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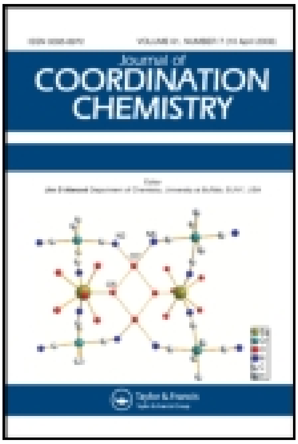

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and crystal structure of a copper(II) complex of 1,10-phenanthroline and succinate

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Published online: 07 Jul 2011.

To cite this article: Hazoor A. Shad , Khalid H. Thebo , Zafar H. Ibupoto , Muhammad A. Malik , Paul O'Brien & James Raftery (2011) Synthesis, characterization, and crystal structure of a copper(II) complex of 1,10-phenanthroline and succinate, Journal of Coordination Chemistry, 64:13, 2353-2360, DOI: 10.1080/00958972.2011.595789

To link to this article: http://dx.doi.org/10.1080/00958972.2011.595789

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Journal of Coordination Chemistry
Vol. 64, No. 13, 10 July 2011, 2353–2360

Synthesis, characterization, and crystal structure of a copper(II) complex of 1,10-phenanthroline and succinate

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(*Received 5 October 2010; in final form 5 April 2011*)

A mixed ligand complex of Cu(II) with 1,10-phenanthroline and succinate has been synthesized from the reaction of hydrated copper nitrate, succinate, and 1,10-phenanthroline. The nature of bonding and the structure of the complex were characterized by elemental analyses, infrared spectrum, TGA/DTA, and X-ray diffraction. The crystal crystallizes in triclinic space group $P\bar{1}$. The complex is polymeric and the geometry around each copper varies from square planar to distorted square pyramidal or octahedral. Each copper coordinates two oxygens of succinate and two nitrogens of 1,10-phenanthroline. The thermal decomposition of the complex has also been studied by TGA and DTA under inert atmosphere.

Keywords: Copper(II) complex; 1,10-Phenanthroline; Succinate; Copper nitrate

1. Introduction

Extensive efforts have been to synthesize mixed ligand complexes [1–3] due to their potential applications. Transition metal complexes, especially first row, play an important role in gas adsorption [4, 5], chemical absorption [6–8], selected gas exchange [9], heterogeneous catalysis [10, 11], and the design of molecular magnetic materials [12–17]. Dicarboxylates have been extensively used as ligands for complexation with various transition metals due to their structural diversity and coordination modes [18–20]. α,ω-Dicarboxylates have been used [21] as effective and flexible bridging ligands, which can link metals into supramolecular architectures with specific topologies. O'Brien prepared copper(II) complexes with oxalate and 2,2′-bipyridine and studied their interconversion properties in the solid state [21, 22]. Fitzgerald *et al.* [23] determined the crystal structures of $[Cu(bipy)(C_2O_4)]\cdot 2H_2O$ and $[Cu(bipy)(C_2O_4)(OH_2)]\cdot 2H_2O$ by X-ray diffraction. Among dicarboxylates, succinate is a versatile and active bridging ligand. In continuation of our previous work on copper(II) complexes of dicarboxylates, $[Cu_2(succ)(bpy)_4](NO_3)_2\cdot 10.5H_2O$, we herein

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.595789

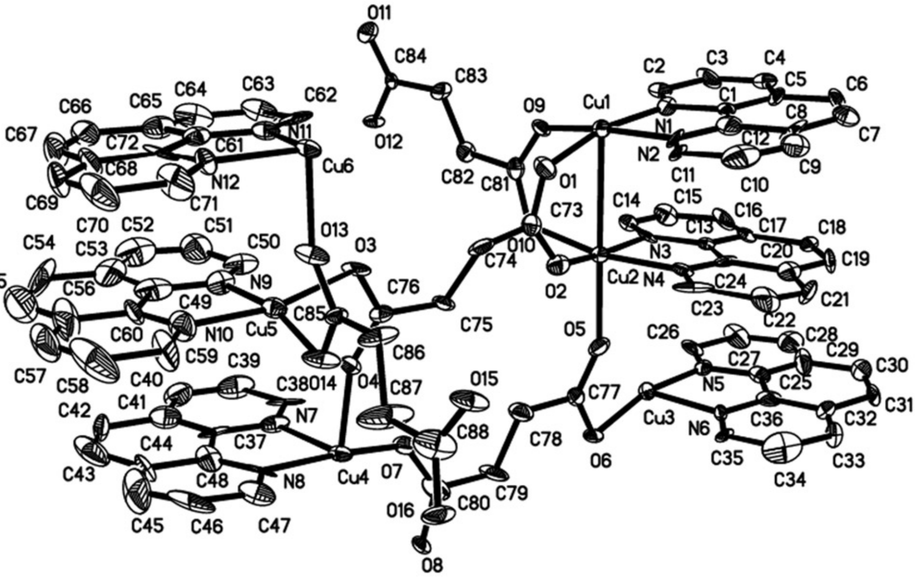

Figure 1. The molecular structure of $[Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$.

Table 1. Crystal data and structural refinement of poly$[Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$.

Empirical formula	$C_{88}H_{64}Cu_6N_{14}O_{27}$
Formula weight	2130.77
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.9222(15)
b	20.261(3)
c	23.167(3)
α	94.434°
β	97.429°
γ	90.089°
Volume ($Å^3$), Z	5068.0(12), 2
Calculated density ($Mg\,m^{-3}$)	1.396
Absorption coefficient (mm^{-1})	1.313
$F(000)$	2160
Crystal size (mm^3)	0.28 × 0.18 × 0.04
θ range for data collection	1.29–28.28
Limiting indices	$-14 \le h \le 14$; $-26 \le k \le 26$; $-30 \le l \le 30$
Reflections collected/unique	44,179/23,098 [R(int) = 0.1239]
Completeness to $\theta = 20.82$ (%)	99.1
Absorption correction	None
Max. and min. transmission	0.9493 and 0.7099
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	23,098/18/1206
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1152$, $wR_2 = 0.3411$
R indices (all data)	$R_1 = 0.2482$, $wR_2 = 0.3965$
Largest difference peak and hole	3.296 and $-2.027\,e\,A^{-3}$

Table 2. Bond lengths (Å) and angles (°) for $\text{poly}[\mathrm{Cu_6(phen)_6(succ)_4}]\cdot 2\mathrm{NO_3}\cdot 5\mathrm{O}$.

Cu(1)–O(1)	1.939(10)	Cu(5)–O(14)	1.953(10)
Cu(1)–O(9)	1.936(9)	Cu(5)–O(3)	1.962(9)
Cu(2)–O(2)	1.931(10)	Cu(6)–O(13)	2.120(10)
Cu(1)–O(11)	2.114(10)	Cu(6)–O(8)	1.944(9)
Cu(1)–Cu(2)	2.966(2)	Cu(6)–O(15)	1.951(10)
Cu(2)–O(10)	1.926(9)	Cu(6)–N(12)	2.008(11)
Cu(4)–O(7)	1.954(10)	Cu(3)–O(6)	1.968(9)
Cu(2)–O(5)	2.131(10)	Cu(4)–O(16)	1.924(10)
Cu(3)–O(12)	1.949(9)	Cu(4)–O(4)	2.072(9)
Cu(1)–N(1)	2.015(13)	Cu(5)–N(9)	1.976(12)
Cu(2)–N(4)	2.005(11)	Cu(2)–N(3)	2.035(11)
Cu(5)–N(10)	2.002(14)	Cu(4)–N(7)	2.025(12)
Cu(1)–N(2)	2.019(11)	Cu(6)–N(12)	2.028(12)
Cu(3)–N(5)	1.981(12)	Cu(3)–N(11)	2.013(12)
Cu(4)–N(8)	2.001(12)	Cu(6)–Cu(4)	2.938(3)
O(1)–Cu(1)–Cu(2)	79.9(3)	O(9)–Cu(1)–Cu(2)	75.6(3)
N(1)–Cu(1)–Cu(2)	90.8(3)	N(2)–Cu(1)–Cu(2)	97.6(3)
O(11)–Cu(1)–Cu(2)	171.1(3)	O(10)–Cu(2)–O(2)	92.5(4)
O(10)–Cu(2)–N(4)	168.3(4)	O(2)–Cu(2)–N(4)	92.4(4)
O(10)–Cu(2)–N(3)	90.6(4)	O(2)–Cu(2)–N(3)	172.5(4)
N(4)–Cu(2)–N(3)	83.3(5)	O(10)–Cu(2)–O(5)	103.0(4)
O(2)–Cu(2)–O(5)	96.3(4)	N(4)–Cu(2)–O(5)	87.0(4)
N(3)–Cu(2)–O(5)	89.5(4)	O(10)–Cu(2)–Cu(1)	81.9(3)
O(2)–Cu(2)–Cu(1)	76.4(3)	N(4)–Cu(2)–Cu(1)	89.0(3)
N(3)–Cu(2)–Cu(1)	97.4(3)	O(5)–Cu(2)–Cu(1)	171.6(3)
O(12)–Cu(3)–O(6)	92.3(4)	O(12)–Cu(3)–N(5)	94.0(4)
O(6)–Cu(3)–N(5)	165.3(4)	O(12)–Cu(3)–N(6)	165.3(4)
O(6)–Cu(3)–N(6)	94.7(5)	N(5)–Cu(3)–N(6)	82.3(5)
O(16)–Cu(4)–O(7)	92.4(5)	O(16)–Cu(4)–N(8)	92.6(5)
O(7)–Cu(4)–N(7)	91.9(5)	N(8)–Cu(4)–N(7)	81.7(5)
O(16)–Cu(4)–O(4)	95.4(4)	N(7)–Cu(4)–O(4)	94.6(4)
O(7)–Cu(4)–O(4)	99.4(4)	N(8)–Cu(4)–O(4)	88.6(4)
O(16)–Cu(4)–Cu(6)	80.0(3)	N(7)–Cu(4)–Cu(6)	90.4(3)
O(7)–Cu(4)–Cu(6)	77.0(3)	N(8)–Cu(4)–Cu(6)	95.5(3)
O(14)–Cu(5)–O(3)	92.4(4)	O(14)–Cu(5)–N(9)	164.3(5)
O(3)–Cu(5)–N(9)	96.4(5)	O(14)–Cu(5)–N(10)	93.4(6)
O(3)–Cu(5)–N(10)	166.4(5)	O(8)–Cu(6)–O(15)	90.9(5)
O(8)–Cu(6)–N(12)	169.6(5)	O(15)–Cu(6)–N(12)	92.2(5)
O(8)–Cu(6)–N(11)	94.3(5)	O(15)–Cu(6)–N(11)	171.3(5)
N(12)–Cu(6)–N(11)	81.5(5)	O(8)–Cu(6)–O(13)	100.6(4)
O(15)–Cu(6)–O(13)	99.0(4)	N(12)–Cu(6)–O(13)	88.8(4)
O(15)–Cu(6)–Cu(4)	76.7(3)	N(12)–Cu(6)–Cu(4)	91.6(3)

Table 3. Tau (τ) values for copper(II).

Cu1	0.053
Cu2	0.070
Cu3	0.000
Cu4	0.030
Cu5	−0.034
Cu6	−0.028

report $\text{poly}[\mathrm{Cu_6(phen)_6(succ)_4}]\cdot 2\mathrm{NO_3}\cdot 5\mathrm{O}$, synthesized from the reaction of 1,10-phenanthroline and succinate with Cu(II). The synthesized complex was characterized by elemental analyses, infrared (IR) spectrum, TGA/DTA, and X-ray diffraction methods.

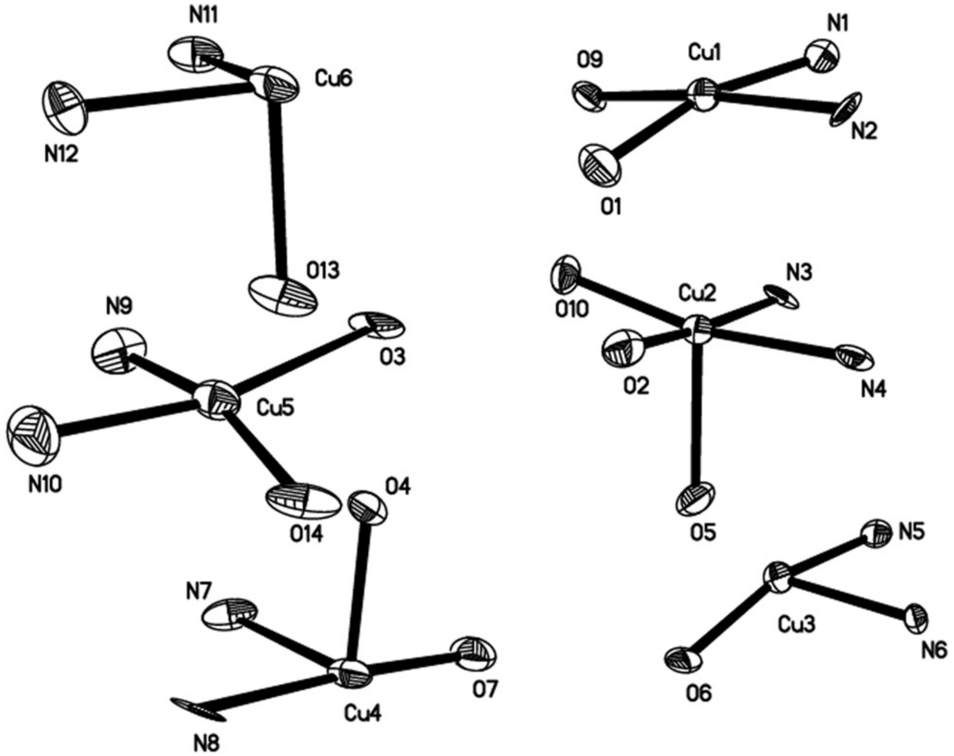

Figure 2. Coordination modes of the copper atoms in $[Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$.

2. Experimental

2.1. *Reagents and techniques*

Copper nitrate trihydrate, disodium succinate, 1,10-phenanthroline, and ethanol were of reagent grade (Sigma-Aldrich) and used without purification. Elemental analyses were carried out with a CHNS/O Analyzer (Thermo Scientific Flash 2000 Organic Elemental Analyzer). Copper analysis was carried out by Fisons Horizon Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). IR spectrum was recorded on a Bio-RAD Merlin (Varian) FTIR spectrometer from 4000 to 200 cm^{-1}.

2.2. *Synthesis of poly$[Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$*

An ethanol solution (25 mL) of 1,10-phenanthroline (0.18 g, 1.0 mmol) was added dropwise to aqueous solution (25 mL) of copper(II) nitrate trihydrate (0.24 g, 1.0 mmol) followed by slow addition of aqueous solution (25 mL) of succinate (0.16 g, 1.0 mmol) with constant stirring. The resulting mixture was stirred for 1 h with monitoring by TLC. After completion of the reaction, the solution was filtered, the resulting greenish solution was reduced to one-third of its volume by rotary evaporation and allowed to stand at room temperature. After 7 days, green crystals were collected from the

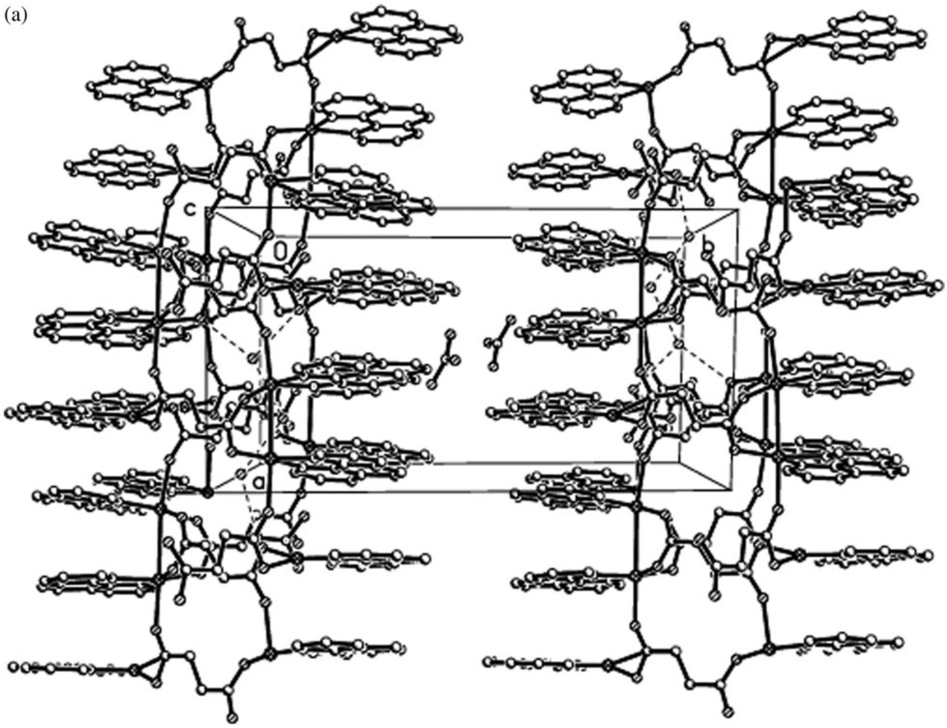

Figure 3. Unit cell packing of poly[$Cu_6(phen)_6(succ)_4$] · $2NO_3 \cdot 5O$.

mother liquor. The crystals were washed several times with cold water followed by diethyl ether and dried in open air. The crystals were stable to air and X-ray exposure. Yield = 80%; m.p. 248°C. Microanalyses: calculated for $C_{88}H_{64}Cu_6N_{14}O_{27}$ (%): C, 49.5; H, 3.0; N, 9.2; Cu, 17.8. Found (%): C, 49.4; H, 3.0; N, 8.9; Cu: 17.5.

2.3. *X-ray crystallography*

The collection of single-crystal XRD data of the title compound was performed with an AXS SMART APEX (Bruker) diffractometer equipped with a graphite-crystal monochromator using Mo-Kα radiation ($k = 0.71073$ Å) at 100(2) K. The structure of the compound was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELX97) [24–26].

3. Results and discussion

3.1. *X-ray crystal structure*

The polymeric molecular structure of poly[$Cu_6(phen)_6(succ)_4$] · $2NO_3 \cdot 5O$ is shown in figure 1. Crystallographic data, selected bond lengths, bond angles, and tau (τ) values are given in tables 1–3, respectively. Each copper of poly[$Cu_6(phen)_6(succ)_4$] · $2NO_3 \cdot 5O$

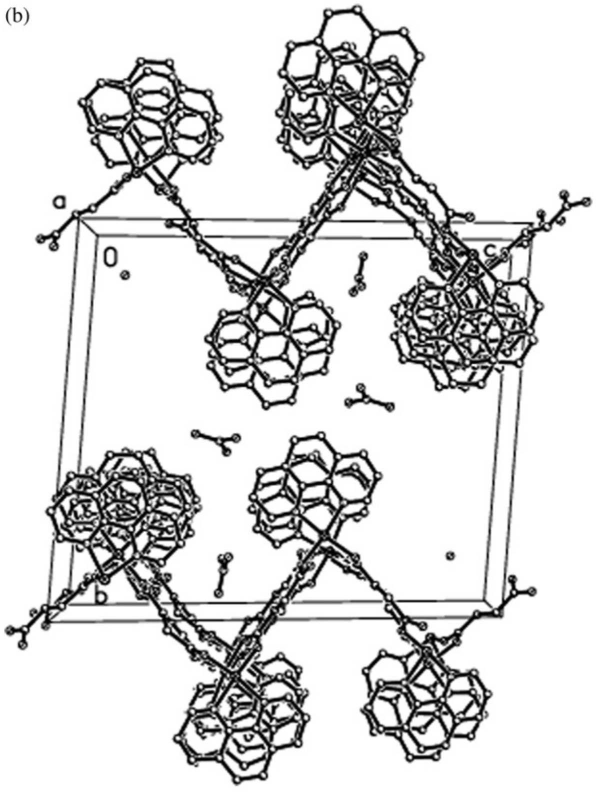

Figure 3. Continued.

is linked through oxygens of two succinates [e.g., Cu(1)–O(1) 1.939(10) Å, Cu(1)–O(9) = 1.936(9) Å], coordinated with 1,10-phenanthroline [Cu(1)–N(1) = 2.015(13) Å, Cu(1)–N(2) = 2.019(11) Å], and may also be coordinated with other oxygens or coppers [e.g., Cu(1)–Cu(2) = 2.966(2) Å] (figure 2). The average Cu–N (2.105 Å) and Cu–O (1.996 Å) distances in the complex are similar [Cu–N = 2.072(9) and Cu–O = 2.235(12) Å] to a previously reported complex [1]. The crystal structure is composed of pleated polymeric sheets, parallel to *c*, of $[Cu(phen)]^{2+}$ ions, stacked along *a*, bridged by the carboxylate of succinate (figure 3a and b). Nitrates lie between the sheets.

The supramolecular structure is very similar to that of a previously reported compound [27] in which all the oxygens of succinate are linked with two coppers. The present complex differs from the reported compound due to one unlinked oxygen. A similar π-stacking interaction is also seen in this structure. These interactions seem to be responsible for the stability of supramolecular chemistry of the complex (figure 3a).

3.2. *IR spectroscopy*

Some characteristic IR spectral bands of poly$[Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$ are given in table 4. The complex exhibited a new and strong band at 428 cm^{-1} assigned to

Table 4. Important IR bands ν(cm^{-1}) observed for poly[$Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$.

O–H (H_2O)	3441 (b)
C=O	1544 (vs)
Cu–O	525 (m)
Cu–N	428 (s)

(b) = broad, (vs) = very strong, (s) = strong, (m) = medium.

metal–nitrogen bonds, clearly indicating the formation of a new bond between 1,10-phenanthroline and copper. Another new band at 525 cm^{-1} assigned to ν(Cu–O) was observed in the spectrum of the copper complex. This new bonding mode indicated coordination through oxygen of succinate. The copper complex showed a strong and broad band at 3441 cm^{-1} assigned to ν(O–H), indicating the presence of water in the complex. The complex showed a strong band at 1544 cm^{-1} assigned to ν(C=O) in succinate.

3.3. *Thermogravimetric analyses*

Thermal decomposition of poly[$Cu_6(phen)_6(succ)_4] \cdot 2NO_3 \cdot 5O$ was performed up to 600°C under nitrogen. The study was carried out at 10°C min^{-1}. The decomposition of the complex takes place in three mass-loss steps before 390°C. The first step completed in the range of 50–100°C, corresponding to the endothermic elimination of NO_3. The experimental mass loss of 6.9% agrees with the calculated mass loss of 5.8%. The degradation of succinate takes place in the second step at 230–260°C, releasing CO_2 (mass loss: found 12.1%; calculated 12.6%) and then $CO_2 + CO$ gas was released simultaneously (mass loss: found 27.7%; calculated 27.2%). In the final step, decomposition of phenanthroline takes place with mass loss (42.5%) and calculated mass (42.0%) agreeing. At the end, the analysis showed (mass loss: found 54.3%; calculated 53.7%) that the final residue is Cu_2O.

4. Conclusion

A polymer copper(II) complex of succinate and 1,10-phenanthroline has been synthesized and characterized by elemental analyses, IR spectroscopy, thermogravimetric analyses, and X-ray diffraction. The X-ray study showed polymeric complex in which each copper is five-coordinate in a distorted square planar environment.

Acknowledgments

The authors are grateful to the Government of Pakistan for financial support and School of Chemistry, the University of Manchester, UK, for providing research facilities.

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