solution (50 mL) β -diketone (0.001mol) were added three drops of ethanolic solution of NaOH. Zinc (II) chloride salt (0.6814g) was then added to the mixture which immediately yielded precipitate. Succinic acid (0.59mol) was added to the precipitate and the suspension was refluxed for 1 hour. The white precipitate formed was cooled washed twice with 10 mL ethanol and dried in a desiccator for 3 days. The yield was 68%. $\text{Zn}_2\text{C}_{24}\text{H}_{28}\text{O}_{12}$: C,45.09; H, 4.41; O,30.03; Found: C,45.38; H,4.43;O,30.45.

2.4 Solubility Tests

The solubility test was carried out in water, ethanol, methanol, and acetone. The test was conducted by dissolving 0.1g of each complex in each of the test-tube containing solvent, the results obtained are shown in the Table 2.

3. RESULTS AND DISCUSSION

We have developed interest in the aspect of coordination polymers as it is one of the most challenging fields of inorganic chemistry. Synthesizing polynuclear species with metal (II) ion is not commonly reported [9]. Our effort to prepare polynuclear metal clusters was successful, as this was investigated through the use of infrared spectroscopy, UV and other techniques.

Copper complex formed blue crystalline solids with relatively high decomposition temperature Table 1. Zn(II) complex gave a yellow crystalline solid. Two complexes prepared were soluble in water, ethanol and methanol while copper complex is sparingly soluble in acetone. The two complexes have high melting point $>240^{\circ}\text{C}$ which is indicative of their resistance to heat Table 1.

Table 1. Color and melting point of the complexes

Complex	Color	Melting point
$[\text{Cu}(\text{acac})_2]_2\text{suc}$	Blue	240°C
$[\text{Zn}(\text{acac})_2]_2\text{suc}$	Yellow	248°C

Table 2. Solubility Test

Complexes	H_2O	Ethanol	Methanol	Acetone
$[\text{Cu}(\text{acac})_2]_2\text{suc}$	S	S	S	SS
$[\text{Zn}(\text{acac})_2]_2\text{suc}$	S	S	S	S

S=soluble SS= slightly soluble

UV- visible spectrum of the copper(II) complex shown in Fig. 2 reveals one peak at around 380nm which should be ascribed to the metal to ligand charge transfer. Two peaks were observed for zinc complex prepared, 380nm which is the major peak and a shoulder at around 660nm.

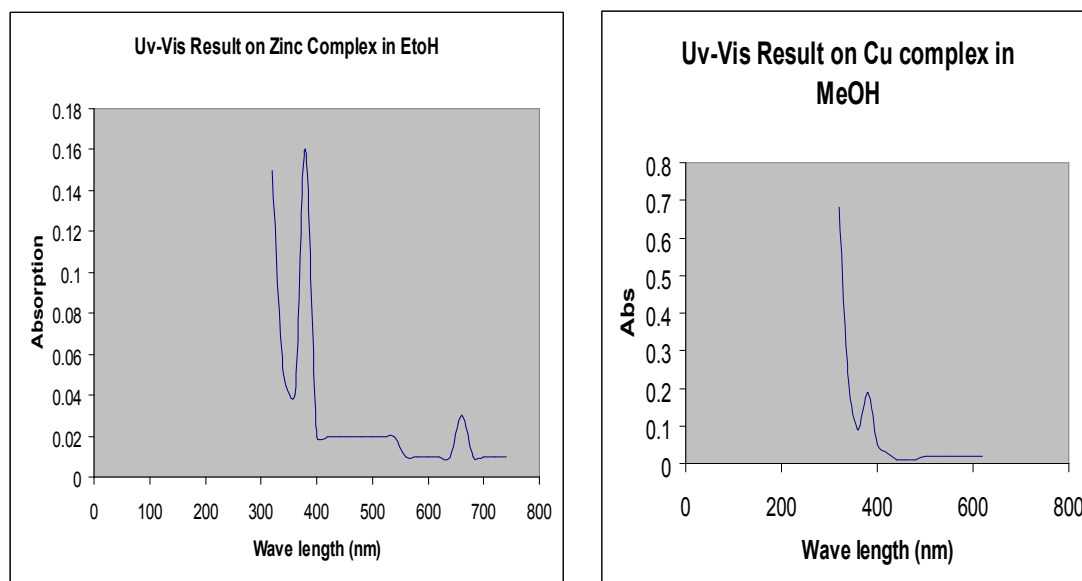


Fig. 2. UV-visible spectra for zinc and copper complexes

The IR spectra of the complexes reveal absorption frequency at 1572 cm^{-1} and 1632 cm^{-1} due to the copper (II)-succinate and zinc (II)-succinate moiety asymmetric vibration respectively. The symmetric CO_2^- vibration bands of the two complexes were found at 1419 cm^{-1} and 1429 cm^{-1} for copper and zinc respectively. These peaks were reported by

Padmanabhan et al. and were ascribed to the bonds that link the two M (acac)₂ moieties [7]. The C-O absorption vibration appears at 1596 and 1583 cm⁻¹ for copper and zinc respectively. The metal-oxygen bond absorbs at 461 cm⁻¹ for copper while that of zinc was recorded at 410 cm⁻¹. The proposed structure is depicted in Fig. 3.

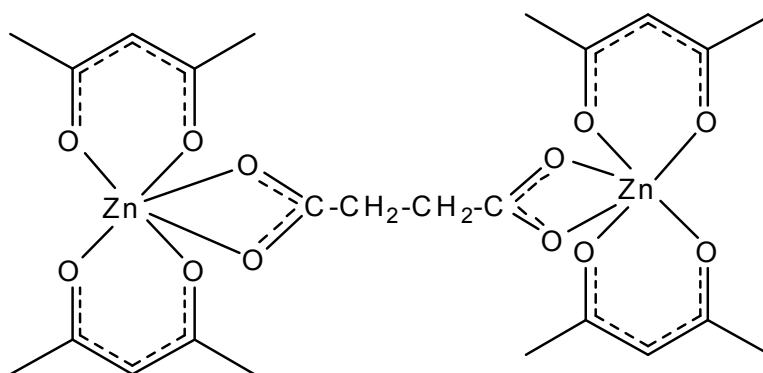


Fig. 3. The depicted structure of the prepared [Zn₂(acac)₂(suc)] complex

4. CONCLUSION

In conclusion we report the synthesis of copper (II) and zinc (II) acetylacetonate complexes of which the monometallic molecule is dimerised through employing molecule as bridging ligand. The UV absorption of the zinc dimer indicated the potentiality of these complexes in biological application.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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