

Theoretical studies on the structural and electronic properties of copper (II) complexes of some β -diketones and their 1,10-phenanthroline adducts.

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Abstract

The copper (II) complexes of 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione(ftbdH), 1-(2-furyl)-1,3-butanedione (fbdH), 1-phenyl-1,3-butanedione (bzacH) and their adducts with 1,10-phenanthroline have been synthesized and characterized accordingly by elemental analysis, solubility, infra-red and electronic spectroscopic methods. The complexes and adducts were insoluble in water, slightly soluble in ethanol but soluble in dimethylformamide, chloroform, tetrachloromethane and acetone. Infrared spectral of the complex and adducts revealed that lower frequency shifts of varying magnitudes were observed in the carbonyl (C=O) and (C=C) aromatic stretching vibrations when compared with that of their ligand values. Electronic spectral data also indicated the geometries of the complex and adducts and transitions in terms of $\pi-\pi^*$. The experimental vibration frequencies are compared with those obtained from semi-empirical (PM3) level of calculations based on the proposed structures.

Keyword: Complex, adducts, spectroscopic, semi-empirical method

Introduction

Di-ketones are carbonyl compounds with two ketonic groups as their functional group. However, separation of these two ketonic groups by a methyl group gives rise to β -diketones. β -diketones and their metal complexes are among the most widely studied coordination compounds due to their wide application in the industries as catalyst (Schwieger, 2009; Xing bang, 2009;

Ferreira, 2002; Poncelet, 2005; Lassahn, 2005; Campelo, 2006) and also as precursors for chemical vapor deposition (Zhang, 2006; Nable et al, 2003; Banger et al, 2001; Dela Rosa et al, 2003). The transition metal complexes of β -diketones have been the subject of many different studies ranging from synthetic, kinetic, antimicrobial and structural topics to catalysis and many others (Plessis, et al, 1998; Campelo et al, 2006; Lassahn et al, 2005; Xingbang et al, 2009; Schwieger et al, 2009). Theoretical methods have been used to study copper complexes of β -diketones in order to gain insight into their structural and electronic interactions as related to their practical uses (Dela Rosa et al, 2003). β -diketonates are a class of high functional compounds with outstanding optical, electric and magnetic properties and the negative ion may act as an excellent chelating agent (Wang, et al., 2006; Halim et al., 2005). The isolation of various substituted β -diketones complexes have been reported (Woods et al, 1994; Odunola et al, 2003).

Thermal transfer printing materials containing metal β -diketonates exhibit good whiteness and image stability (Miura et al, (1993)). It has been found that toners containing metal complexes of β -diketones are stable, controllable and capable of producing clear colour images even at high temperatures and high humidity without producing copier stain (Hiroshi and Katsuhiko, 1987). Studies on the effect of substituent on the spectra properties of metal β -diketonates have been reported (Nakamoto et al, 1959; Nakamoto et al, 1962; Patel and Woods, 1990; Woods and Patel, 1994). However, there is dearth of information on 2-substituted-1-phenyl-1, 3-butanedione copper (II) complexes and their 2,2'-bipyridine and 1,10-phenanthroline adducts. Therefore, in this work we concentrate on the synthesis, spectroscopic and theoretical studies of the Copper (II) substituted-1-phenyl-1, 3-butanedione, 4,4,4-trifluoro-1-(3-pyridyl)-1, 3 butanedione, 1-(2-furyl)-1,3-butanedione and their adducts with 1,10-phenanthroline.

The complexes and its adducts are modeled based on the spectroscopic interpretations using Spartan program (Spartan 06) implemented on an Intel Pentium M 2.0GHz computer. The optimization and frequency calculation of the Cu (II) complex and its adducts were performed using semi-empirical method (PM3), since PM3 has been successfully used either alone or with other theoretical methods for structural analysis of Cu(II) complexes (Johnson et al, 2000; Bernabe et al, 2001; Seguel et al, 2005; Adeoye et al, 2010; Sequel et, al, 2010 and Adekunle et al, 2011; Oladipo et al, 2012). The Mulliken charges and highest molecular orbitals (HOMO) of adducts and the metal complexes were reported.

Results and discussion

The results of the elemental analysis, colour, percentage yield, melting points/decomposition temperatures and room temperature magnetic moments (U_{eff}) of the complexes are given in Table 1.

colour

All the compounds were obtained as various shades of green and blue except for Cu (fbd)₂.2H₂O and Cu(Ftbd)₂phen₃ that were yellow.

Elemental analysis

The results of elemental analysis of the complexes and adducts studied are shown in Table 1. The observed results agree well with the expected ones suggesting that the complexes were 1: 2 metal: ligand as expected for divalent complexes while the addition compounds were obtained as 1: 1 adducts.

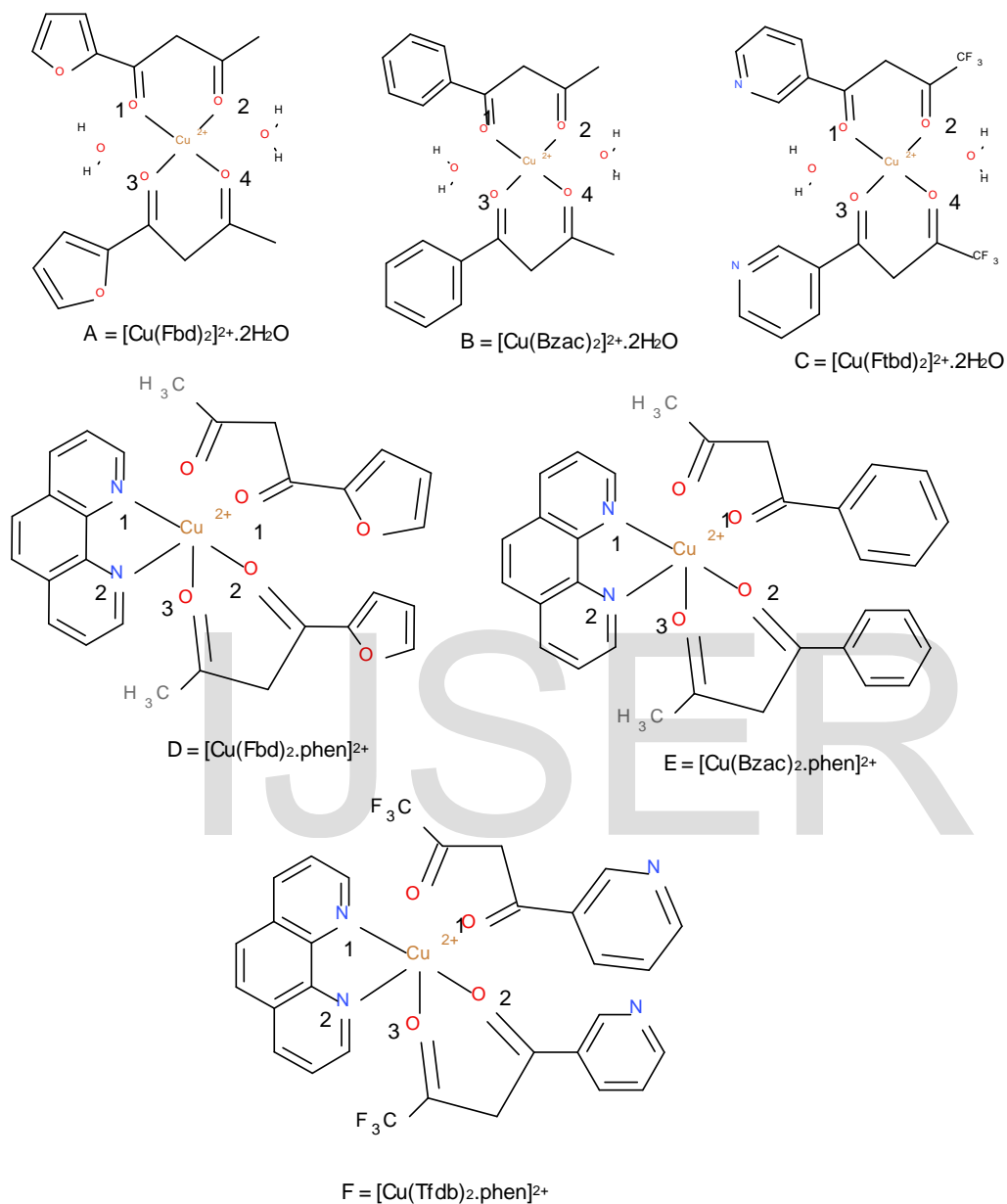


Figure 1: The proposed structures of the complexes and adducts with numbering of atoms.

Table1: elemental data of complexes and adducts

Compound	Molecular mass	Color	% Yield	Melting point	%Cu		%C		%H		μ_{eff} B.M
					Ex	Ob	Ex	Ob	Ex	Ob	
Cu(ftbd) ₂ .2H ₂ O	541.93	Green	83	>220	11.73	11.56	35.16	35.24	2.23	2.19	2.06
Cu(fbd) ₂ .2H ₂ O	1046.5	Yellow	39	18-220	6.07	6.00	59.68	59.62	3.08	3.04	1.90
Cu(Bzac) ₂ .2H ₂ O	421.94	Blue	92	162-164	15.06	15.07	56.93	56.90	5.26	5.25	2.03
Cu(fbd) ₂ .phen	566.12	Green	27	220	11.22	12.51	67.89	68.02	4.99	5.23	1.89
Cu(Bzac) ₂ .phen	566.115	Green	21	208-210	11.22	12.51	67.89	68.10	4.99	4.70	2.19
Cu(Ftbd) ₂ phen ₃	1046.522	Yellow	39	218-220	6.07	6.00	59.68	59.62	3.08	3.04	1.99

Solubility

The complexes and adducts had varying degree of solubilities in both coordinating and non-coordinating solvents. They were all insoluble in water, slightly soluble in ethanol but very soluble in dimethylformamide, chloroform, tetrachloromethane and acetone.

Infrared spectra

The observed and theoretical vibrational frequencies of the complexes and adducts and their tentative assignments are presented in Table 2. The spectra of β -diketonates have been studied and assignment made for the different bands in the spectra of the compounds overlap in the absorption frequencies of most vibrational modes of these ligands due to electron delocalization in the chelate ring results in appreciable coupling of the different vibrational modes (Nakamoto, k, 1970). The most important bands in the β -diketone ligands are the C=O and C=C and the CH₃ rocking vibration because they are metal-sensitive. In 1-phenyl-1,3-butanedione, the asymmetric stretching vibration of C=O + C=C appear as three (1590cm⁻¹, 1550cm⁻¹ and 1515cm⁻¹). Conversely, in 1-(2-furyl)-1,3-butanedione, these bands appear around 1725cm⁻¹ and 1610cm⁻¹ while in 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, they were at

1655 cm^{-1} and 1620 cm^{-1} , the CH_3 group being replaced by CF_3 . The position of the $\nu_{\text{asc}=\text{o}}$ + $\nu_{\text{asc}=\text{c}}$ stretching vibrations which is higher in fbdH than in ftbdH could probably be attributed to a more electronegative oxygen atom in the furyl ring than sulphur and nitrogen in the thienyl ring which had affected the extend of the mesomeric interactions occurring between these five membered heterocyclic rings and possibly the corresponding metal chelate ring. Fluorine substitution shifts the $\nu_{\text{asc}=\text{o}}$ + $\nu_{\text{asc}=\text{c}}$ band to higher frequencies, a phenomenon commonly found with fluorinated β -diketones.

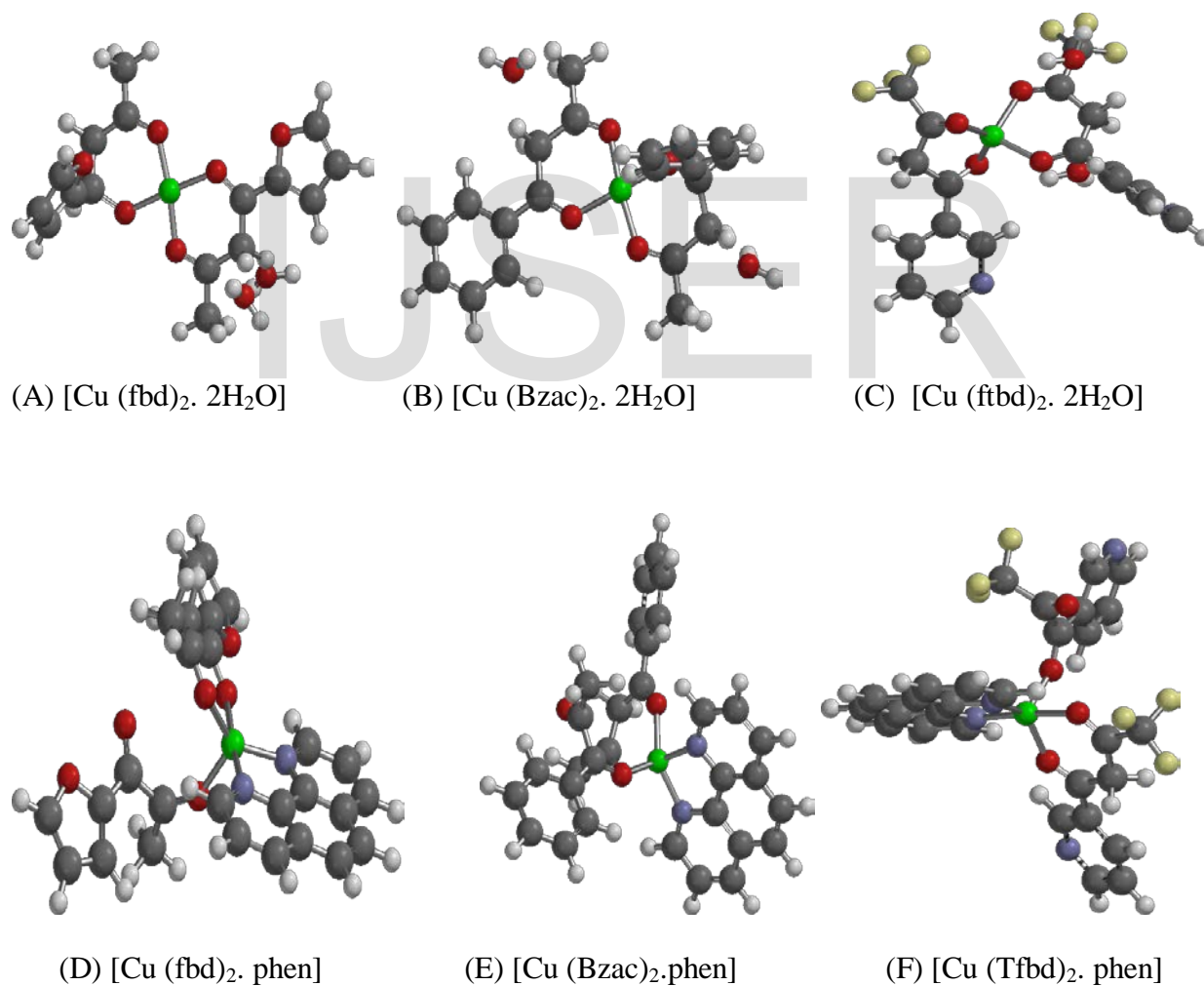


Figure 2: Optimized structures of the complexes and adducts at PM3 level of semi-empirical method

The main stretching modes in the infrared spectra of the complexes and adducts were shifted to shorter wavelength of absorption in the complex relative to the parent ligand. The $\nu_{C=O}$ (cm^{-1}) modes of copper complexes observed at lower frequency shifts relative to the parent ligands could be an indication of stronger Cu-O bonds in the chelate ring due to increased electron delocalization. The infrared spectra of the complexes and adducts showed that lower frequency shifts were observed in the carbonyl stretching frequencies on complexation. This was evident in all the complexes and adducts. For instance, $\nu_{C=O}$ vibrational frequency for FbdH was found at 1725cm^{-1} but in the complex and adduct, it was found at 1558cm^{-1} and 1600cm^{-1} respectively. Theoretically, these were calculated to be 1772 , 1543 and 1603cm^{-1} for FbdH, complex and adduct respectively. Infrared studies on diketones have shown that electron releasing substituent give rise to low $\nu_{C=O}$ (cm^{-1}). This indicates that the β -diketonate ligands adopt a chelating coordination mode (Harding, et. al. 2008). Although calculated vibrational frequencies at PM3 were higher than the experimental values, the scaled vibrational frequencies agreed very well with experimental values. The $\nu_{C=O}$ stretching frequencies of adducts were relatively lower than that of the parent ligands and complexes, this was consistent with the theoretical results.

Table 2: Experimental and theoretical vibration bands in ligands, complexes and adducts

Compound	Experimental $\nu_{C=O}$ (cm^{-1})	Computational (unscaled) $\nu_{C=O}$ (cm^{-1})	Computational (scaled with 0.895) $\nu_{C=O}$ (cm^{-1})
FtbdH	1655, 1620	2012, 1970	1801, 1763
FbdH	1725, 1610.	1980, 1963	1772, 1757

BzacH	1590(m), 1550(s)	1979, 1963	1771, 1757
Cu(ftbd) ₂ .2H ₂ O	1580 _(s) , 1545 _(s)	1916, 1849	1714, 1655,
Cu(ftbd) ₂ .2H ₂ O	1558 _(w) , 1525 _(w)	1724, 1678	1543, 1501
Cu(Bzac) ₂ .2H ₂ O	1600 _s , 1568 _s , 1534 _s , 1504 _s	1738, 1724, 1647, 1623	1555, 1543, 1474, 1452
Cu(Bzac) ₂ .phen	1595 _w , 1570 _s , 1510 _s	1853, 1805, 1703	1604, 1562, 1474
Cu(ftbd) ₂ phen ₃	1575(s), 1540(s)	1860, 1780, 1763	1665, 1593, 1578
Cu(ftbd) ₂ .phen	1600 _w , 1576 _w , 1560 _w	1852, 1815, 1612	1603, 1570, 1439

Electronic Spectra

The electronic spectra of the diketones, their copper complexes and adducts both in methanol and chloroform are in Table 3. The assignment of the bands have been made based on related compounds. (Frackler, 1966, Singh and Sahai, 1969, Fleming and Thorton, 1975). The π - π^* intraligand transitions within the phenyl, furyl and thienyl rings were observed within the 36000-41000 cm^{-1} region. This could be due to semi-empirical calculations on the π – electron system. (Brailer et al, 1973). The π_3 - π_4^* transitions appeared in the 28000-34000 cm^{-1} region. However, the d-d bands of the compounds were found 14000-18000 cm^{-1} region. On complexation, bathochromic shifts were observed in the π_3 - π_4^* transitions of the complexes in methanol and chloroform except Cu(Fbd)₂ with hypsochromic in methanol. The electronic spectra of copper(II) complexes are difficult to interpret due to different ordering of the energy levels [Fackler et al, 1963]. The six coordinate copper (II) ion with a 2E_g ground state in an octahedral field is subject to Jahn-Teller distortion. The visible absorption bands of copper(II) β -diketonates are more intense and located at lower in methanol (a coordinating solvent) than in chloroform (a non-coordinating solvent) [Golchoubian and Khoshiar, 2012]. The effect of ligand and solvent variation in these spectra has been interpreted in some cases as indicating square pyramidal

structure. A shift to lower frequency of the d-d transitions in these complexes in methanol could be in indication of a change from four coordinate, square planar stereochemistry to five coordinate geometry, a shift to higher frequency indicates a change from five coordinate to six coordinate while no spectral shift indicates six coordinate copper(II) species [Addison et al, 1981].

In the Copper(II) complexes studied, a plausible four coordinate geometry is proposed based on the spectra shifts of the d-d transitions. There are shifts to lower frequencies of these transitions. The $\pi_3-\pi_4^*$ transitions of the complexes in methanol were accompanied by bathochromic shifts on adduct formation while the d-d transitions of these complexes were accompanied by hypsochromic shifts on adduct formation. In the adduct $\text{Cu}(\text{Ftbd})_2\text{phen}_3$, there was a shift of the $\pi_3-\pi_4^*$ transitions to lower frequency because of the presence of fluorine. The hypsochromic shifts probably indicate weaker delocalization as a result of stronger copper-base interaction. There was a high frequency shift of the d-d transitions of the adducts on changing solvent from chloroform to methanol. This is consistent with the coordinating ability of methanol resulting in six-coordinate copper(II) ions and could be an indication of a change from five coordinate, possibly square pyramidal, stereochemistry to six-coordinate geometry in methanol. Consequently, a probable five coordinate geometry is proposed for the adducts.

Table 3: Experimental electronic spectra of complex and adducts.

Compound	d-d $\times 10^3 \text{ cm}^{-1}$ transition		$\pi_3-\pi_4^* \times 10^3 \text{ cm}^{-1}$		$\pi-\pi^* \times 10^3$ (ph, Fu & py)	
	Methanol	Chloroform	Methanol	Chloroform	methanol	Chloroform
FbdH			28.28(502)	28.61(12505)	36.80(4271)	36.93(21883)
Ftbdh			28.01(678s)	29.26(13604)	35.42(5244)	36.20(20484)
BzacH			32.68(1070)	33.33(17440)	40.65(397)	40.80(33363)
$\text{Cu}(\text{Ftbd})_2 \cdot 2\text{H}_2\text{O}$	14.62(21)	14.95(40)	29.76(39149)	29.64(37680)	36.90(13940)	35.71(13200)
$\text{Cu}(\text{Fbd})_2 \cdot 2\text{H}_2\text{O}$	15.15(27.43)	IN	30.21(31686)	IN	36.23(16643)	IN

Cu(Bzac) ₂ .2H ₂ O	14.90(38)	15.42(49) 17.91(49)	31.45(39382)	31.56(38000)	39.84(25598)	-
Cu(Fbd) ₂ .Phen	16.26(73)	14.16(56)	29.59(49097)	30.67(43532)	33.78(102790)	33.67(17925)
Cu(Ftbd) ₂ .Phen ₃	15.61(46)	15.88(60)	28.70(38568)	28.68(37589)	37.45(100438)	35.71(142685)
Cu(Bzac) ₂ .Phen	16.50(106)	14.22(53)	30.36(17000)	30.58(17273)		40.49(27902)

NB: Values in bracket indicates the absorptivity of the band.

Magnetic properties

The room temperature magnetic moments for the copper (II) complexes and adducts were between 1.90-2.10 B.M which is within the range expected for magnetically dilute copper(II) ion(Earnshaw and Greenwood, 1984). An increase in the moment was observed in the adducts as compared with the parent complexes. This probably indicates reduced electron density in the chelate ring.

Computational studies

Optimized geometries

The schematic structures and optimized structures of both complexes and adducts are shown in Figures 1 and 2 respectively. The complexes and adducts were modeled based on the data obtained from infrared spectra, electronic spectra and elemental analysis of complex and adducts. The geometric parameters calculated at PM3 level of the semi-empirical method are listed in Table 4. The calculated bond distances of Cu-O1, Cu-O2, Cu-O3, and Cu-O4 are 1.849, 1.822, 1.847 and 1.842Å for complex A respectively. These bond distances were 1.851, 1.826, 1.852 and 1.845Å for Complex B and 1.925, 1.874, 1.910 and 1.955Å for complex C respectively. The average four Cu-O bond distances from the metal ion-ligand complexation for

A, B and C are 1.840, 1.844 and 1.916Å respectively, therefore Cu-O is stronger in complex A as compared to either A or C; the order Cu-O bond in the complexes are $A > B > C$.

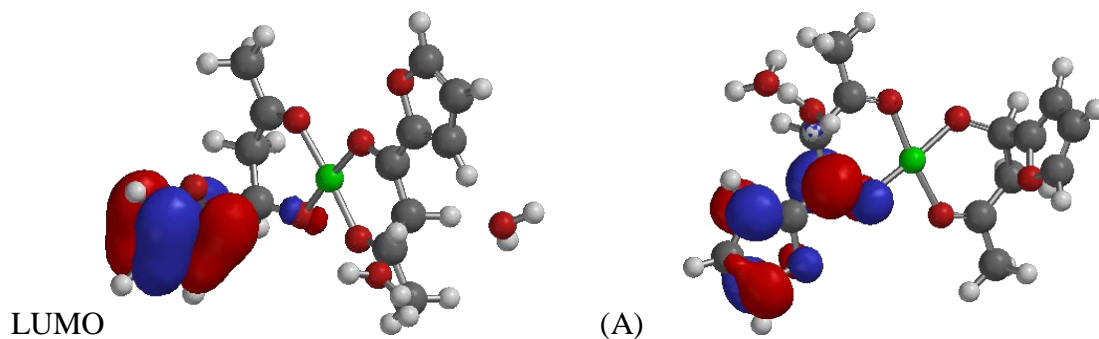
Table4: Geometry parameters for the complexes using PM3 level of semi-empirical method.

Bond Distance (Å)	A [Cu(fbd) ₂ .2H ₂ O]	B [Cu(Bzac) ₂ .2H ₂ O]	C [Cu(ftbd) ₂ .2H ₂ O]
Cu1-O1	1.849	1.851	1.925
Cu1-O2	1.822	1.826	1.874
Cu1-O3	1.847	1.852	1.910
Cu1-O4	1.842	1.845	1.955
Average Cu-O	1.840	1.844	1.916
BOND ANGLES (°)			
O1-Cu1-O2	99.30	97.43	127.97
O1-Cu1-O3	83.50	83.81	107.00
O1-Cu1-O4	173.27	171.47	110.70
O2-Cu1-O3	176.30	176.66	104.67
O2-Cu1-O4	73.98	75.93	105.33
O3-Cu1-O4	103.20	102.94	96.61

In adducts, the Cu-O1, Cu-O2 and Cu-O3 bond distances are 1.967, 1.932 and 1.924Å for D, these bonds are calculated to be 1.959, 1.928 and 1.930Å for E respectively. In adduct F; these bonds are 1.960, 1.931 and 1.936Å respectively (Table 5). The average Cu-O bond distances for adducts D, E and F are 1.940, 1.939 and 1.942Å respectively, therefore Cu-O is relatively shortened in the complexes than that of adducts, thus Cu-O bonds are stronger in the complexes than in adducts. This is consistent with the both experimental and calculated infrared spectra which show lower frequency shifts indicating stronger Cu-O bonds in the complexes. The Cu-N1 (Cu-N2) bond distances for adducts D, E and F are 1.924 (1.915), 1.922 (1.918) and 1.919Å (1.916Å) respectively. Comparing the values of Cu-O and Cu-N bond distances, Cu-N bonds are stronger than Cu-O bonds (longer bond distances) in adducts, therefore adducts

formation weakened the Cu-O bonds which are consistent with experimental infrared spectra obtained.

HOMO



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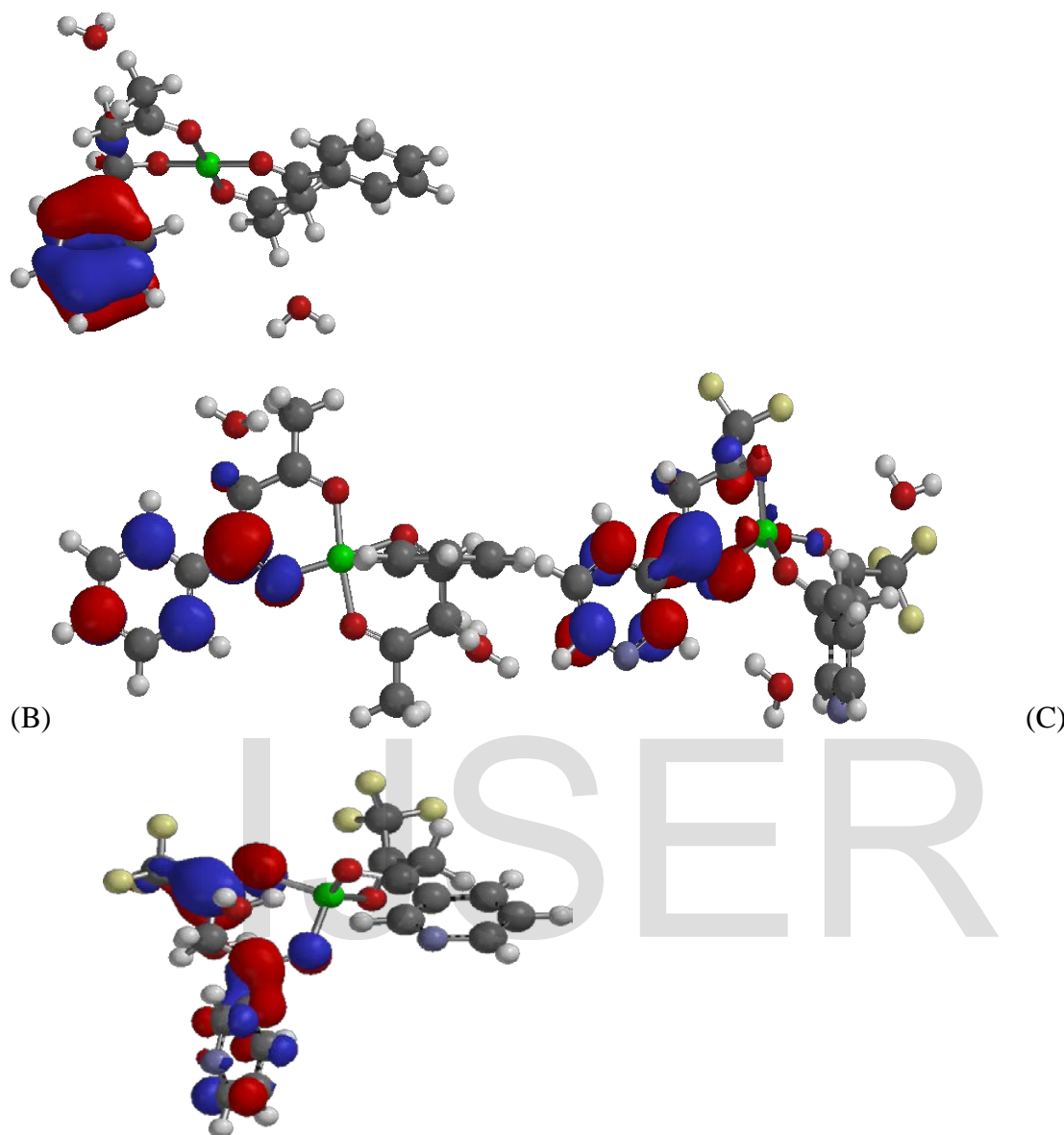


Figure 3: Frontier Molecular orbitals: HOMO and LUMO of the complexes.

The O1-Cu-O2, O1-Cu-O4, O2-Cu-O4 and O3-Cu-O4 bond angles are 99.30, 173.27, 73.98 and 103.20° respectively for complexes A. These bond angles are 97.43, 171.47, 75.93 and 102.94° for complex B and 127.97, 110.70, 105.33 and 96.61° respectively for complex C. From the Table 4, it could be suggested that complexes A and B adopted square planar geometries and complex C tetrahedral geometry.

In adducts, O1-Cu-O2, O1-Cu-O3 and O2-Cu-O3 bond angles are 115.24, 88.39 and 90.01° for adduct D; 115.21, 88.80 and 89.41° for adduct E and 98.39, 88.67 and 88.90° for adduct F respectively. The N1-Cu-N2, O1-Cu-N1, O2-Cu-N1, O2-Cu-N2 and O3-Cu-N2 bond angles are 90.79, 103.93, 140.72, 87.36 and 174.44° for D; 90.78, 104.43, 141.32, 87.01 and 174.62° for E and 94.77, 94.90, 175.44, 89.61 and 138.15° for adduct F respectively. The trigonal bipyramidal geometry was proposed for adducts.

Table 5. Geometry parameters for adducts using PM3 level of semi-empirical method.

BOND DISTANCE (Å)	D [Cu(fbd) ₂ .phen]	E [Cu(Bzac) ₂ .phen]	F Cu(Ftbd) ₂ .Phen
Cu1-O1	1.967	1.959	1.960
Cu1-O2	1.932	1.928	1.931
Cu1-O3	1.922	1.930	1.936
Cu1-N1	1.924	1.922	1.919
Cu1-N2	1.915	1.918	1.916
Ave. Cu-O	1.940	1.939	1.942
	BOND ANGLES (°)		
O1-Cu1-O2	115.24	115.21	98.39
O1-Cu1-O3	88.39	88.80	88.67
O2-Cu1-O3	90.01	89.41	88.90
O1-Cu1-N1	103.93	104.43	94.90
O1-Cu1-N2	97.17	96.34	123.38
O2-Cu1-N1	140.72	141.32	175.44
O2-Cu1-N2	87.36	87.01	89.61
O3-Cu1-N1	88.14	89.50	87.78
O3-Cu1-N2	174.44	174.62	138.15
N1-Cu1-N2	90.79	90.78	90.77

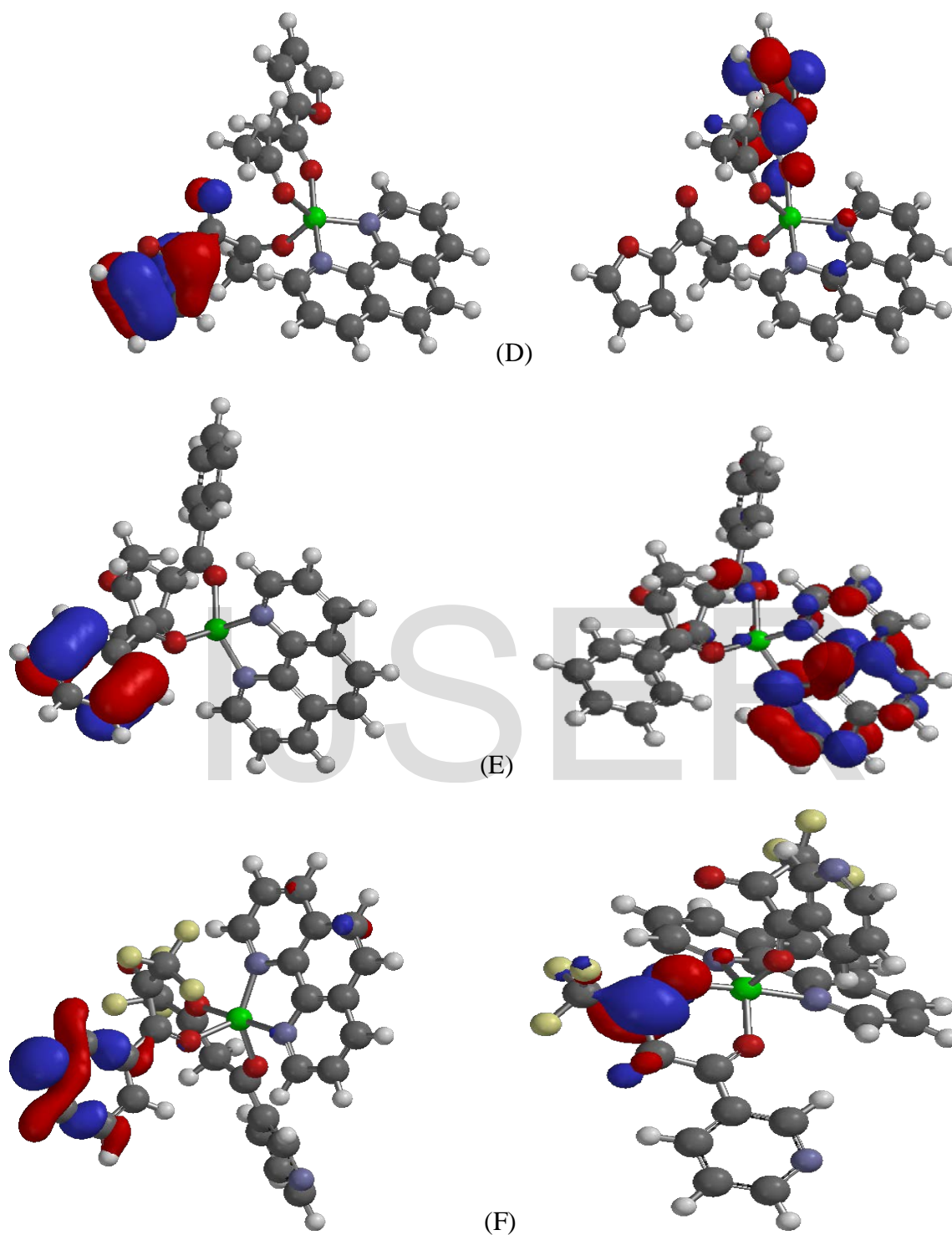


Figure 4: Frontier Molecular orbitals: HOMO and LUMO of adducts.

The contour plots of HOMO and LUMO orbitals of the complexes and adducts computed at the PM3 level of semi-empirical are displayed in Figures 3 and 4 respectively. The HOMO of complex A was localized on the furan ring of one of the ligand, while the LUMO is principally localized on one furan and C=O of 1-furyl-1,3-butanedione. For complex B, the HOMO is localized on one of the benzene rings of the ligand and LUMO is localized mainly on the one of the benzene rings and C=O of 1-phenyl-1,3-butanedione of the ligand. For complex C, both HOMO and LUMO are localized on pyridinyl-1,3-butanedione.

For adducts D, E and F (i.e. [Cu (Bzac)₂.phen], [Cu (fbd)₂.phen] and [Cu(Tfbd)₂.phen]), the HOMOs are localized on the furan ring of 1-furyl-1,3-butanedione, benzene ring of 1-phenyl-1,3-butanedione and pyridine ring of the pyridinyl-1,3-butanedione in D, E and F respectively (i.e. the HOMO map of these adducts is on the ligand that used one of its C=O in bonding to copper ion). The LUMO map of adducts is mainly localized on the phenanthroline. The HOMO-LUMO band gap of the complexes suggested that the complexes and adducts could have good stability.

Table 6: Mulliken charges of the complexes.

Atom	A [Cu(fbd) ₂ .2H ₂ O]	B [Cu(Bzac) ₂ .2H ₂ O]	C [Cu(ftbd) ₂ .2H ₂ O]
Cu1	-0.149	-0.169	-0.381
O1	-0.011	-0.025	-0.143
O2	-0.132	-0.116	-0.236
O3	-0.049	-0.052	0.008
O4	0.050	0.058	0.018
Atom	D [Cu(fbd) ₂ .phen]	E [Cu(Bzac) ₂ .phen]	(F) [Cu(Tfbd) ₂ .phen]
Cu1	-0.353	-0.363	-0.370
O1	-0.141	-0.170	-0.178
O2	-0.112	-0.110	-0.047
O3	-0.150	-0.152	-0.144
N1	0.504	0.507	0.502
N2	0.500	0.506	0.493

The Mulliken charges on copper atom in the complexes A, B and C are -0.149, -0.169 and -0.381 respectively, this is an indication that electrons were donated into d-orbital of the copper atom from the ligands. The charges on copper ion in complex C is higher than that of A and B which implied that more electrons are available in the d-orbital of copper ion of complex C. This might be due to the three atoms of chlorine which behaved as electron donating specie rather than electron abstracting specie coupled with higher electron donating ability of pyridine over furan and benzene. The same argument could be used to explain a Mulliken charge on copper ions of adducts D, E and F. The Mulliken charges of D, E and F are -0.353, -0.363 and -0.370e respectively (Table 6). Evidence of electrons transfer during complexation could be seen in the Mulliken charges on coordinated carbonyl oxygen atoms; the charges on O1 (O2) in complexes A, B and C are -0.011 (-0.132), -0.025 (-0.116) and -0.143 (-0.236e) respectively as compared to -0.231 (-0.286), -0.216 (-0.284) and -0.223 (-0.196e) in FbdH, BzacH and FtbdH ligands respectively. The Mulliken charges on O4 are all positive; 0.050, 0.058 and 0.018e in complexes A, B and C respectively.

The Mulliken charges on O1 (O2) for adducts D, E and F are -0.141 (-0.112), -0.170 (-0.110) and -0.178 (-0.047) respectively which are reduced as compared to the ligands. This supports experimental results that more lone pair of electrons is donated to Copper from the ligands. The Mulliken charges on nitrogen atoms are all positive depicting that the lone pair of electrons on nitrogen atoms have been donated to the central Copper ion in the formation of adducts. The nitrogen atoms N1 (N2) have Mulliken charges 0.504 (0.500), 0.507 (0.506) and 0.502e (0.493e) in complex D, E and F respectively.

Conclusion

Copper (II) complex of 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione (FtbdH), (1-(2-furyl)-1,3-butanedione (FbdH) and 1-phenyl-1,3-butanedione, (BzachH) were synthesized and characterized by elemental analysis, infrared and electronic spectra . The metal analysis agreed with the expected theoretical values. There was a hypsochromic shift in the carbonyl stretch vibrational band on ligand-metal ion complexation and also in adduct formation. This was in agreement with the theoretical results. The proposed structures of the complexes and adducts based on the electronic spectra results were modeled by quantum chemical software package. The geometries parameters were calculated at PM3 level of semi empirical methods, the HOMO, LUMO and Mulliken charges of the complexes and adduct were also reported.

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