

Synthesis and crystal structure of poly{bis-(3-nitro-2,4-pentanediono)-copper(II)}, [Cu(NO₂-acac)₂]_n

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ABSTRACT

The organo-inorganic polymer, poly[{Cu(NO₂-acac)₂]₃]_n, has been prepared and its crystal structure was determined. The structure consists of a trimeric unit in which, acetylacetone ligated symmetrically to copper atoms that pose in the center of octahedrons. The three octahedral fragments of the trimer are linked to each other through nitro group. Crystal Data: C₁₀H₁₂CuN₂O₈, *M_r* = 351.76, triclinic, P-1 (No. 2), a = 5.8237(2) Å, b = 7.7963(3) Å, c = 7.8847(3) Å, α = 81.988(2)°, β = 75.294(2)°, γ = 72.217(2)°, V = 328.98(2) Å³, T = 143(2) K, Z = 1, Z' = 0.5, μ(Mo Kα) = 1.703, 3021 reflections measured, 1421 unique (*R_{int}* = 0.0156) which were used in all calculations. The final *wR*₂ was 0.0686 (all data) and *R*₁ was 0.0217 (*I* > 2σ (*I*)).

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1. Introduction

Coordination polymers are a class of polymers whose repeated units are coordination complexes. A subclass of these is the metal-organic frameworks that are coordinated with organic ligands containing potential voids [1]. Coordination polymers are relevant to many fields such as organic-, inorganic-, bio-, electro-chemistry; material science and pharmacology. Many potential applications led to extensive studies in the past few decades [2,3].

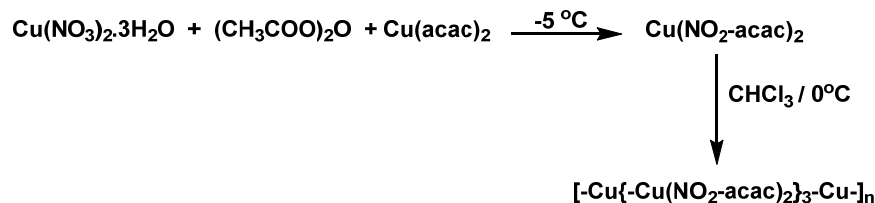
Coordination polymers have many applications such as dyes [4], molecular storages [5], catalysts, ion exchange, electrical conductors [6-10], bioactive molecules, sensors, and single molecule magnet [11]. Also, they can be used in the fields of molecular electronics, medicine, luminescence and optics [12].

The identity and oxidation state of metal [13], the length and geometry of the organic ligand [14] and the relative orientation of the ligand donor group [15,16] are the fundamental aspects to direct the overall architecture. Also, the coordination geometry of the metal ion, the coordination site and the flexibility of the pre-organized ligand donor show the same effects.

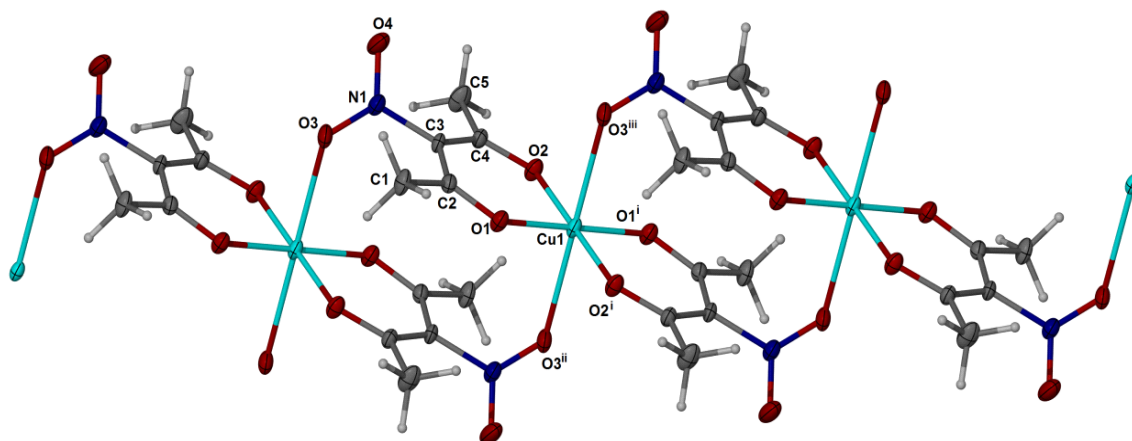
Transition metals are commonly used as nodes or hubs and the electronic structure of these partially filled *d*-orbitals causes some of them to exhibit multiple coordination geometries particularly copper ion. Thus, the synthetic study of the ternary Cu(II)/malemate (-1)/1,10-phenanthroline reaction system showed: mononuclear, binuclear and polymeric complexes [11].

The family of organic ligands used many at times in combination with terminal *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 [17]. Baker *et al.* synthesized 2,2'-bipyrimidine adducts of the β-diketones complexes of lanthanides metal-ion. Thus the 2,2'-bipyrimidine has been used as a bridging moiety and as a channel for energy and electron transfer [18].

Herein, we report the synthesis of the poly{bis-(3-nitro-2,4-pentanediono)-copper(II)} linked via nitro group as bridging agent. Thus, we believe that this moiety can be functioned as a channel for energy and electron transference, presenting the X-ray single crystal structure of [-Cu-{Cu(NO₂-acac)₂]₃-Cu-]_n.



Scheme 1

Figure 1. X-ray single crystal structure of $[-\text{Cu}\{\text{Cu}(\text{NO}_2\text{-acac})_2\}_3\text{-Cu-}]_n$.

2. Experimental

2.1. Instrumentation

Single crystal X-ray structural study of poly{bis-(3-nitro-2,4-pentanediono)-copper(II)}, $[-\text{Cu}\{\text{Cu}(\text{NO}_2\text{-acac})_2\}_3\text{-Cu-}]_n$, was carried out using an X-ray single crystallographic instrument located at the Faculty of Science, University of Malaya, Malaysia. Data collection of this work was carried out on a Bruker APEXII CCD diffractometer using a green single crystals with dimensions of $0.49 \times 0.11 \times 0.03$ mm with graphic monochromatic MoK α radiation ($\lambda = 0.71073$ Å).

2.2. Preparation of bis-(nitroacetylacetonato)copper(II), $\text{Cu}(\text{NO}_2\text{-acac})_2$

The complex $\text{Cu}(\text{NO}_2\text{-acac})_2$ was prepared by the reaction of acetylacetonone (2 mmol) in 40 mL acetic anhydride with solid copper(II) nitrate (2.3 mmol) [19]. The resultant mixture was stirred vigorously at an ice bath to control the exothermic reaction. The green oily product was separated and solidified by the addition of ethanol, then filtered and recrystallized from methylene chloride-ethanol mixture.

2.3. Synthesis of poly{bis-(3-nitro-2,4-pentanediono)-copper(II)} $[-\text{Cu}\{\text{Cu}(\text{NO}_2\text{-acac})_2\}_3\text{-Cu-}]_n$

Bis-(Nitroacetylacetonato)copper(II) (0.5 g, 5 mmole) was dissolved in 10-12 mL of chloroform and the resultant solution was placed in an ice bath with stirring for 15 min, then the mixture was transferred into a 50 mL two necks-flask fitted with a condenser, then refluxed for 3 hrs at room temperature. The solid product was filtered, and recrystallized from acetone. Green crystals were collected, dried and stored under vacuum. A suitable crystal for crystallographic measurements was chosen as a green crystal of dimensions $0.49 \times 0.11 \times 0.03$ mm. Scheme 1 shows the overall synthesis route.

3. Results and discussion

The crystal structure of the unit of polymer (triclinic) obtained is illustrated in Figure 1, while the crystal data and refinement parameters are given in Table 1. The atomic coordination and isotropic displacement parameters for the prepared compound are also listed in Table 2. Tables 3 and 4 are showing the selected bond distances and bond angles of $[-\text{Cu}\{\text{Cu}(\text{NO}_2\text{-acac})_2\}_3\text{-Cu-}]_n$, respectively. The structure was solved by SHELXS97 and refined with SHELXL2013 [20]. The technique used was θ/ω scan with θ limits ($2.677 \leq \theta \leq 26.991$) at a temperature of 143(2) K. A total of 3021 reflections were measured, of which 1421 were unique. Hydrogen atoms were included in calculating positions with C-H = 0.98 Å, while the displacement parameters for the hydrogen atoms were set equal to 1.496 Å times U_{eq} for the attached carbon.

The three repeating units are linked via the nitro group as bridged moiety attached to α -position of the acetylacetonato ligand. The base plane of each monomeric unit being formed with the four oxygen atoms, namely O_1 , O_1' , O_2 and O_2' belongs to the acac ligand coordinated to the central Cu-atom. Cu atom is bonded axially to O_3'' and O_3''' of the nitro groups whose belong to the prepared monomers adopting distorted octahedral geometry in each monomer. Thus, it seems that the axial Cu- O_3'' and Cu- O_3''' are longer than the equatorial $\text{Cu}_1\text{-O}_1$ (1.9233(13) Å) and $\text{Cu}_1\text{-O}_2$ (1.9195(13) Å) led to distorted octahedral geometry, in which the Cu atom is located at its center. These $\text{Cu}_1\text{-O}_1$ and $\text{Cu}_1\text{-O}_2$ distances are longer than those observed for $\text{Cu}(\text{acac})_2$ complexes, 1.914(4) and 1.912(4) Å reported by Lebrun et al. [21]. However, $\text{Cu}_1\text{-O}_1$ bond distance is slightly longer than that observed by Golchoubian [22], 1.9214(11) Å; whereas $\text{Cu}_1\text{-O}_2$ is shorter than reported by the same author, 1.9234(116) Å. Both chelate angles $\text{O}_2\text{-Cu-O}_1$ and $\text{O}_2'\text{-Cu-O}_1'$ of the prepared polymer are $92.16(6)^\circ$, less than those observed by Lebrun et al. [21], $93.2(2)^\circ$ and Golchoubian [22], $93.58(5)^\circ$, while both dihedral angles: $\text{O}_2'\text{-Cu}_1\text{-O}_2'$ and $\text{O}_1'\text{-Cu}_1\text{-O}_1'$ are 180.0° .

Table 1. Crystal data and structure refinement for [Cu(NO₂-acac)₂]_n.

Empirical formula	C ₁₀ H ₁₂ CuN ₂ O ₈
Formula weight	351.76
Temperature (K)	143(2)
Color	Green
Crystal system	Triclinic
Space group	P-1
a (Å)	5.8237(2)
b (Å)	7.7963(3)
c (Å)	7.8847(3)
α (°)	81.988(2)
β (°)	75.294(2)
γ (°)	72.217(2)
Volume (Å ³)	328.98(2)
Z	1
ρ _{calc} (g/cm ³)	1.776
μ (mm ⁻¹)	1.703
F(000)	179.0
Crystal size (mm ³)	0.490 × 0.110 × 0.030
Radiation	MoKα (λ = 0.71073)
2θ range for data collection (°)	5.354 to 53.982
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -9 ≤ l ≤ 10
Reflections collected	3021
Independent reflections	1421 [R _{int} = 0.0156, R _{sigma} = 0.0241]
Data/restraints/parameters	1421/0/99
Goodness-of-fit on F ²	1.188
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0217, wR ₂ = 0.0560
Final R indexes [all data]	R ₁ = 0.0228, wR ₂ = 0.0686
Largest diff. peak/hole (e Å ⁻³)	0.31/-0.42

Table 2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for [Cu(NO₂-acac)₂]_n. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U _{eq}
Cu1	0	0	10000	15.95(12)
O1	3162(2)	-1441.9(18)	8797.8(18)	19.5(3)
O2	1001(2)	2176.6(18)	9391.5(18)	20.3(3)
O3	9166(2)	524(2)	6924.8(19)	23.5(3)
O4	6951(3)	2574(2)	5403(2)	36.5(4)
N1	7158(3)	1367(2)	6574(2)	20.4(3)
C1	7067(4)	-2337(3)	6875(3)	23.4(4)
C2	4956(3)	-914(3)	7827(2)	17.3(4)
C3	4927(3)	926(3)	7628(2)	17.5(4)
C4	3017(3)	2375(3)	8415(2)	18.2(4)
C5	3299(4)	4251(3)	8230(3)	29.4(5)

Table 3. Selected bond distances for [Cu(NO₂-acac)₂]_n.

Atom	Atom	Length(Å)
Cu1	O2	1.9195(13)
Cu1	O2 ¹	1.9195(13)
Cu1	O1	1.9233(13)
Cu1	O1 ¹	1.9233(13)
O1	C2	1.271(2)
O2	C4	1.270(2)
Cu1	O3 ⁱⁱ	3.0107(78)
Cu1	O3 ⁱⁱⁱ	3.0107(78)
O3	N1	1.233(2)
O4	N1	1.224(2)
N1	C3	1.464(2)
C1	C2	1.496(3)
C2	C3	1.416(3)
C3	C4	1.406(3)
C4	C5	1.504(3)

¹ -x, -y, 2-z.**Table 4.** Selected bond angles for [Cu(NO₂-acac)₂]_n.

Atom	Atom	Atom	Angle (°)
O2	Cu1	O2 ¹	180.0
O2	Cu1	O1	92.16(6)
O2 ¹	Cu1	O1	87.84(6)
O2	Cu1	O1 ¹	87.84(6)
O2 ¹	Cu1	O1 ¹	92.16(6)
O1	Cu1	O1 ¹	180.0
C2	O1	Cu1	128.30(12)
C4	O2	Cu1	128.06(13)
O4	N1	O3	122.76(17)
O4	N1	C3	118.79(16)
O3	N1	C3	118.43(15)
O1	C2	C3	121.80(17)
O1	C2	C1	116.23(16)
C3	C2	C1	121.95(17)
C4	C3	C2	126.68(17)
C4	C3	N1	116.02(16)

Table 4. (Continued).

Atom	Atom	Atom	Angle (°)
C2	C3	N1	117.22(16)
O2	C4	C3	122.58(17)
O2	C4	C5	115.69(17)
C3	C4	C5	121.64(17)

¹ -x, -y, 2-z.

4. Conclusion

A single crystal of nitro-acetylacetonato copper polymer was grown and all the structural dimensions and symmetrical information's were collected and studied crystallographically.

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Supplementary data

CCDC-1533625 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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