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Physicochemical studies of copper(II) β-diketonate: Magnetic and spectral properties of copper(II) complexes of 2-alkyl-1-phenyl-1,3-butanedione, their 2,2′-bipyridine and 1,10-phenanthroline adducts

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ABSTRACT

A series of copper(II) complexes of 2-alkyl-1-phenyl-1,3-butanedione (2-R-BzacH) and their 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts have been synthesized and characterized by microanalysis, conductance, magnetic and spectral measurements. The conductivity measurements in nitromethane indicate that the complexes are non-electrolytes while the adducts are 1:1 electrolytes except $Cu(n\text{-}Pr\text{-}bzac)_2bipy$, $Cu(n\text{-}Pr\text{-}bzac)_2phen$, $Cu(i\text{-}Pr\text{-}bzac)_2bipy$ *and* $Cu(i\text{-}Pr\text{-}bzac)_2phen$ *that are non-electrolytes. The room temperature magnetic moments suggest that they are magnetically dilute compounds while the visible absorption spectra of the compounds showed the influence of variation of solvents and suggest plausible 4- and 5- coordinate geometries (Square planar and square pyramidal) which have been proposed, respectively.*

Key words: 2-Substituted-1-phenyl-1,3-butanedione, spectra studies, magnetic susceptibility studies, elemental analysis.

INTRODUCTION

β-diketonates complexes have been found useful as catalysts in polymerization of Styrene [1,2] Hydrogenation of benzene [3], oxidation of ethylbenzene [4,5], Hydrogenation of butadiene-styrene copolymers [6], hydrocracking of Athabasca bitumen [7], olefin epoxidation [8] and hydrogenation of methyl acetoacetate [9].

We have reported the isolation of various substituted β-diketonates complexes [10-15]. In this paper, we discuss the conductivity, the magnetic and spectral properties of bis(2-substituted-1-phenyl-1,3-butanedionato)copper(II) complexes, $Cu(R\text{-}Bzac)_2$ (R= Methyl (Me), Ethyl (Et), n-

Butyl (n-Bu) and their adducts with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) with the objective of determining the effect of substituents on these properties.

MATERIALS AND METHODS

The following reagents were used: 1-phenyl-1,3-butanedione or benzoylacetone (bzacH) (Aldrich chemicals), Copper acetate, 2,2′-bipyridine, and 1,10-phenanthroline (Analytical grade). Solvents were purified by standard methods [16].

Preparation of Ligands

The ligands, 2-alkyl-1-phenyl-1,3-butanediones were prepared by refluxing the appropriate alkyl iodide and anhydrous potassium carbonate with 1-phenyl-1,3-butanedione [17,18].

Synthesis of the Complexes and Adducts

Synthesis of $Cu(Me\text{-}bzac)_2$

(1.27 g, 6.35 mmol) of copper acetate was added to 2 mL 2-methy-1-phenyl-1,3-butanedione(2.24 g, 12.7 mmol) in 100 mL of methanol while stirring. The precipitated solids were washed with 40% methanol and dried over silica gel. Similar procedure was used for preparation of the other Cu(II) complexes.

Synthesis of $Cu(Me\text{-}bzac)_2phen$

(0.79 g, 3.99 mol) of 1,10-phenanthroline was dissolved in 15 mL of hot chloroform and (0.5 g, 1.21 mmoles) of $Cu(Me\text{-}bzac)_2$ was added while stirring. The mixture was concentrated, acetone was added and scratched to aid precipitation. The precipitates obtained were filtered, washed with few drops of acetone and dried in vacuo. Similar procedure was used for preparation of the other bipyridine and phenanthroline adducts.

Physical Measurements

Elemental analyses for C, H, N was determined by the Geological Survey of Ethiopia while percentage copper was determined titrimetrically with EDTA [19]. The magnetic susceptibilities of the compounds at room temperature were measured by MSB-AUTO (Sherwood scientific). The molar conductivities of the soluble compounds in nitromethane at room temperature were determined using Digital conductivity meter (Labtech). The electronic spectra of the compounds in methanol and chloroform were recorded on a Unicam UV-Visible Spectrophotometer using 1cm glass cell. The infrared spectra were measured as pressed KBr disc on Perkin Elmer Spectrophotometer BX FT-IR.

RESULTS AND DISCUSSION

The complexes were obtained by reaction of appropriate ligands with copper(II) acetate monohydrate in reasonable yields. The general equation for the preparation of the complexes is:

$CuAc_2 + 2R\text{-}BzacH \rightarrow Cu(R\text{-}Bzac)_2 + 2AcH$

Ac=acetate ion

The adducts were prepared in hot chloroform and precipitation was aided by addition of acetone. The representative equation is:

$Cu(R\text{-}Bzac)_2 + XN\text{-}N \rightarrow Cu(R\text{-}Bzac)_2N\text{-}N_x$

(N-N=bipyridine or phenanthroline; and X=1, 2.)

All the compounds were obtained as various shades of green except [Cu(bzac)(phen)](bzac) which displayed a yellow colour. Tables 1 and 2 list the analytical data, colours, %yields and room temperature effective magnetic moments (μ_{eff}) of the complexes. The elemental analyses were consistent with the proposed structure.

The room temperature magnetic moments of the synthesized copper complexes are presented in Table 1. A moment of 1.73-2.2 B.M. is usually observed for magnetically dilute copper(II) compounds, with compounds whose geometry approaches octahedral having moments at the lower end while those approaching tetrahedral geometry are at the higher end [15]. The prepared 2-alkyl-1-phenyl-1,3-butanedionato copper(II) complexes had moments in the range 1.74-1.96 B.M. except $Cu(n\text{-}Bu\text{-}bzac)_2$ with magnetic moment of 1.55 B.M. which is indicative of dimerization with the possibility of Cu-Cu linkage [20]. An increase was observed on substituting the hydrogen in $Cu(bzac)_2$ with alkyl groups except $Cu(Me\text{-}bzac)_2$ and $Cu(n\text{-}Bu\text{-}bzac)_2$ which had decreased moment. Reduction in moment may probably be due to increase in electron density around the metal leading to reduction in orbital contribution and therefore lower moment.

The observed magnetic moments of 2,2′-bipyridine and 1,10-phenanthroline adducts of 2-alkyl-1-phenyl-1,3-butanedionato copper(II) complexes are in the range 1.91-2.2 B.M. An increase in magnetic moments was observed in all the adducts as compared with the parent complexes except $Cu(Me\text{-}bzac)_2phen$ which had reduced moment compared with the parent complex. $Cu(Me\text{-}bzac)_2phen$ had a moment of 1.61 B.M. which is indicative of dimerization with the possibility of Cu-Cu linkage [20]. Magnetic moment of $Cu(n\text{-}Pr\text{-}bzac)_2bipy$ could not be measured due to difficulty in packing the glass tube. A decrease in moment was observed on comparing the bipyridine/phenanthroline adduct of $Cu(R\text{-}bzac)_2$ with the unsubstituted bipyridine and phenanthroline adducts. Reduction in moment is attributed to increase electron density around the copper leading to reduction in orbital contribution and therefore lower moments were obtained.

In the spectra of the copper(II) complexes studied, lower frequency shifts of the carbonyl bands were observed upon chelation, which indicates the formation of stronger metal-oxygen bonds. The position of the perturbed carbonyl band is influenced by the interaction of the carbonyl with neighbouring π or d-orbitals and the relative electron density of the σ bond [21]. The lower frequency shifts of the asymmetric $\nu(C{=}O)+\nu(C{=}C)$ stretching vibrations were observed in the order: $Cu(i\text{-}Pr\text{-}bzac)_2$ ($\Delta\nu = 205\ cm^{-1}$) > $Cu(Et\text{-}bzac)_2$ ($\Delta\nu = 163\ cm^{-1}$) > $Cu(Me\text{-}bzac)_2$ ($\Delta\nu = 151\ cm^{-1}$) > $Cu(n\text{-}Bu\text{-}bzac)_2$ ($\Delta\nu = 129\ cm^{-1}$) > $Cu(n\text{-}Pr\text{-}bzac)_2$ ($\Delta\nu = 93\ cm^{-1}$) > $Cu(bzac)_2$ ($\Delta\nu = 10\ cm^{-1}$).

There is a lot of controversy on assignment of bands in the infrared spectrum of metal β-diketonates [21-24].

In a study, the strong bands found at 1554 cm^{-1} and one at 1534 cm^{-1} have been assigned to a mode consisting of 75% C=O stretch and 25% C=O stretch [23] while lower frequency bands at 1430-1465 cm^{-1} were assigned to 50% C=O stretching and 50% C-H in plane bending. Furthermore, the bands at 1274 cm^{-1} have been assigned to a mode consisting of 28% C=C stretch and 50% $C\text{-}CH_3$ stretch [25]. Similar studies have also assigned this band to C-C str + C-R str of copper complex of dibenzoylmethane while bands in the region 902-945 cm^{-1} have been assigned to $C\text{-}C_6H_5$ str [26].

In the complexes studied, bands in the 1559-1593 cm^{-1} have been assigned as $\nu_{as}(C{=}O) + \nu_{as}(C{=}C)$. Some of these bands are strong while a few are of weak intensity. Bands of strong and medium intensity observed at 1441-1488 cm^{-1} in the complexes have been assigned to $\nu_s(C\text{-}O) + \delta C\text{-}H$ vibrational modes. A decrease in $\nu_s(C\text{-}O) + \delta C\text{-}H$ of copper(II) complexes of 2-Substituted-1-phenyl-1,3-butanedione was observed as the length of the alkyl group increases except $Cu(n\text{-}Pr\text{-}bzac)_2$, and $Cu(n\text{-}Bu\text{-}bzac)_2$ which had increased frequency. The decrease in frequency indicates the positive inductive effect of the alkyl group on the system. Bands in the region 1355-1418 cm^{-1} have been assigned as methyl deformation bands. Bands below 700 cm^{-1} have been assigned to coupled copper-oxygen and copper-nitrogen stretching vibrations. Higher frequency shifts of varying magnitude were observed in the $\nu_{as}(C{=}O) + \nu_{as}(C{=}C)$ vibrations of all the adducts relative to the parent complex. Similarly, higher frequency shifts of $\nu_{as}(C{=}O) + \nu_{as}(C{=}C)$ were observed on comparing the bipyridine adduct of $Cu(R\text{-}bzac)_2$ with [Cu(bzac)(bipy)](bzac) (unsubstituted adduct) in the order: [Cu(Me-bzac)(bipy)](Me-bzac) ($\Delta\nu = 3\ cm^{-1}$) < $[Cu(n\text{-}Bu\text{-}bzac)(bipy)(H_2O)](n\text{-}Bu\text{-}bzac)$ ($\Delta\nu = 4\ cm^{-1}$) < $Cu(i\text{-}Pr\text{-}bzac)_2bipy$($\Delta\nu = 7\ cm^{-1}$) < $[Cu(Et\text{-}bzac)(bipy)(H_2O)](Et\text{-}bzac)$ ($\Delta\nu = 10\ cm^{-1}$) < $Cu(n\text{-}Pr\text{-}bzac)_2bipy$($\Delta\nu = 131\ cm^{-1}$). The phenanthroline adduct of copper(II) complexes of 2-Substituted-1-phenyl-1,3-butanedione also displayed higher frequency shifts of $\nu_{as}(C{=}O) + \nu_{as}(C{=}C)$ relative to [Cu(bzac)(phen)](bzac), the unsubstituted adduct.

CH deformation bands of 2,2′-bipyridine were observed as strong bands in the 765-778 cm^{-1} region while those of the 1,10- phenanthroline adducts appeared as very prominent bands around 717-724 cm^{-1} and 849-856 cm^{-1} region.

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 [15,25,27].

Upon chelation, $\pi_3\text{-}\pi_4^*$ bathochromic shifts of varying magnitude were observed in all the complexes in chloroform and methanol. Hypsochromic shifts of the $\pi_3\text{-}\pi_4^*$ band were observed in the complexes on substituting the 2-position of $Cu(bzac)_2$ with methyl, ethyl, n-propyl, i-propyl and n-butyl in chloroform and methanol except $Cu(Et\text{-}bzac)_2$ in methanol which had no shift and $Cu(i\text{-}Pr\text{-}bzac)_2$ which had bathochromic shift in methanol. The hypsochromic shift probably indicates the presence of positive inductive effect of the alkyl group. The magnitude of these shifts in chloroform is in the order: $Cu(Et\text{-}bzac)_2 > Cu(n\text{-}Bu\text{-}bzac)_2 = Cu(Me\text{-}bzac)_2 > Cu(i\text{-}Pr\text{-}bzac)_2 > Cu(bzac)_2$. The bands observed in the ultraviolet region of the complexes between 31,056-34,014 cm^{-1} in methanol and chloroform have been assigned to π_3-π_4^* transition while bands between 38,760-43,860 cm^{-1} have been assigned as σ_L-3d$_{xy}$/benzenoid transition.

The ligand field spectra of Cu(II) β-diketonates have been subject of intense experiment and theoretical research [25,28-30] and coordinating solvents have been found to have a particular dramatic effect on the spectra [15,31]. As a result of this, when there is a higher frequency shift in the ligand field spectra band of the copper compounds in coordinating solvent (methanol) 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 frequency band position remains unchanged in both coordinating and non-coordinating solvents. Thus, the various synthesized Cu(R-bzac)$_2$ complexes have probable four-coordinate square planar geometry due to their lower frequency shifts in methanol relative to chloroform. The visible bands shifted to higher frequencies on replacement of hydrogen by alkyl groups and the magnitude of the shift is about the same in all the solvents. Lengthening of the alkyl side chain produces no further change in the formation constants [32]. In the synthesized complexes, higher frequency shifts were observed in the complexes on substituting the 2-position of Cu(bzac)$_2$ with alkyl groups in chloroform.

The spectra of the bipyridine adducts in methanol and chloroform had bands in the 38,168-42,735 cm^{-1} region while phenanthroline adducts had bands in the 36,900-44,843 cm^{-1} region. In the bipyridine adducts, the π-π (bipy) were observed as single bands in methanol solution spectra of [Cu(bzac)(bipy)](bzac), [Cu(Me-bzac)(bipy)](Me-bzac), [Cu(Et-bzac)(bipy)(H$_2$O)](Et-bzac) and [Cu(n-Bu-bzac)(bipy)(H$_2$O)](n-Bu-bzac) while additional bands were observed in chloroform solution. The visible spectra of copper(II) β-diketonates are more intense and located at lower frequency in coordinating solvents [33,34,35] and could be an indication of a probable four-coordinate square planar geometry while a higher frequency shifts were observed in the synthesized compounds in methanol relative to chloroform which is an indication of a probable five-coordinate square pyramidal structure except [Cu(bzac)(bipy)](bzac), [Cu(bzac)(phen)](bzac), [Cu(Me-bzac)(bipy)](Me-bzac), [Cu(Me-bzac)phen](Me-bzac) and [Cu(Et-bzac)(phen)](Et-bzac).H$_2$O which had lower frequency shifts in methanol relative to chloroform and therefore probably indicates square planar geometry.

The electronic reflectance spectra of the ligands (R-bzacH), copper(II) complexes and adducts in calcium carbonate are listed in Table 5. The assignments of bands were made by reference to similar compounds in the literature [11]. The intraligand π-π* and ligand to metal charge transfer (LMCT) transitions were observed in the 34,130-45,045 cm^{-1} region for the complexes. The spectra of copper complexes of the aryl substituted ligands exhibit two bands, which were assigned to π_3-π_4^* and σ_L-3d$_{xy}$. Complexes without aryl-substituents have smaller π_3-π_4^* bands compared with aryl substituted complexes. This feature suggests that in aryl series the 40,000 cm^{-1} band acquires additional intensity from a chromophore which is unique to this series i.e. the phenyl ring. The 40,000 cm^{-1} band comprises the combined intensities of the benzenoid and σ_L-3d$_{xy}$ transitions in the copper complexes of aryl-substituted ligands [30].

In the synthesized complexes, π_3-π_4^* transitions were observed in the 34,130-35,971 cm^{-1} region and there was no splitting of the band. Bands in the 40,000-44843 cm^{-1} region have been assigned as benzenoid/σ_L-3d$_{xy}$ transitions [30].

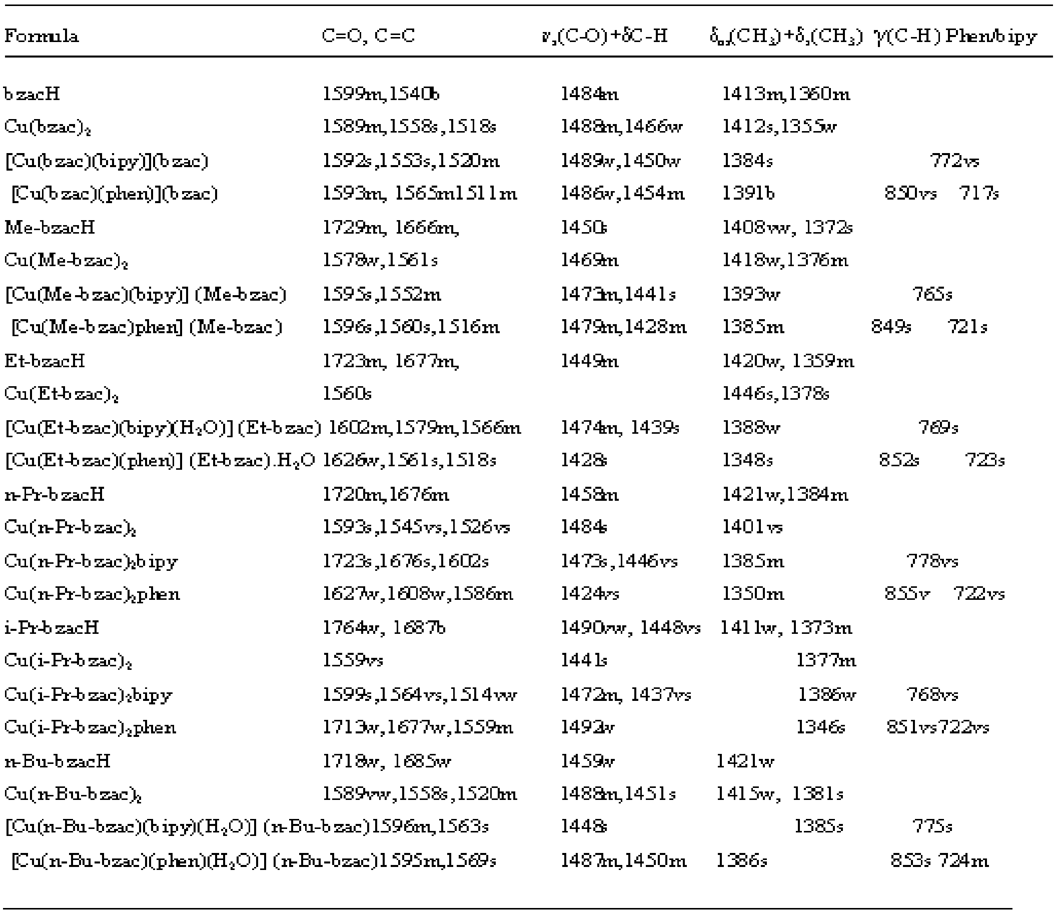
Table 1: Analytical and physical data of copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione and their adducts

Formula	MM	Colour	M.Pt (˚C)	Yield (%)	μ_{eff} (B.M.)
Cu(bzac)$_2$	385.86	Dark green	187-189	95.52	1.81
[Cu(bzac)(bipy)](bzac)	542.06	Yellowish green	172-174	35.59	1.91
[Cu(bzac)(phen)](bzac)	566.08	Yellow	142-144	47.74	1.98
Cu(Me-bzac)$_2$	413.94	Dark green	205-207	57.79	1.74
Cu(Me-bzac)(bipy)] (Me-bzac)	570.13	Dark green	122-124	40.82	2.04
[Cu(Me-bzac)phen] (Me-bzac)	594.14	Dark green	163-165	51.38	1.61
Cu(Et-bzac)$_2$	442.00	Dark green	188-190	33.33	1.87
[Cu(Etbzac)(bipy)(H$_2$O)] (Et-bzac)	616.20	Light green	138-140	60.59	2.01
[Cu(Et-bzac)(phen)](Et-bzac).H$_2$O	712.32	Dark green	99-101	61.40	2.13
Cu(n-Pr-bzac)$_2$	470.06	Dark green	331-333	86.54	1.93
Cu(n-Pr-bzac)$_2$bipy	626.24	Dark green	341-343	33.73	-
Cu(n-Pr-bzac)$_2$phen	650.26	Dark green	317-319	44.76	2.2
Cu(i-Pr-bzac)$_2$	470.06	Y.green	234-236	70.48	1.96
Cu(i-Pr-bzac)$_2$bipy	626.24	Dark green	256-258	51.36	2.00
Cu(i-Pr-bzac)$_2$phen	650.26	Dark green	124-126	43.5	1.98
Cu(n-Bu-bzac)$_2$	498.12	Dirty green	147-149	53.97	1.55
[Cu(n-Bu-bzac)(bipy)(H$_2$O)](n-Bu-bzac)	672.32	Bluish green	96-98	30.23	1.96
[Cu(n-Bu-bzac)(phen)(H$_2$O)](n-Bu-bzac)	696.34	Dark green	194-196	54.61	2.03

Table 2: Microanalytical data of copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione and their adducts

Emperical formula	%Found				%Calculated			
	C	H	N	Metal	C	H	N	Metal
Cu(bzac)$_2$	62.59	4.91	-	16.46	62.25	4.71	-	16.48
[Cu(bzac)(bipy)](bzac)	66.68	4.54	4.97	11.65	66.47	4.84	5.17	11.71
[Cu(bzac)(phen)](bzac)	68.09	4.86	5.15	11.60	67.89	4.64	4.95	11.22
Cu(Me-bzac)$_2$	63.29	5.02	-	15.06	63.83	5.37	-	15.34
[Cu(Me-bzac)(bipy)] (Me-bzac)	67.27	5.18	5.08	11.24	67.41	5.31	4.91	11.41
[Cu(Me-bzac)phen] (Me-bzac)	69.00	4.98	4.59	10.24	68.73	5.10	4.71	10.69
Cu(Et-bzac)$_2$	65.11	5.70	-	14.83	65.21	5.94	-	14.37
[Cu(Et-bzac)(bipy)(H$_2$O)] (Et-bzac)	68.18	5.59	4.76	10.22	66.27	5.74	4.68	10.31
[Cu(Et-bzac)(phen)](Et-bzac).H$_2$O	60.35	5.95	4.14	8.86	60.70	6.24	3.93	8.91
Cu(n-Pr-bzac)$_2$	66.69	6.80	-	13.77	66.43	6.45	-	13.51
Cu(n-Pr-bzac)$_2$bipy	69.18	6.35	4.72	9.86	69.04	6.13	4.47	10.14
Cu(n-Pr-bzac)$_2$phen	69.92	5.40	4.20	10.04	70.18	5.90	4.31	9.77
Cu(i-Pr-bzac)$_2$	66.19	6.54	-	13.31	66.43	6.45	-	13.51
Cu(i-Pr-bzac)$_2$bipy	69.23	5.98	4.24	9.98	69.04	6.13	4.47	0.14
Cu(i-Pr-bzac)$_2$phen	70.23	5.84	4.09	4.79	70.18	5.90	4.31	4.77
Cu(n-Bu-bzac)$_2$	67.34	6.51	-	12.56	67.51	6.89	-	2.75
[Cu(n-Bu-bzac)(bipy)(H$_2$O)] (n-Bu-bzac)	68.05	6.48	3.92	9.54	67.88	6.61	4.16	9.44
[Cu(n-Bu-bzac)(phen)(H$_2$O)] (n-Bu-bzac)	68.62	6.12	3.90	8.89	68.99	6.38	4.02	9.12

Table 3: Relevant Infrared Spectra bands (cm-^{1}) of Copper(II) Complexes of 2-Substituted-1-Phenyl-1,3-butanedione and their Adducts



Formula	C=O, C=C	ν_s(C-O)+δC-H	$\delta_{as}(CH_3)+\delta_s(CH_3)$	γ(C-H) Phen/bipy
bzacH	1599m,1540b	1484m	1413m,1360m	
Cu(bzac)$_2$	1589m,1558s,1518s	1488m,1466w	1412s,1355w	
[Cu(bzac)(bipy)](bzac)	1592s,1553s,1520m	1489w,1450w	1384s	772vs
[Cu(bzac)(phen)](bzac)	1593m, 1565m1511m	1486w,1454m	1391b	850vs 717s
Me-bzacH	1729m, 1666m,	1450s	1408vw, 1372s	
Cu(Me-bzac)$_2$	1578w,1561s	1469m	1418w,1376m	
[Cu(Me-bzac)(bipy)] (Me-bzac)	1595s,1552m	1473m,1441s	1393w	765s
[Cu(Me-bzac)phen] (Me-bzac)	1596s,1560s,1516m	1479m,1428m	1385m	849s 721s
Et-bzacH	1723m, 1677m,	1449m	1420w, 1359m	
Cu(Et-bzac)$_2$	1560s		1446s,1378s	
[Cu(Et-bzac)(bipy)(H$_2$O)] (Et-bzac)	1602m,1579m,1566m	1474m, 1439s	1388w	769s
[Cu(Et-bzac)(phen)] (Et-bzac).H$_2$O	1626w,1561s,1518s	1428s	1348s	852s 723s
n-Pr-bzacH	1720m,1676m	1458m	1421w,1384m	
Cu(n-Pr-bzac)$_2$	1593s,1545vs,1526vs	1484s	1401vs	
Cu(n-Pr-bzac)$_2$bipy	1723s,1676s,1602s	1473s,1446vs	1385m	778vs
Cu(n-Pr-bzac)$_2$phen	1627w,1608w,1586m	1424vs	1350m	855v 722vs
i-Pr-bzacH	1764w, 1687b	1490vw, 1448vs	1411w, 1373m	
Cu(i-Pr-bzac)$_2$	1559vs	1441s	1377m	
Cu(i-Pr-bzac)$_2$bipy	1599s,1564vs,1514vw	1472m, 1437vs	1386w	768vs
Cu(i-Pr-bzac)$_2$phen	1713w,1677w,1559m	1492w	1346s	851vs722vs
n-Bu-bzacH	1718w, 1685w	1459w	1421w	
Cu(n-Bu-bzac)$_2$	1589vw,1558s,1520m	1488m,1451s	1415w, 1381s	
[Cu(n-Bu-bzac)(bipy)(H$_2$O)] (n-Bu-bzac)	1596m,1563s	1448s	1385s	775s
[Cu(n-Bu-bzac)(phen)(H$_2$O)] (n-Bu-bzac)	1595m,1569s	1487m,1450m	1386s	853s 724m

The visible spectra of all the complexes studied displayed three bands with varying λ_{max} between 12,005-20,921 cm^{-1} which is consistent with square planar geometry for copper(II) complexes. Single bands were displayed by the adducts in the visible region between 13,553-14,698 cm^{-1} which is consistent with square pyramidal geometry for copper(II) compounds [11] except, [Cu(Me-bzac)(bipy)](Me-bzac), [Cu(Me-bzac)(phen)](Me-bzac) and [Cu(Et-bzac)(bipy)(H$_2$O)](Et-bzac) which had additional bands at 19,011-21,598 cm^{-1} corresponding to square planar structure [36].

The molar conductivities of these complexes are very low with Λ_m values of 18.9-23.8 ohm^{-1}cm^{2}mole^{-1}, which suggests that they are non-electrolytes. The molar conductivities of the Cu(R-bzac)$_2$ adducts indicate that most are non-electrolytes except [Cu(bzac)(bipy)](bzac), [Cu(bzac)(phen)](bzac), [Cu(Me-bzac)(bipy)](Me-bzac), [Cu(Me-bzac)phen](Me-bzac), [Cu(Et-bzac)(bipy)(H$_2$O)](Et-bzac), [Cu(Et-bzac)(phen)](Et-bzac).H$_2$O, [Cu(n-Bu-bzac)(bipy)(H$_2$O)](n-Bu-bzac) and [Cu(n-Bu-bzac)(phen)(H$_2$O)](n-Bu-bzac), which were 1:1 electrolytes with an outer sphere anion.

Table 4: The electronic solution spectra of Copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione and their adducts

Emperical Formula	π_{3}-π_{4}*(cm^{-1})		d-d	
	$CHCl_3$	CH_3OH	$CHCl_3$	CH_3OH
bzacH	32,258(7242)	32,258(18259)	-	-
Cu(bzac)$_2$	31,056(36730)	31,250(26813)	18,248* 15,198(48)	15,773(93) 11,820(53)
[Cu(bzac)(bipy)](bzac)	32,468(36161)	33,333(28353)	18,868* 14,368(210)	16,393(106)
[Cu(bzac)(phen)](bzac)	34,014* 31,056(48249)	33,784(34634) 31,546*	18,939* 15,152(67)	16,234(84)
Me-bzacH	34,364(?)	33,557(?) 31,056(?)	-	-
Cu(Me-bzac)$_2$	31,250(51038)	31,447(31142)	18,360* 15,198(146)	16,287(147)
[Cu(Me-bzac)(bipy)] (Me-bzac)	34,014(?) 32,051*	34,014(21953) 32,258*	13,966(?)	13,870(177)
[Cu(Me-bzac)phen] (Me-bzac)	IS	34,014(26672)	IS	14,620(132)
Et-bzacH	32,680(?)	34,014(?)	-	-
Cu(Et-bzac)$_2$	31,447(43328)	31,250(14359)	19,157(149) 15,152(129)	16,260(123) 11,792(120)
[Cu(Et-bzac)(bipy)(H_2O)] (Et-bzac)	33,557(15078)	33,557(49780)	14,493(191)	16,340(160)
[Cu(Et-bzac)(phen)](Et-bzac).H_2O	34,014(33409)	34,014(32030)	18,340(478) 13,624(446)	13,812(223)
i-Pr-bzacH	35,336(?)	35,088(?)	-	-
Cu(i-Pr-bzac)$_2$	31,153(?)	31,153(?)	19,608(?) 15,314(?)	13,245(?)
Cu(i-Pr-bzac)$_2$bipy	33,898(?)	33,557(?)	14,085(?)	13,947(?)
Cu(i-Pr-bzac)$_2$phen	33,333(?)	35,461(?)	13,569(?)	13,831(?)
n-Pr-bzacH	35,088(?)	35,461(?)	-	-
Cu(n-Pr-bzac)$_2$	IS	34,014(?)	IS	12,937(?)
Cu(n-Pr-bzac)$_2$bipy	IS	33,445(?)	IS	14,085(?)
Cu(n-Pr-bzac)$_2$phen	IS	34,247(?)	IS	13,870(?)
n-Bu-bzacH	33,003(?)	33,784(?)	-	-
Cu(n-Bu-bzac)$_2$	31,250(39515)	31,348(16578)	19,531(117) 17,668(107)	16,234(105) 11,792(62)
[Cu(n-Bu-bzac)(bipy)(H_2O)] (n-Bu-bzac)	33,557(39563)	33,333(?)	14,493(378)	16,835(?)
[Cu(n-Bu-bzac)(phen)(H_2O)] (n-Bu-bzac)	34,014(?)	34,014(22021)	13,850(?)	15,480(96)

The thermogravimetric measurements for [Cu(bzac)(phen)](bzac) and [Cu(Et-bzac)(phen)](Et-bzac).H_2O were studied by the DSC-TGA technique. The phenanthroline adducts were found to be stable at room temperature. There was no loss of water molecule in [Cu(bzac)(phen)](bzac) which signifies the absence of water whereas Cu(Et-bzac)$_2$phen.H_2O showed loss of water molecule below 100°C indicating that the water is hanging in the lattice.

Table 5: The electronic solid reflectance spectra of Copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione and their adducts

Emperical Formula	π_3-π_4*(cm^{-1})	d-d
bzacH	31,056	-
Cu(bzac)$_2$	35,971	20,790, 16,260, 12,019
[Cu(bzac)(bipy)](bzac)	35,461	20,790, 19,724, 12,531
[Cu(bzac)(phen)](bzac)	33,670	21,978*, 17,575, 12,107
Me-bzacH	35,587, 32,680	-
Cu(Me-bzac)$_2$	35,336	20,833*, 17,065, 12,438
[Cu(Me-bzac)(bipy)](Me-bzac)	32,787	21,231, 19,011, 12,019
[Cu(Me-bzac)phen] (Me-bzac)	31,056	19,531, 12,225
Et-bzacH	35,088, 31,153	-
Cu(Et-bzac)$_2$	35,460	20,576, 17,452, 12,739
[Cu(Et-bzac)(bipy)(H_2O)] (Et-bzac)	35,971, 32,468	14,692
[Cu(Et-bzac)(phen)] (Et-bzac).H_2O	31,056	21,598,19,531, 18,349
n-Pr-bzacH	33,003	-
Cu(n-Pr-bzac)$_2$	34,130	20,576, 19,011,12,107
Cu(n-Pr-bzac)$_2$bipy	33,003	14,608
Cu(n-Pr-bzac)$_2$phen	34,602	14,698
n-Bu-bzacH	33,670	-
Cu(n-Bu-bzac)$_2$	35,971	20,921, 17,271, 12,005
[Cu(n-Bu-bzac)(bipy)(H_2O)] (n-Bu-bzac)	35,971	14,342
[Cu(n-Bu-bzac)(phen)(H_2O)](n-Bu-bzac)	34,247	14,194

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