

Synthesis and Physicochemical Studies of Some 2-substituted-1-phenyl-1,3-butanedionato Nickel(II) and Copper(II) Complexes And Their 2,2'-Bipyridine and 1,10-Phenanthroline Adducts

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Abstract

The nickel(II) and copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione (2-R-bzacH, R=Cl, NO₂) 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 all the adducts are electrolytes except Ni(NO₂-bzac)₂bipy and Cu(NO₂-bzac)₂phen which are non-electrolytes. The room temperature magnetic moments suggest that the Cu(NO₂-bzac)₂ is a dimer while the visible absorption spectra of the compounds suggest plausible 4-, 5- and 6-coordinate geometry for these compounds. The infrared spectra of the complexes showed that lower frequency shifts of varying magnitudes were observed in the carbonyl stretching frequencies on complexation.

Keywords: 2-substituted-1-phenyl-1,3-butanedione, Spectra studies, Magnetic moments, Conductance measurement

1. Introduction

A survey of the literature reveals that metal β -diketonates have found use as fuel additives, trace metal analysis by gas chromatography and numerous other extraction applications (Wenzel et al, 1985). The dissolution of chelating agents in supercritical fluids has been explored as a possible route to waste cleanup (Laintd et al, 1992; Lalntz et al, 1994; Wang et al, 1995; Wang et al, 1994). Complexes of β -diketones are reported to have potentially useful pharmacological properties (Onawumi et al, 2008).

Literature is available on the introduction of halogens and nitronium ion at the central carbon atom of β -diketones [(R₁COCH₂COR₂) where R₁=R₂=CH₃](Singh and Sahai, 1967a; Singh and Sahai, 1967b; Woods and Patel, 1994; Patel and Woods, 1990a; Collman et al, 1962; Ebeid et al, 1966; Tanaka et al, 1969) whereas little work has been carried out on the synthesis and characterization of the nickel(II) and copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione (2-R-bzacH, R=Cl, NO₂) and their 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) adducts. In continuation of our work on substituted β -diketones (Woods et al, 2009a; Woods et al, 2009b), we report the results of our investigations on the nickel(II) and copper(II) complexes of some 2-substituted-1-phenyl-1,3-butanediones (2-R-bzacH, R=Cl, NO₂) and their adducts with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen).

2. Experimental

The following reagents were used: 1-phenyl-1,3-butanedione or benzoylacetone (bzacH) (Aldrich chemicals), sulphuryl chloride, copper nitrate, nickel acetate, copper acetate, 2,2'-bipyridine and 1,10-phenanthroline (analytical grade).

2.1 Synthesis of the Ligands

The ligands, 2-chloro-1-phenyl-1,3-butanedione (Tanaka et al, 1969) and 2-nitro-1-phenyl-1,3-butanedione (Singh and Sahai, 1967a) were prepared by literature methods.

2.2 Synthesis of the Complexes and Adducts

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

Cl-bzacH (2.00 mL, 12.4 mmol) in 6 mL acetone was added to copper(II) acetate monohydrate (1.24 g, 6.2 mmol) in 50 mL 60% methanol in drops. The mixture was stirred for 1 hour and the precipitates formed were filtered, washed with 60% methanol and dried in the vacuo. All the other complexes were prepared using similar procedure.

2.2.2 Synthesis of $\text{Cu}(\text{Cl-bzac})_2\text{phen}$

The phenanthroline adduct of $\text{Cu}(\text{Cl-bzac})_2$ was prepared by adding the solid complex (0.50 g, 1.1 mmol) while stirring to phenanthroline (0.72 g, 3.6 mmol) dissolved in 10 mL hot chloroform solution. The mixture was further stirred for 15 minutes and the precipitates formed were filtered and washed with acetone. This was dried in vacuo over anhydrous calcium chloride. Other adducts were prepared using similar procedures.

2.3 Physical measurements

Elemental analyses for C, H, N were determined at Department of Chemistry, Loughborough University, UK. The % metal in the nickel(II) and copper(II) compounds were determined titrimetrically using 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 the Ligands, nickel(II) and copper(II) compounds in methanol and chloroform were recorded on a Unicam UV-Visible Spectrophotometer using 1cm glass cell. The reflectance spectra of the Ligands, nickel(II) and 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.

3. Results and discussion

Table I shows the analytical data, colours, %yield and room temperature magnetic moments (μ_{eff}) of the prepared nickel(II) and copper(II) compounds. The elemental analyses were in good agreement with those calculated for the proposed formula (Table 2). The nickel(II) compounds prepared from 2-chloro-1-phenyl-1,3-butanedione were generally pink in colour except $\text{Ni}(\text{Cl-bzac})_2 \cdot 2\text{H}_2\text{O}$ which had green colour while those prepared from 2- NO_2 -1-phenyl-1,3-butanedione were obtained as various shades of green except $[\text{Ni}(\text{NO}_2\text{-bzac})(\text{phen})_2](\text{NO}_2\text{-bzac})$ which was obtained as Light brown. All the copper(II) complexes and their adducts were obtained as various shades of green colour.

The magnetic moment data as shown in Table 1 depicts the paramagnetic nature of the compounds. The nickel(II) compounds had values in the range 2.9-3.28 B.M. which is in agreement with the range expected for octahedral nickel(II) complexes (2.9-3.3 B.M) (Patel and Woods, 1990b). 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 (Patel and Woods, 1990c). The prepared 2-substituted-1-phenyl-1,3-butanedionato copper(II) compounds had moments in the range 1.44-2.19 B.M. The magnetic moment of $\text{Cu}(\text{NO}_2\text{-bzac})_2$ (1.44 B.M.) is lower than the spin only value of 1.73 B.M. which is indicative of dimerization with the possibility of Cu-Cu linkage (Cotton and Wilkinson, 1988).

The molar conductivity of the complexes in nitromethane were in the range 17-21 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that they are non-electrolytes. The adducts had values between 62-198 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ except $\text{Ni}(\text{NO}_2\text{-bzac})_2\text{bipy}$ and $\text{Cu}(\text{NO}_2\text{-bzac})_2\text{phen}$ which are non-electrolytes (13 and 46 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ respectively).

The principal IR absorption bands of the prepared complexes are listed in Table 3. In the spectrum of $\text{NO}_2\text{-bzacH}$, the band at 1600 cm^{-1} has been assigned as $\nu_{\text{as}}(\text{C=O}) + \nu_{\text{as}}(\text{C=C}) + \nu_{\text{as}}(\text{NO}_2)$ vibrations while those at 1360 cm^{-1} and 820 cm^{-1} are assigned as $\nu_s(\text{NO}_2)$ and $\nu(\text{C-N})$ or $\delta\text{N-O}$ respectively. Bathochromic shifts of varying magnitude were observed in the asymmetric C-O and C-C stretching vibrations of the complexes relative to their respective ligands whereas hypsochromic shifts were observed in all the adducts relative to the complexes. Multiple bands of $\nu_s(\text{C-O}) + \delta\text{C-H}$ were observed in all the compounds except $[\text{Ni}(\text{Cl-bzac})(\text{bipy})(\text{H}_2\text{O})_2](\text{Cl-bzac})$, $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](\text{Cl-bzac})$ and $[\text{Ni}(\text{Cl-bzac})(\text{phen})(\text{H}_2\text{O})_2](\text{Cl-bzac})$ which had single band. Studies have shown

that methyl deformation band occurred at around 1425 cm^{-1} in acetylacetone (Holtzclaw and Collman, 1957; Belford et al, 1956) while bands in the $1420\text{--}1350\text{ cm}^{-1}$ region have been assigned as $\delta_{\text{as}}(\text{CH}_3) + \delta_{\text{s}}(\text{CH}_3)$ vibrations (Singh and Sahai, 1967b; Tanaka et al, 1969; Patel and Woods, 1990b; Koshimura et al, 1973; Nakamoto et al, 1961). Furthermore, the $\nu\text{M-O}+\nu\text{C-N}$ vibrational modes occurred below 700 cm^{-1} (Patel and Woods, 1990a; Patel and Woods, 1990c). The C-H deformation bands ($\delta\text{C-H}$) for the bipyridine appeared at around 768 cm^{-1} while that of the phenanthroline adducts were observed at 852 cm^{-1} and 727 cm^{-1} .

The electronic spectra of the ligands in CHCl_3 and methanol are listed in Table 4. Single bands of the $\pi_3\text{--}\pi_4^*$ were observed in the $31,250\text{--}31,154\text{ cm}^{-1}$ region in Cl-bzacH and $\text{NO}_2\text{--bzacH}$ ligands. Bathochromic shift of the $\pi_3\text{--}\pi_4^*$ were observed in Cl-bzacH and $\text{NO}_2\text{--bzacH}$ as compared to bzacH in chloroform. $\pi_3\text{--}\pi_4^*$ Hypsochromic shifts of varying magnitude were observed in the $\text{Ni}(\text{Cl-bzac})_2\cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_2\text{--bzac})_2\cdot 2\text{H}_2\text{O}$ complexes in chloroform and methanol. Upon adduct formation, $\pi_3\text{--}\pi_4^*$ Hypsochromic shifts were observed in all the adducts in chloroform except $[\text{Ni}(\text{Cl-bzac})(\text{bipy})(\text{H}_2\text{O})_2](\text{Cl-bzac})$ which had bathochromic shift. The ligand field spectra band of $\text{Ni}(\text{Cl-bzac})_2\cdot 2\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_2\text{--bzac})_2\cdot 2\text{H}_2\text{O}$ were typically of an octahedral geometry (Lever, 1986) while the shift observed in $\text{Cu}(\text{Cl-bzac})_2$ and $\text{Cu}(\text{NO}_2\text{--bzac})_2$ suggest a four coordinate square planar geometry. Lower frequency shifts were observed in $\text{Cu}(\text{Cl-bzac})_2$ and $\text{Cu}(\text{NO}_2\text{--bzac})_2$ in methanol relative to chloroform [$18,031\text{ cm}^{-1}$ in chloroform $\rightarrow 15,625\text{ cm}^{-1}$ in methanol for $\text{Cu}(\text{Cl-bzac})_2$] and [$18,349\text{ cm}^{-1}$ in chloroform $\rightarrow 15,198\text{ cm}^{-1}$ in methanol for $\text{Cu}(\text{NO}_2\text{--bzac})_2$] which is an indication that the complexes are square planar in structure. Nickel(II) species have a large number of stereochemical forms in which the ion occurs, hence equilibrium between these forms are usually set up which are generally temperature, solvent and sometimes concentration dependent (Bailar et al, 1973). In solution, Ni(II) β -diketonates sometimes exhibit a monomer $\leftrightarrow$ trimer, square planar $\leftrightarrow$ octahedral equilibrium (Cotton and Wilkinson, 1980). Three transitions are expected for an octahedral nickel(II) ion in the region $7,000\text{--}13,000\text{ cm}^{-1}$, $11,000\text{--}20,000\text{ cm}^{-1}$, $19,000\text{--}27,000\text{ cm}^{-1}$ which are assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ respectively. In the synthesized nickel(II) adducts, bands in the $11,442\text{--}12,821\text{ cm}^{-1}$ and $13,908\text{--}19,455\text{ cm}^{-1}$ region have been assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ transitions respectively (Lever, 1986; Osowole et al, 2000). The visible spectra of the synthesized copper(II) adducts had a single band between $14,006\text{--}15,625\text{ cm}^{-1}$ which is consistent with the adoption of square pyramidal geometry for copper(II) compounds (Odunola et al, 2003). In addition, higher frequency shifts were observed in the ligand field spectral of the copper(II) adducts in methanol as compared with chloroform. $[\text{Cu}(\text{Cl-bzac})(\text{bipy})(\text{H}_2\text{O})](\text{Cl-bzac})$ had a band in the $14,205\text{ cm}^{-1}$ region in chloroform and this band was shifted to $16,393\text{ cm}^{-1}$ in methanol. This is an indication that the compound is a five coordinate square pyramidal geometry (Patel and Woods, 1990a). The electronic reflectance spectra of the ligands, complexes and adducts in the ultraviolet region exhibited single peak between $31,056\text{--}37,453\text{ cm}^{-1}$ with an additional peak observed between $39,683\text{--}48,544\text{ cm}^{-1}$ which have been assigned to $\pi_3\text{--}\pi_4^*$ and charge transfer (CT) respectively. The visible region of the spectra showed that the nickel(II) compounds were octahedral in geometry while the copper(II) complexes and adducts were square planar and square pyramidal in geometry respectively.

4. Conclusion

Probable six coordinate octahedral geometry is suggested for all the nickel(II) compounds while a probable five coordinate, square pyramidal geometry is suggested for the copper(II) compounds except $\text{Cu}(\text{Cl-bzac})_2$ and $\text{Cu}(\text{NO}_2\text{--bzac})_2$ which are square planar in structure.

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

Formula	M.Wt	Colour	M.P. (°C)	Yield (%)	μ_{eff} (B.M.)
Ni(Cl-bzac) ₂ .2H ₂ O	486.09	Green	128-130	51.58	2.90
[Ni(Cl-bzac)(bipy)(H ₂ O) ₂](Cl-bzac)	642.28	Pink	124-126	61.86	2.93
[Ni(phen) ₃ (H ₂ O) ₂](Cl-bzac) ₂	1026.71	Pink	138-140	40.36	3.28
[Ni(phen) ₂ (H ₂ O) ₂](Cl-bzac) ₂	846.49	Pink	198-200	82.67	3.08
Ni(NO ₂ -bzac) ₂ .2H ₂ O	507.10	L.Green	168	52.32	2.96
Ni(NO ₂ -bzac) ₂ .bipy	627.25	Green	218-219	77.78	3.02
[Ni(NO ₂ -bzac)(phen) ₂](NO ₂ -bzac)	831.47	L.Brown	196-198	69.42	3.18
Cu(Cl-bzac) ₂	454.84	Green	220-222	61.34	1.79
[Cu(Cl-bzac)(bipy)(H ₂ O)](Cl-bzac)	629.05	D.Green	175-177	89.13	2.19
Cu(Cl-bzac)(phen)(H ₂ O)](Cl-bzac)	653.06	D.Green	207-209	34.82	1.98
Cu(NO ₂ -bzac) ₂	475.85	Green	145-147	89.13	1.44
[Cu(NO ₂ -bzac)(bipy)(H ₂ O)]	650.06	Green	170-172	56.03	1.73
Cu(NO ₂ -bzac) ₂ .phen	656.05	Green	185-187	25.67	2.01

D = dark, L = light

Table 2. Microanalytical data of nickel(II) and 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
Ni(Cl-bzac) ₂ .2H ₂ O	50.17	4.10	-	11.78	49.41	4.16	-	12.08
[Ni(Cl-bzac)(bipy)(H ₂ O) ₂](Cl-bzac)	55.70	4.55	4.02	9.42	56.10	4.40	4.36	9.42
[Ni(phen) ₃ (H ₂ O) ₂](Cl-bzac) ₂	65.69	4.03	7.83	6.22	65.51	4.33	8.18	5.72
[Ni(phen) ₂ (H ₂ O) ₂](Cl-bzac) ₂	62.04	3.98	7.02	6.80	62.43	4.30	6.62	6.85
Ni(NO ₂ -bzac) ₂ .2H ₂ O	46.97	4.28	5.82	11.33	47.37	3.98	5.52	11.58
Ni(NO ₂ -bzac) ₂ .bipy	56.94	4.05	9.12	9.11	57.44	3.86	8.92	9.34
[Ni(NO ₂ -bzac)(phen) ₂](NO ₂ -bzac)	64.01	4.32	9.82	7.50	63.55	3.89	10.10	7.06
Cu(Cl-bzac) ₂	52.24	3.84	-	13.7	52.81	3.55	-	13.96
[Cu(Cl-bzac)(bipy)(H ₂ O)](Cl-bzac)	56.83	4.07	4.15	10.19	57.28	4.17	4.45	10.09
[Cu(Cl-bzac)(phen)(H ₂ O)](Cl-bzac)	59.09	3.77	4.79	9.40	58.85	4.02	4.29	9.72
Cu(NO ₂ -bzac) ₂	50.18	3.20	5.82	13.33	50.48	3.40	5.88	13.34
[Cu(NO ₂ -bzac)(bipy)(H ₂ O)]	55.81	3.92	9.01	9.47	55.43	4.04	8.61	9.77
Cu(NO ₂ -bzac) ₂ .phen	58.58	3.69	8.54	9.68	58.50	3.86	8.63	9.62

Table 3. Relevant Infrared Spectra bands (cm^{-1}) of nickel(II) and copper(II) complexes of 2-substituted-1-phenyl-1,3-butanedione and their adducts

Formula	C=O, C=C	$\nu_s(\text{C-O})+\delta\text{C-H}$	$\delta_{\text{as}}(\text{CH}_3)+\delta_s(\text{CH}_3)$	$\delta(\text{C-H})$ Phen/bipy
bzacH	1599m, 1540b	1484m	1413m, 1360m	-
Cl-bzacH	1749w 1724w 1686m	1449w	1359w	
Ni(Cl-bzac) $_2$.2H $_2$ O	1689w1591s 1563s	1487m 1448w	1352w	
[Ni(Cl-bzac)(bipy)(H $_2$ O) $_2$](Cl-bzac)	1598s 1570m 1509m	1443m	1406m 1355w	768s
[Ni(phen) $_3$ (H $_2$ O) $_2$](Cl-bzac) $_2$	1626m 1587m 1516s	1462w	1424s 847s	726s
[Ni(phen) $_2$ (H $_2$ O) $_2$](Cl-bzac) $_2$	1736b 1627w 1594s	1457s	1399s 851s	727s
NO $_2$ -bzacH	1600m 1567w	1462m	1412w1360m	
Ni(NO $_2$ -bzac) $_2$.2H $_2$ O	1592s 1561s 1516s	1484m 1452s	1403m	
Ni(NO $_2$ -bzac) $_2$.bipy	1595vs 1570vs 1506vs	1484vs 1456s	1358w	772vs
[Ni(NO $_2$ -bzac)(phen) $_2$](NO $_2$ -bzac)	1624w 1593s 1564s	1484m 1457m	1399s 851s	727s
Cu(Cl-bzac) $_2$	1553s 1516m	1487w 1443m	1395m	
[Cu(Cl-bzac)(bipy)(H $_2$ O)](Cl-bzac)	1592s 1589m1521s	1490m 1448s	1385s	764s
[Cu(Cl-bzac),phen)(H $_2$ O)](Cl-bzac)	1597m 1564m 1518s	1486m 1450m	1388s 852s	724s
Cu(NO $_2$ -bzac) $_2$	1587m 1565s 1523s	1488m 1453m	1401s 1360m	
[Cu(Cl-bzac),phen)(H $_2$ O)](Cl-bzac)	1666s 1589s 1561s	1488s 1451m	1390s	774s
Cu(NO $_2$ -bzac) $_2$.phen	1716w 1595s 1568s	1486m 1450m	1387s 852s	724s

b=broad, s=strong, v=very, w=weak, m=medium

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

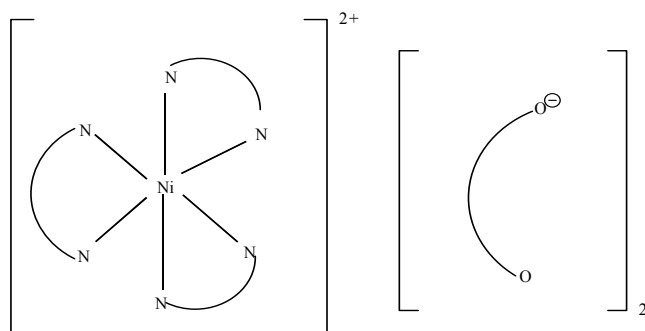
Empirical Formula	$\pi_3, \pi_4^*(\text{cm}^{-1})$		d-d	
	CHCl_3	CH_3OH	CHCl_3	CH_3OH
bzacH	32,258(7247)	32,258(18259)	-	-
Cl-bzacH	31,250*	32,051(?)	-	-
$\text{Ni}(\text{Cl-bzac})_2 \cdot 2\text{H}_2\text{O}$	33,333*	34,247*	17,422(67) 13,850(59)	15,974(16)
$[\text{Ni}(\text{Cl-bzac})(\text{bipy})(\text{H}_2\text{O})_2](\text{Cl-bzac})$	33,113(?)	33,784(29412) 12,690(?)	17,730(?) 12,755(41)	17,544(60)
$[\text{Ni}(\text{phen})_3(\text{H}_2\text{O})_2](\text{Cl-bzac})_2$	34,014(?)	34,014(18085)	19,048(?) 13,908(?)	19,455(56) 12,755(8) 11,442(8)
$[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](\text{Cl-bzac})_2$	34,247(31759)	34,247(26188)	17,857(89) 12,853(73)	18,450(24) 12,563(8)
$\text{NO}_2\text{-bzacH}$	32,154(27141)	32,051(22717)	-	-
$\text{Ni}(\text{NO}_2\text{-bzac})_2 \cdot 2\text{H}_2\text{O}$	34,014*	34,483*	15,723(15)	18,587(43) 12,821(15)
$\text{Ni}(\text{NO}_2\text{-bzac})_2 \cdot \text{bipy}$	34,420(29568)	34,480(29765)	17,870(60) 12,600(55)	17,560(68) 12,080(40)
$[\text{Ni}(\text{NO}_2\text{-bzac})(\text{phen})_2](\text{NO}_2\text{-bzac})$	34,247(30811)	34,247(39952)	17,373(98) 12,987(72)	18,587(43) 12,821(15)
$\text{Cu}(\text{Cl-bzac})_2$	32,468(12998)	31,056(?)	12,690(113)	15,625(?) 11,848(?)
$[\text{Cu}(\text{Cl-bzac})(\text{bipy})(\text{H}_2\text{O})](\text{Cl-bzac})$	33,557(66659)	33,333(53582)	14,205(489)	16,393(161)
$[\text{Cu}(\text{Cl-bzac})(\text{phen})(\text{H}_2\text{O})](\text{Cl-bzac})$	34,014(?)	34,014(44970)	14,006(?)	16,129(137)
$\text{Cu}(\text{NO}_2\text{-bzac})_2$	31,447(36456)	33,898*	18,349* 15,060(128)	15,198(70)
$[\text{Cu}(\text{NO}_2\text{-bzac})(\text{bipy})(\text{H}_2\text{O})]$	32,258(58721)	32,680(31224)	15,625(82)	16,447(96)
$\text{Cu}(\text{NO}_2\text{-bzac})_2 \cdot \text{phen}$	34,014(31249)	34,014(38037)	14,164(224)	16,287(185)

? Compounds partially soluble in the solvent.

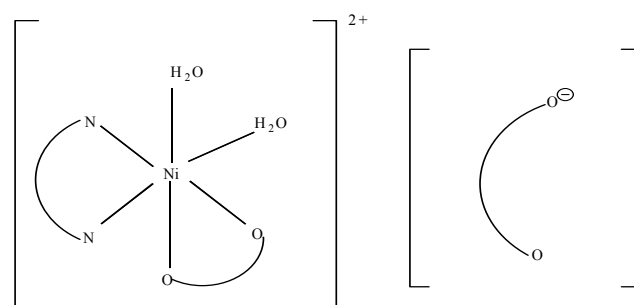
*Shoulder

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

Emperical Formula	$\pi_3.\pi_4^*(\text{cm}^{-1})$	d-d
Cl-bzacH	35,971	-
Ni(Cl-bzac) ₂ .2H ₂ O	32,154	18,484, 12,019
[Ni(Cl-bzac)(bipy)(H ₂ O) ₂](Cl-bzac)	36,364	20,325, 14,749, 12,642
[Ni(phen) ₃ (H ₂ O) ₂](Cl-bzac) ₂	31,056	21,645, 15,480, 12,048
[Ni(phen) ₂ (H ₂ O) ₂](Cl-bzac) ₂	31,348	20,790, 14,749, 12,739
NO ₂ -bzacH	37,453	-
Ni(NO ₂ -bzac) ₂ .2H ₂ O	36,900	18,349, 12,063
Ni(NO ₂ -bzac) ₂ .bipy	36,630	20,325, 13,587, 12,642
[Ni(NO ₂ -bzac)(phen) ₂](NO ₂ -bzac)	31,157	19,802, 14,306, 12,500
Cu(Cl-bzac) ₂	34,364	20,000, 17,007, 12,121
[Cu(Cl-bzac)(bipy)(H ₂ O)](Cl-bzac)	36,101	14,724
[Cu(Cl-bzac)(phen)(H ₂ O)](Cl-bzac)	34,247	14,305
Cu(NO ₂ -bzac) ₂	31,847	20,284, 16,155, 12,210
[Cu(NO ₂ -bzac)(bipy)(H ₂ O)]	36,101	15,325
Cu(NO ₂ -bzac) ₂ .phen	35,345	14,987



1:2 ELECTROLYTE



1:1 ELECTROLYTE

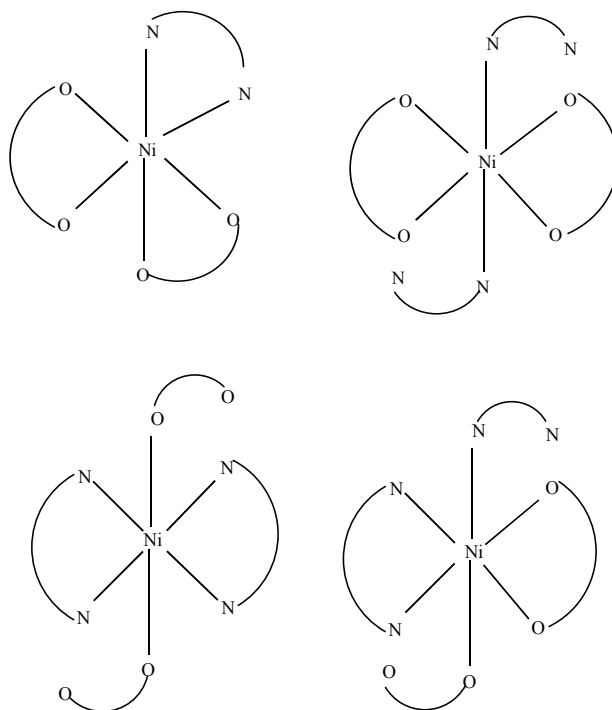


Figure 1. Proposed structures for Nickel adducts

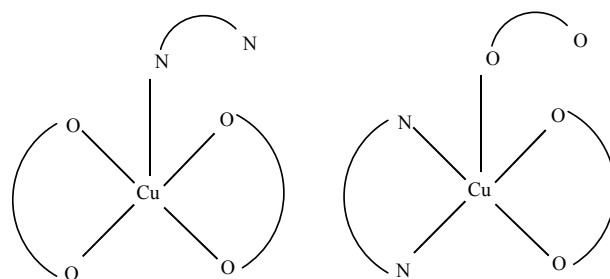
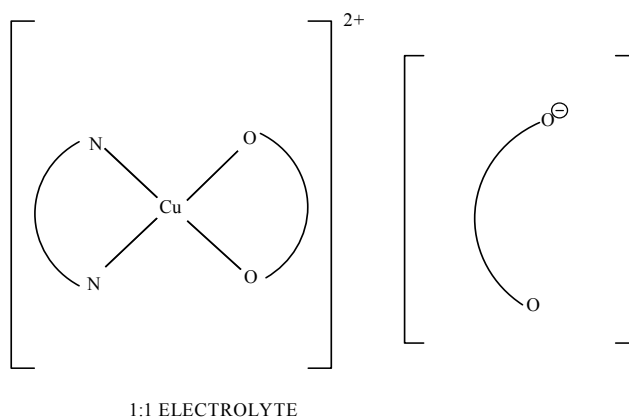


Figure 2. Proposed structures for Copper adducts