Synthesis, Spectroscopic Properties and Structural Studies of Copper(II) Complexes of 2-Substituted-1,3-Diphenyl-1,3-Propanedione, Their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts

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Abstract

The complexes of 2-substituted-1,3-diphenyl-1,3-propanedione with copper(II) ion and their 2,2'-bipvridine and 1,10-phenanthroline adducts were synthesised and characterised by microanalysis, conductance, magnetic and spectral measurements. The conductance data showed that [Cu(dbm)(phen)](dbm) and [Cu(Me-dbm)(phen)](Me-dbm) are 1:1 electrolytes. The infrared spectra revealed the different shifts of the carbonyl frequency. While the electronic solid reflectance spectra of the prepared complexes exhibited three peaks with varying λ_{max} between 12,121-21,505 cm⁻¹, the adducts displayed single bands in the visible region between 13,553-14,698 cm⁻¹ except for [Cu(dbm)(phen)](dbm) and [Cu(Me-dbm)(phen)](Me-dbm) with additional two peaks. These peaks have been assigned as d-d transitions. Using Density Functional Theory (DFT) and Semi-empirical PM3, the modeled compound showed a distorted five coordinate square pyramidal geometry.

Keywords: 2-substituted-1-phenyl-1,3-butanedione, spectra studies, magnetic susceptibility, elemental analyses, DFT

1. Introduction

β-diketonates have been used as shift reagents for the structural determination of steroids and other complex molecules (Hinckley, 1969, 1970). Metal β-diketonates have also been used in fuel additives; trace metal analysis by gas chromatography and other numerous extraction applications (Wenzel, 1985). We have recently reported the magnetic nickel(II) and spectral properties of complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their 2,2'-bipyridine and 1,10-phenanthroline adducts and were able to correlate the band shifts with the positive inductive effect of the substituted alkyl group on the system (Woods et al., 2009). These studies have been extended to the copper(II) derivatives of 2-substituted-1,3-diphenyl-1,3-propanedione [R-dbmH, where R = methyl (Me), ethyl (Et) and normal-butyl (n-Bu)] and their 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts to investigate the effects of these substituents on the properties of these compounds. Density functional theory is a widely used method for electronic structure calculations and provides useful predictions for molecular parameters (Perdew et al., 2005). In this paper, we present our report on synthesis, microanalysis, conductance, magnetic and spectral measurements of Copper(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione, their 2,2'-bipyridine and 1,10-phenanthroline adducts and the DFT and PM3 calculations of Cu(Me-dbm)₂bipy.

2. Method

The following reagents were used: 1,3-diphenyl-1,3-propanedione or dibenzoylmethane (dbmH) (Aldrich chemicals), potassium carbonate, copper acetate, methyl iodide, ethyl iodide, n-butyl iodide (Aldrich chemicals), 2,2'-bipyridine and 1,10-phenanthroline (Analytical grade).

2.1 Synthesis of the Ligands

2-alkyl-1,3-diphenyl-1,3-propanediones were prepared as previously reported (Patel & Woods, 1990a).

2.2 Synthesis of the Complexes and Adducts

2.2.1 Synthesis of Cu(dbm)₂

1,3-diphenyl-1,3-propanedione (1.7972 g, 8 mmol) which was dissolved in 10 mL acetone, was added to copper(II) acetate tetrahydrate(0.8 g, 4 mmol) in 25 mL 40% methanol. The precipitated solids were washed with 40% methanol and acetone and dried over silica gel. Similar procedure was used for preparation of the other copper(II) complexes.



Equation 1. Preparation of copper(II) complex

2.2.2 Synthesis of Cu(Me-dbm)₂bipy

Solid Cu(Me-dbm)₂ (0.3 g, 0.556 mmol) was added pinchwise to solution of 2,2'-bipyridine (0.286 g, 1.833 mmol) in 15 mL chloroform. This mixture was stirred for 30minutes and the precipitates formed were filtered and washed with chloroform.



Equation 2. Preparation of copper(II) adduct

2.3 Physical Measurements

Elemental analyses for C, H, N were determined at Department of Chemistry, Loughborough University, UK. The % metal in the copper(II) complexes and adducts was determined titrimetrically with EDTA. The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech).

The solution spectra of the compounds in methanol and chloroform were recorded on a Unicam UV-Visible Spectrophotometer using 1cm glass cell. The reflectance spectra of the copper(II) compounds were recorded on a Perkin-Elmer Lambda 950 UV/VIS spectrophotometer at the Department of Chemical Engineering, Faculty of

Technology, Addis Ababa University, Ethiopia using calcium carbonate as reference. The infrared spectra of the compounds, as pressed KBr disc, were recorded on Perkin-Elmer Spectrophotometer BX FT-IR.

2.4 Computational Methods

Complete geometrical optimisation without symmetry constraint was performed using DFT (Density Functional Theory) with Becke's three parameter exchange functional, along with the Lee-Yang-Parr correlation functional and with LANL2DZ basis set. All calculations were done with Spartan '06 V112 (Shao et al., 2006). The vibrational wavenumbers were calculated using the PM3 method and a C1 point group. The positive value of all the calculated wavenumbers indicates the stability of the optimised geometry.

3. Results and Discussion

The analytical and the physical data are shown in Table 1. Different shades of green colour were observed for all the copper(II) compounds. The Microanalytical data, as depicted in Table 2, shows that the elemental analyses are consistent with the proposed stoichiometry.

The prepared 2-substituted-1,3-diphenyl-1,3-propanedionato copper(II) complexes have moments in the range 1.75-2.00 B.M. An increase was observed on substituting the 2-position of Cu(dbm)₂ with alkyl groups except Cu(n-Bu-dbm)₂ with decreased moment. The observed magnetic moments of the synthesised 2,2'-bipyridine and 1,10-phenanthroline adducts of 2-substituted-1,3-diphenyl-1,3-propanedionato copper(II) complexes are in the range 1.95-2.10 B.M. This shows that they are magnetically dilute compounds and that there is no intermolecular magnetic interaction. An increase in magnetic moments was observed in all the adducts as compared with the appropriate parent complexes.

Formula	MM	Colour	M.Pt (°C)	Yield (%)	µeff (B.M)
Cu(dbm) ₂	510.00	Y. green	300-302	16.52	1.75
Cu(dbm) ₂ bipy	666.20	D. green	290-292	15.50	2.04
[Cu(dbm)(Phen)](dbm)	690.22	Y. Green	235-237	62.42	1.95
Cu(Me-dbm) ₂	538.08	Y. green	203	20.4	1.78
Cu(Me-dbm) ₂ bipy	694.26	D. green	290-292	55.69	2.10
[Cu(Me-dbm)(Phen)](Me-dbm)	736.30	D. green	283-285	64.23	2.08
Cu(Et-dbm) ₂	566.14	Y. green	306-308	57.03	2.00
Cu(Et-dbm) ₂ bipy	722.32	Green	319-321	30.86	2.06
Cu(Et-dbm) ₂ phen	746.34	Y. Green	314-316	24.2	2.10
Cu(n-Bu-dbm) ₂	622.26	Y. green	317-319	65.58	1.97
Cu(n-Bu-dbm) ₂ bipy	778.44	B. green	220-222	42.89	2.10
Cu(n-Bu-dbm) ₂ phen	802.46	B. green	329-331	45.96	2.10

Table 1. Analytical and physical data of Copper(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their adducts

D = dark, Y = yellowish, G = greenish, B = bright.

The molar conductivities of these complexes were very low with Λ_m values of 4.2-29.7 ohm⁻¹ cm² mole⁻¹, which suggests that they are non-electrolytes. Similarly, the molar conductivities of the Cu(R-dbm)₂ adducts indicate that they are non-electrolytes except [Cu(dbm)(phen)](dbm) and [Cu(Me-dbm)(phen)](Me-dbm), which are 1:1 electrolytes with an outer sphere anion as reflected in the Λ_m values of 82-84 ohm⁻¹ cm² mole⁻¹.

The carbonyl and carbon-carbon double bonds have less double bond character and more single bond character in the conjugated ring, which accounted for the large frequency shifts usually observed. Studies have revealed that three factors determine the position of the perturbed carbonyl band in the spectrum of a given chelate: the masses of the groups attached at the ends of the ligand molecule to the carbonyl groups; interaction of the carbonyl with neighbouring π or d-orbitals and the relative electron density of the σ bond. Moreover, the comparison of the infrared spectra taken at low temperature with those at room temperature shows that there is a sharpening up of the bands in the low temperature spectrum owing to the decreased population of the higher vibrational states of the molecule (Fackler et al., 1968).

In the complexes studied, the frequencies of the asymmetric C=O and C=C stretching vibrations were lowered from their free ligand values (Table 3). The $v_{as}(C=O) + v_{as}(C=C)$ vibrations of the copper(II) complexes occurred as multiple bands in the 1514-1653 cm⁻¹ region. Single band of $v_s(C-O) + \delta C$ -H were observed in Cu(dbm)₂ while Cu(Me-dbm)₂, Cu(Et-dbm)₂ and Cu(n-Bu-dbm)₂ had double bands. Upon adduct formation, hypsochromic shifts of the $v_{as}(C=O) + v_{as}(C=C)$ in all the adducts relative to the parent complexes were observed except Cu(Me-dbm)₂bipy, Cu(Me-dbm)₂phen, and Cu(Et-dbm)₂phen which had bathochromic shifts. The observed shifts can be used to predict the type of bonds in the adducts (Holtzclaw & Collman, 1957; Tanaka et al., 1969). The hypsochromic shifts probably indicate stronger Cu-N and C-O bonds and weaker Cu-O bonds while the reverse is applicable for bathochromic shifts. The symmetric and asymmetric methyl bending vibrations of the adducts appeared with varying shifts as compared with the complexes. CH deformation bands of 2,2'-bipyridine were observed as strong bands in the 745-778 cm⁻¹ region. Coupled Cu-O and Cu-N stretching vibrational modes occurred in the range 420-696 cm⁻¹ in the 2,2'-bipyridine and 1,10- phenanthroline adducts (Patel & Woods, 1990b).

Table 2. Microanalytical data of Copper(II) complexes of 2-substituted-1,3-diphenyl-1,3-propanedione and their adducts

Compound		% Calculated (Observed)				
		С	Н	Ν	М	
1.	Cu(dbm) ₂	70.64(70.51)	4.36(4.37)	-	12.45(12.83)	
2.	Cu(dbm) ₂ bipy	72.11(72.28)	4.55(4.72)	4.20(4.18)	9.53(9.73)	
3.	[Cu(dbm)(phen)](dbm)	73.08(73.12)	4.39(4.46)	4.06(4.02)	9.20(8.97)	
4.	Cu(Me-dbm) ₂	71.42(71.52)	4.88(5.07)	-	11.80(11.96)	
5.	Cu(Me-dbm) ₂ bipy	72.66(72.59)	4.95(5.29)	4.03(3.92)	9.15(8.81)	
6.	[Cu(Me-dbm)(phen)](Me-dbm)	71.77(71.52)	4.94(4.89)	3.80(4.05)	8.62(8.32)	
7.	Cu(Et-dbm) ₂	72.13(71.90)	5.35(5.09)	-	11.22(11.45)	
8.	Cu(Et-dbm) ₂ bipy	73.16(73.09)	5.31(5.51)	3.88(4.09)	8.79(8.98)	
9.	Cu(Et-dbm) ₂ phen	74.02(73.88)	5.14(4.90)	3.75(3.86)	8.51(8.64)	
10.	Cu(n-Bu-dbm) ₂	73.34(73.18)	6.17(5.92)	-	10.20(10.59)	
11.	Cu(n-Bu-dbm) ₂ bipy	74.06(73.10)	5.97(6.15)	3.60(3.81)	8.16(7.84)	
12.	Cu(n-Bu-dbm) ₂ phen	74.83(75.04)	5.79(5.60)	3.49(3.52)	7.91(8.21)	

The solution spectra of the copper(II) complexes were studied in chloroform and methanol. The assignments of the bands have been made with the help of literature on similar compounds (Fackler et al., 1968; Patel & Woods, 1990b, 1990c). Hypsochromic shift of the π_3 - π^*_4 band was observed in Cu(Et-dbm)₂ as compared with Cu(dbm)₂ in chloroform. Cu(Me-dbm)₂ had bathochromic shift while Cu(n-Bu-dbm)₂ had no shift. Coordinating solvents have been found to have a particular dramatic effect on the ligand field spectra of copper(II) compounds (Patel & Woods, 1990b). As a result of this, when there is a higher frequency shift in the ligand field spectra band of the copper compounds in coordinating solvents relative to non-coordinating (chloroform), it indicates a probable square pyramidal structure. A probable four coordinate square planar structure is observed when there is lower frequency shift in coordinating solvent relative to non-coordinating. For six-coordinate octahedral geometry, the band position remains unchanged in both coordinating and non-coordinating solvents. Thus, the various synthesised Cu(R-dbm)₂ have probable, four-coordinate, square planar geometry due to their lower frequency shifts in methanol relative to chloroform. Copper(II) complexes with square planar stereochemistry commonly exhibit a broad structured band between 13,000 to 20,000 cm⁻¹. They have absorption that shows little structure between 18,000 to 21,000 cm⁻¹ and no electronic absorption below 10,000 cm⁻¹ (Lever, 1986). In the synthesised complexes, the little structure absorption was observed between 18,051-18,087 cm⁻¹ in chloroform, which also shows that the various synthesised Cu(R-dbm)₂ have probable four-coordinate, square planar geometry.

Formula	C=0 $C=C$	v (C-O)+8C-H	$\delta_{as}(CH_3)+$	γ(C-H)	
Torniula	0,00	V _s (C-O)+0C-II	$\delta_s(CH_3)$	Phen/bipy	
dbmH	1598b, 1540b	1466b	-	-	
Cu(dbm) ₂	1593s,1545b,1526b	1484m	-	-	
Cu(dbm) ₂ bipy	1618w,1593s,1515s	1484m	-	745s	
[Cu(dbm)(phen)](dbm)	1624w,1594m,1551s	1478m,1451m	-	843m,721s	
Me-dbmH	1689m,1664m,1595m	1450s	1346s		
Cu(Me-dbm) ₂	1653vw,1582m,1514s	1498m,1471w	1418m,1370m		
Cu(Me-dbm) ₂ bipy	1594s,1546m,1525m	1484m,1455m	1400s	764w	
[Cu(Me-dbm)(phen)] (Me-dbm)	1630w,1587w,1518s		1343m	852s,722s	
Et-dbmH	1687vs,1665s,1697vs	1466b, 1449m	1356s		
Cu(Et-dbm) ₂	1595s,1542m,1524m	1475s,1457m	1402vs		
Cu(Et-dbm) ₂ phen	1587m,1546m,1516vs	1456w,1424vs,1401w	854vs	721vs	
n-Bu-dbmH	1693s,1667s,1596m	1447s	1380vw,1348m		
Cu(n-Bu-dbm) ₂	1598s,1532b	1482m, 1456m	1398vs		
Cu(n-Bu-dbm)2bipy	1606s,1572m,1551w	1470s,1442vs,1382m		774vs	
Cu(n-Bu-dbm)₂phen	1627w,1584m,1514s	1496w,1426vs,1373w		856vs,718vs	

Table 3. Relevant Infrared Spectra bands (cm⁻¹) of 1,3-diphenyl-1,3-propanedione, the Copper(II) complexes and their adducts

B = broad, s = strong, v = very, w = weak, m = medium.

In a study, the visible bands shifted to higher frequencies on replacement of hydrogen by alkyl groups and the magnitude of the shift was about the same in all the solvents. This was attributed to the inductive effect of the alkyl groups leading to a higher ligand field. It was also detected that lengthening of the alkyl side chain produced no further change in the formation constants (Graddon & Schulz, 1965). Transitions in Copper(II) of β -diketonates with absorption at energies higher than 24,000 cm⁻¹ originate from charge transfer from β -diketones ion to the metal (Melnik et al., 1996; Gorbenko et al., 1997). In the prepared complexes, high-energy absorption was observed at 27,855 cm⁻¹ in Cu(dbm)₂.

The tentative assignment of the reflectance spectra of the ligands (R-dbmH), copper(II) complexes and their adducts in calcium carbonate are presented in Table 5. The visible spectra of all the complexes studied displayed three bands in this region with varying λ_{max} between 12,121-21,505 cm⁻¹, which is consistent with square planar geometry for copper(II) complexes. The spectra of the Cu(R-dbm)₂ adducts displayed single bands in the visible region between 13,553-14,698 cm⁻¹. This is also consistent with square pyramidal geometry for copper(II) compounds (Odunola et al., 2003) except [Cu(dbm)(Phen)](dbm) and [Cu(Me-dbm)(Phen)](Me-dbm) with little structure absorption at 18,149-21,978 cm⁻¹ which corresponded with square planar structures (Lever, 1986). In the synthesised complexes, π_3 - π_4 * transitions were observed in the 31,153-33,445 cm⁻¹ region. Splitting of this band was not observed in any of the prepared complexes. Bands in the 40,000-44,843 cm⁻¹ regions have been assigned as benzenoid/ σ_L - $3d_{xy}$ transitions (Johnson & Thornton, 1975). The ultraviolet region of the solid reflectance spectra of the adducts showed hypsochromic shift of the π_3 - π_4 * transition upon adduct formation. In the adducts, π_3 - π_4 * transition appeared as single bands at 32,154-35,971 cm⁻¹ region except Cu(Et-dbm)₂bipy which had an additional band.

Emperical Formula	$\pi_{3}\pi_{4}^{*}(\text{cm}^{-1})$		d	d-d	
Emperiedi Formula	CHCl ₃	CH ₃ OH	CHCl ₃	CH ₃ OH	
dbmH	34,483(20567)	34,364(23114)			
Cu(dbm) ₂	34,722*	-	18,051*	-	
	34,014(45546)		15,337(7735)		
Cu(dbm) ₂ bipy	33,445(?)	32,895(?)	-	13,947(?)	
[Cu(dbm)(phen)](dbm)	34,014*	34,014(24354)	20,325*	16,340(116)	
			13,966(225)		
Me-dbmH	34,247(5282)	-			
Cu(Me-dbm) ₂	34,014*	35,971(?)	15,991(?)	15,649(?)	
		34,247(?)		14,164(?)	
Cu(Me-dbm) ₂ bipy	33,333(7462)	33,113(11609)	16,181(59)	16,831(62)	
			12,531(555)		
[Cu(Me-dbm)(phen)](Me-dbm)	34,114(37393)	34,483(57112)	20,492(405)	16,129(234)	
			13,966		
Et-dbmH	32,259(20203)	34,602(6951)			
Cu(Et-dbm) ₂	34,965(?)	-			
Cu(Et-dbm) ₂ bipy	34,602(?)	33,445(?)	14,970(?)	15,966(?)	
		32,258(?)			
Cu(Et-dbm) ₂ phen	34,722*	34,843(?)	-	15,314(?)	
n-Bu-dbmH	35,211(?)	35,088(?)			
Cu(n-Bu-dbm) ₂	34,722*	34,965*	18,087*	17,422(?)	
			14,903(?)		
Cu(n-Bu-dbm) ₂ bipy	33,557(?)	33,223(?)	15,015(?)	15,947(?)	
Cu(n-Bu-dbm) ₂ phen	33,784(?)	34,364(?)	15,823(?)	15,928(?)	

Table 4. The electronic solution spectra of 2-substituted-1,3-diphenyl-1,3-propanedione Copper(II) complexes and their adducts

(?) Compounds are partially soluble in the solvent.

Emperical Formula	$\pi_{3}\pi_{4}*(cm^{-1})$	d-d
dbmH	35,211	-
Cu(dbm) ₂	33,445	19,493, 16,892, 12,121
Cu(dbm) ₂ bipy	35,842	14,048
[Cu(dbm)(Phen)](dbm)	33,557	21,322*, 18,149, 12,092
Me-dbmH	34,398	-
Cu(Me-dbm) ₂	33,014	18,360*15,198, 12,170
Cu(Me-dbm) ₂ bipy	33,557	14,305
[Cu(Me-dbm)(Phen)](Me-dbm)	34,965	21,142*, 18,282, 12,048
Et-dbmH	35,088, 33,003	
Cu(Et-dbm) ₂	31,153	21,505, 19,455,12,195
Cu(Et-dbm)2bipy	35,971, 32,154	13,692, 14,531
Cu(Et-dbm) ₂ phen	34,014	14,493
n-Bu-dbmH	35,971	
Cu(n-Bu-dbm) ₂	33,113	19,531, 17,123, 12,225
Cu(n-Bu-dbm)2bipy	34,843	14,455
Cu(n-Bu-dbm) ₂ phen	34,602	13,692

Table 5. The electronic solid reflectance spectra of 2-substituted-1,3-diphenyl-1,3-propanedione, Copper(II) complex and its adducts



Figure 1. a) Infrared spectra of 1,3-diphenyl-1,3-propancedione, copper(II) complex and its adducts
b) Infrared spectra of 2-Methyl-1,3-diphenyl-1,3-propancedione, copper(II) complex and its adducts
Figure 2. a) Visible spectra of Cu(dbm)₂ and its adduct in chloroform
b) Visible spectra of Cu(Me-dbm)₂ and its adduct in chloroform

4. Computational Studies

4.1 Geometry and Structural Data

Density Functional Theory at B3LYP/LANL2DZ was used for geometry optimisation and electronic structure determination (Karakas & Sayin, 2013; Malecki et al., 2010). The optimised geometry of the Cu(Me-dbm)₂bipy is shown in Figures 3(a) and (b). Table 6 shows the selected calculated bond distances, angles, of the modeled compound and the experimental X-ray crystallographic data (Zheng et al., 1991) of a five-coordinated copper(II) complex of 2,2'-bipyridine. The optimised bond distances at both semi-empirical PM3 and B3LYP levels are comparable with the corresponding values obtained from the X-ray diffraction as can be seen in Table 6 (Zheng et al., 1991). The DFT calculated angles/bite angles for O(1)–Cu-O(2), O(1)-Cu-O(3), O(1)-Cu-N(2), N(1)-Cu-N(2) and O(2)-Cu-N(1) are 89.37°, 87.97°, 109.26°, 77.7°, and 92.40° respectively. The variation from the ideal value could be attributed to the distortion from the perfect square pyramidal structure around the Copper(II) ion of the compound. Figures 3(c) and 3(d) show the HOMO and LUMO orbitals of the Copper(II) compound. The HOMO is predominantly located on the 2,2'-Bipyridine moiety and the LUMO is essentially spread around the 2 units of 2-Methyl-1,3-diphenyl-1,3-propanedione. The B3LYP modeled molecular structure is five coordinate Copper(II) adduct and consists of 2 units of 2-Methyl-1,3-diphenyl-1,3-propanedione and one unit of 2,2'-Bipyridine. The coordinated environment around the Copper(II) is a distorted square pyramidal with three oxygen atoms of 2-Methyl-1,3-diphenyl-1,3-propanedione and two nitrogen atom of 2,2'-Bipyridine.



Figure 3. (a) FB3LYP Optimized structure of Cu(Me-dbm)₂bipy; (b) Optimized structure of Cu(Me-dbm)₂bipy (Tube form); (c) Lumo plot of Cu(Me-dbm)₂bipy; (d) Homo plot of Cu(Me-dbm)₂bipy

The molecular data from DFT calculation are summarized in Table 7. The energy gap between LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) is 0.329 eV. The low energy gap indicates high reactivity (Fan et al., 2007; Herrag et al., 2010; Obot & Obi-Egbedi, 2010; Obot et al., 2012). The dipole moment is 28.93 debye. The value of the dipole moment indicates that Cu(Me-dbm)₂bipy is polar and has

Numbering	PM3	B3LYP/LANL2DZ	Exp ^a
Cu-O ₁	1.853	1.902	1.935
Cu-O ₂	1.866	1.958	1.920
Cu-O ₃	1.859	1.961	2.204
Cu-N ₁	1.881	2.015	1.983
Cu-N ₂	1.978	2.269	1.991
O_1 - C_1	1.299	1.326	1.274
O ₂ -C ₁₀	1.307	1.304	1.260
N ₁ -C ₃₅	1.383	1.360	1.356
N ₁ -C ₃₆	1.368	1.348	1.335(8)
N ₂ -C ₃₃	1.384	1.357	1.341
N ₂ -C ₄₃	1.367	1.346	1.336
C ₃₃ -C ₃₅	1.483	1.485	1.478
C_{33} - C_{41}	1.399	1.403	1.373
C ₃₄ -C ₃₈	1.393	1.397	1.36(1)
C ₃₄ -C ₃₇	1.389	1.398	1.36(1)
C ₃₅ -C ₃₈	1.399	1.403	1.36(1)
C ₃₆ -C ₃₇	1.396	1.395	1.38(1)
C ₃₉ -C ₄₃	1.395	1.398	1.37(1)
C ₃₉ -C ₄₂	1.388	1.398	1.37(1)
C_{41} - C_{42}	1.393	1.398	1.38(1)
O ₁ -Cu-O ₂	97.31	89.37	92.2
O ₁ -Cu-O ₃	89.77	87.97	93.3
O ₁ -Cu-N ₂	100.13	109.26	91.9
O ₁ -Cu-N ₁	167.76	1732.60	167.3
O ₂ -Cu-N ₁	86.28	92.40	92.2
$O_1 - C_1 - C_8$	128.37	126.15	123.6
$O_2-C_{10}-C_8$	127.54	123.64	127.9
N ₁ -Cu-N ₂	90.78	77.70	81.2
N_1 -Cu- O_3	83.38	88.04	97.6
N ₂ -Cu-O ₃	96.91	102.57	92.8
N ₁ -C ₃₆ -C ₃₇	120.71	121.56	122.1
N ₁ -C ₃₅ -C ₃₃	117.53	116.99	114.2
N_1 - C_{35} - C_{38}	119.52	119.58	121.4
N_2 - C_{33} - C_{41}	120.74	120.78	121.7
N ₂ -C ₃₃ -C ₃₅	116.69	115.83	114.3
$C_1 - C_8 - C_{10}$	119.72	119.99	123.8
C_{36} - N_1 - C_{35}	120.43	121.13	118.4
C_{43} - N_2 - C_{33}	118.65	120.11	119.0
C ₄₃ -N ₂ -Cu	135.06	129.08	125.7

Table 6. Selected calculated bond distances, angles, of the modeled compounds and the experimental X-ray crystallographic data

a. Ref. (Sheela, Sampathkrishnan, Kumar, & Muthu, 2013).

high tendency to react with other charged compounds (Herrag et al., 2010). The modeled Copper(II) complex has 83 atoms, 234 normal modes of fundamental vibrations and possesses C1 point group. By using semi-empirical PM3 method, the vibrational frequencies of the modeled Copper(II) complex were calculated in the ground state. Calculated vibrational frequencies are scaled by a factor 0.974, that was recommended by Scott and Radom (Scott & Radom, 1996). Fourteen calculated vibrational frequencies are selected and reported in Table 8. Some of the calculated vibrational wavenumbers were found to agree quite well with the available experimental data. Discrepancy between calculated and experimental values could be due, in part, to anharmonicity and the tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry (Sheela et al., 2013).

Table 7. The DFT Molecular parameters of Cu(Me-dbm)₂bipy

E _{LUMO} (eV) -3.509866
$E_{HOMO}(eV) = -3.838417$
$\Delta E = E_{LUMO} - E_{HOMO} = 0.329$
Dipole moment = 28.93 debye

Table 8. Comparison of the observed and calculated vibrational wavenumber (cm^{-1}) of $Cu(Me-dbm)_2$ bipy with PM3 method

Mode No	PM3 Calculated Unscaled	PM3 Calculated Scaled	INT. IR	FT-IR Exp.	Assignments as in Table 6
1	790.72	767	26.24	-	
2	792.16	768	179.29	764w	γ(C-H) Phen/bipy
3	797.32	777	30.40	-	
4	1442.63	1405	42.06	1400s	$\delta_{as}(CH_3)+\delta_s(CH_3)$
5	1485.90	1447	152.06	1455m	$\nu_s(C-O)+\delta C-H$
6	1498.69	1460	558.22	-	
7	1523.18	1484	112.26	1484m	ν _s (C-O)+δC-H
8	1536.51	1497	5.53	-	
9	1539.15	1499	13.54	-	
10	1589.84	1549	6.63	1525m	$v_{as}(C=O) + v_{as}(C=C)$
11	1601.65	1560	7.95	1546m	$v_{as}(C=O) + v_{as}(C=C)$
12	1604.66	1563	145.3	-	
13	1609.33	1567	72.14	-	
14	1636.41	1594	577	1594s	$v_{as}(C=O) + v_{as}(C=C)$

 v_s = symmetric stretching; γ = out of plane bending; δ_{as} = assymetric; Int = IR intensity.

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References

Fackler Jr., J. P., Mittleman, M. I., Weigold, H., & Barrow, G. M. (1968). Spectra of metal β-ketoenolates. The electronic spectrum of monomeric nickel(II) acetylacetonate and the infrared spectra of matrix-isolated acetylacetonates of cobalt(II), nickel(II), copper(II) and zinc(II). *Journal of Physical Chemistry*, 7(13),

4631-4636. http://dx.doi.org/10.1021/j100859a046

- Fan, D., Afzaal, M., Mallik, M., Nguyen, C., & O'Brien, P. (2007). Using Coordination Chemistry to develop new routes to semiconductor and other materials. *Coordination Chemistry Reviews*, 251, 1878-1888. http://dx.doi.org/10.1016/j.ccr.2007.03.021
- Gorbenko, O. Y., Troyanov, S. I., Meetsma, A., & Bosak, A. A. (1997). Crystal structure of copper(II) pivaloyltrifluoroacetonate adducts with o-phenanthroline and 2,2'-dipyridyl. *Polyhedron*, *16*(12), 1999-2004. http://dx.doi.org/10.1016/S0277-5387(96)00519-0
- Graddon, D. P., & Schulz, R. A. (1965). Adducts of copper(II) β-diketone chelates with heterocyclic bases. II. Chelates with 3-alkylacetylacetones. *Australian Journal of Chemistry*, 18, 1731-1742. http://dx.doi.org/10.1071/CH9651731
- Hassan, W. M., Zayed, E. M., Elkholy, A. K., Moustafa, H., & Mohamed, G. G. (2012). Spectroscopic and Density Functional Theory Investigation of Novel Schiff Base Complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 103, 378-387.
- Herrag, L., Hammouti B., Elkadiri, S., Aouniti, A., Jama, C., Vezin, H., & Bentiss, F. (2010). Adsorption properties and inhibition of mild steel corrosion in hydrochloric solution by some newly synthesised diamine derivatives: Experimental and theoretical investigations. *Corros. Sci., 52*, 3042-3051. http://dx.doi.org/10.1016/j.corsci.2010.05.024
- Hinckley, C. C. (1969). Paramagnetic shifts in solutions of cholesterol and the dipyridine adducts of trisdipivaloylmethanatoeuropium (III). A shift reagent. *Journal of the American Chemical Society*, 91(18), 5160-5162. http://dx.doi.org/10.1021/ja01046a038
- Hinckley, C. C. (1970). Applications of rare earth nuclear magnetic resonance shift reagents. I. The assignment of the methyl proton magnetic resonance of d-camphor. *Journal of Organic Chemistry*, 35(8), 2834-2836. http://dx.doi.org/10.1021/jo00833a090
- Holtzclaw, H. F. Jr., & Collman, J. P. (1957). Infrared absorption of metal chelate compounds of 1,3-diketones. *Journal of American Chemical Society*, 79, 3318-3322. http://dx.doi.org/10.1021/ja01570a006
- Johnson, P. R., & Thornton, D. A. (1975). Electronic spectra of copper(II) β-ketoenolates: intraligand and charge transfer transitions. *Journal of Molecular Structure*, 29, 97-103. http://dx.doi.org/10.1016/0022-2860(75)88010-0
- Karakas, D., & Sayin, K. (2013). DFT and TD-DFT studies on copper(II) complexes with tripodal tetramine ligands. *Indian Journal of Chemistry*, 52A, 480-485.
- Lever, A. B. P. (1986). Inorganic Electronic Spectroscopy (4th ed.). London: Elsevier.
- Malecki, J. G., Machura, B., & Switlicka, A. (2011). X-ray studies, spectroscopic characterization and DFT calculations for Mn(II), Ni(II) and Cu(II) complexes with 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine. *Struct Chem.*, 22, 77-87. http://dx.doi.org/10.1007/s11224-010-9686-7
- Melnik, M., Potocnak, I., Macaskova, L., Miklos, D., & Holloway, C. E. (1996). Spectral study of copper(II) flufenamates: crystal and molecular structure of bis(flufenamato)di(N-N-diethylnicotinamide)di(aqua)copper(II). Polyhedron, 15, 2159-2164. http://dx.doi.org/10.1016/0277-5387(95)00486-6
- Obot, I. B., & Obi-Egbedi, N. O. (2010). Adsorption properties and inhibition of mild steel corrosion in sulphuric solution by Ketoconazole: Experimental and theoretical investigation. *Corrosion Science*, *52*, 198-204. http://dx.doi.org/10.1016/j.corsci.2009.09.002
- Odunola, O. A., Oladipo, M. A., Woods, J. A. O., & Gelebe, A. C. (2003). Synthesis and structural studies of some ternary copper(II) complexes containing β-diketones with 1,10-phenanthroline and 2,2'-bipyridyl and x-ray structure of [Cu(C₆H₅COCHCOCH₃)(bipy)Cl]. Synthesis and Reactivity of Inorganic and Metal Organic Chemistry, 33(5), 857-871. http://dx.doi.org/10.1081/SIM-120021651
- Patel K. S., & Woods, J. A. O. (1990a). Synthesis and properties of nickel(II) complexes of various 3-alkyl-2,4-pentanediones and their adducts with 2,2-bipyridine and 1,10-phenanthroline. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 20(4), 409-424 and the references therein.
- Patel, K. S., & Woods, J. A. O. (1990b). Synthesis and physico-chemical properties of Bis(3-akyl-2,4-pentanedionato) copper(II) complexes and their adducts with 2,2'-bipyridine and 1,10-phenanthroline. Synthesis and Reactivity of Inorganic and Metal Organic Chemistry, 20(7), 909-922.

http://dx.doi.org/10.1080/00945719008048184

- Patel, K. S., & Woods, J. A. O. (1990c). Preparation and physico-chemical studies of some 3-substituted-2,4-pentanedionato copper(II) complexes and their adducts. *Synthesis and Reactivity of Inorganic and Metal Organic Chemistry*, 20(1), 97-109. http://dx.doi.org/10.1080/00945719008049873
- Perdew, J. P., Ruzsinszky, A., Tao, J., Staroverov, V. N., Scuseria, G. E., & Csonka, G. I. (2005). Prescription for the desighn and selection of density functional approximations: More constraint satisfaction with fewer fits. *Journal of Chemical Physics*, 123, 62201-9. http://dx.doi.org/10.1063/1.1904565
- Scott, A. P., & Radom, L. (1996). Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Moller-Plesset, Quadratic Configuration; Density Functional Theory, and Semi empirical Scale Factors. J. Phys. Chem., 100, 16502-16513. http://dx.doi.org/10.1021/jp960976r
- Shao, Y., Molnar, L. F., Jung, Y., Kussmann, J., Ochsenfeld, C., Brown, S. T., & Martin Head-Gordon. (2006). Advances in methods and algorithms in a modern quantum chemistry program package. *Phys. Chem. Chem. Phys.*, 8, 3172-3191.
- Sheela, N. R., Sampathkrishnan, S., Kumar, M. T., & Muthu, S. (2013). Synthesis, spectroscopic (FT-IR, FT-Raman, ¹³C, ¹H, UV) study, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of 2(2-Hydroxyphenyl)-N-(4-Methyphenyl)Nitrone. SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy, 109, 272-281. http://dx.doi.org/10.1016/j.saa.2013.03.030
- Tanaka, M., Shono, T., & Shinra, K. (1969). Tautomerism in 3-substituted 2,4-pentanediones and their copper chelates. *Bulletin of the Chemical Society of Japan, 42*, 3190-3194. http://dx.doi.org/10.1246/bcsj.42.3190
- Wenzel, T. J., Williams, E. J., Haltiwanger, R. C., & Sievers, R. E. (1985). Studies of metal chelates with the novel ligand 2,2,7-trimethyl-3,5-octanedione. *Polyhedron*, 4(3), 369-378. http://dx.doi.org/10.1016/S0277-5387(00)86994-6
- Woods, J. A. O., Omoregie, H. O., Retta, N., Chebude, Y., & Capitelli, F. (2009). Synthesis and Physicochemical Studies of Nickel(II) Complexes of 2-substituted-1,3-diphenyl-1,3-propanedione, their 2,2'-bipyridine and 1,10-phenanthroline Adducts and X-Ray Structure of (2,2'-bipyridine)Bis(1,3-diphenyl-1, 3-propanedionato) Nickel(II). Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39(10), 694-703.
- Xu, Z., Gou, S. H., You, X. Z., Liu, S. X., Lin, C. C., Yu, Y. P., & Zhu, D. L. (1991). Structure of a five-coordinate Copper(II) complex: (2,2'-bipyridine)[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-O][4,4,4-trifluoro-1-(2-thienyl)butane-1,3 -dionato-O,O'] copper(II). Acta Cryst., C47, 81-83. http://dx.doi.org/10.1107/S0108270190005807

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