Synthesis, Characterization and Quantum Chemical Studies of Some Co(II) and Cu(II) Complexes of Acetoacetic Acid Hydrazide

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New complexes of cobalt(II) and copper(II) acetoacetic acid hydrazides have been synthesized and characterized by elemental analysis, infrared and electronic reflectance spectra and room temperature magnetic susceptibility measurements. The infrared spectra of the complexes revealed the coordination to the metal ion occurs at the carbonyl oxygen and the amino nitrogen of the hydrazide moiety. This was supported by theoretical calculations. The conjoint of the electronic spectra and magnetic susceptibility measurements suggests plausible octahedral geometry for the cobalt(II) complexes while the copper(II) complexes adopt a square planar geometry. The stereochemistry of the modeled structures calculated by semi-empirical (PM3) and density functional theory (DFT) methods are also consistent with those experimentally deduced.

Key Words: Synthesis, Infrared, Hydrazides, DFT, Electronic spectra.

INTRODUCTION

Transition metal complexes of hydrazides have been intensely investigated by coordination chemists because of their interesting structural properties and their wide ranging applications[1-5]. Aliphatic carboxylic acid hydrazides among many other uses are employed as metal ion removal from waste waters[6], aromatic hydrazides are used as stabilizers for rigid PVC against therm-oxidative degradation[7]. Hydrazides are also used for the extraction of non-ferrous metals and rare earth from aqueous solutions[8-10,11]. The coordinating ability of hydrazides to a variety of elements particularly transition metals afford the study of the metals in such systems.

In continuation of our studies on alkyl acetoacetate hydrazides[12,13] we present the results of our investigations on the synthesis, spectral and the theoretical studies of Co(II) and Cu(II) complexes of acetoacetic acid hydrazide. The complexes are new and represent the first systematic study of acetoacetic acid hydrazide series.

EXPERIMENTAL

Reagents grade cobalt(II) acetate tetrahydrate, cobalt(II) chloride hexahydrate, cobalt(II) sulphate heptahydrate, copper(II) acetate monohydrate, copper(II) chloride dihydrate, copper(II) sulphate pentahydrate, copper(II) nitrate pentahydrate, ethylacetoacetate, hydrazine hydrate, methanol were available from BDH.

Preparation of acetoacetic acid hydrazide: Ethylaceto acetate (51 mL, 0.04 mol) was added dropwisely to hydrazine hydrate (19.4 mL 0.04 mol) in quick fit conical flask fitted with a reflux condenser. The orange coloured suspension obtained was refluxed for 15 min and on addition of 170 mL of ethanol a clear yellow solution was obtained. The resultant solution was refluxed for an additional 4 h after which the ethanol was distilled off. The remaining solution was transferred to a 250 mL beaker and left overnight at room temperature. The precipitate was filtered by suction, washed with deionized water and dried in a desiccator over calcium chloride (yield 17.2 g; 63 %).

Synthesis of [Cu(AAAH)₂](OAc)₂: Acetoacetic acid hydrazide (3.48 g, 0.003 mol) dissolved in 10 mL methanol was added dropwisely to $Cu(OAc)_2 \cdot 4H_2O$ (2.99 g, 0.0015 mol) dissolved in methanol (30 mL, 40 %) with stirring on a magnetic stirrer. Ammonia was added to raise the pH to 9 to aid precipitation. The resulting mixture was left to stir for 1 h after which it was filtered by suction, washed with 40 % methanol and deionized water and dried over calcium chloride (yield 3.4 g 55 %). The other complexes of Co(II) and Cu(II) were similarly prepared.

Physical measurements: Microanalysis for carbon, hydrogen and nitrogen for the ligand and complexes were determined using a Perkin-Elmer 240C elemental analyzer. The percentage metal was determined using complexometric method[14]. Infrared spectra were recorded on a Nicolet Avatar

330 FT-IR spectrophotometer in nujol. Electronic reflectance spectra of the ligand and complexes in nujol were recorded using Genesys 10 scanning spectrophotometer (Thermo Electron Corporation).

Computational details: The Co(II) and Cu(II) complexes were modeled based on the spectroscopic interpretations which involved the O2 and N2 atoms (Fig. 1) forming coordinate bonds with metal ions using Spartan program (Spartan 06) implemented on an Intel Pentium M 2.0 GHz computer. Other possibilities involving O1 and N2 in ligand-metal bonds were considered. Three copper(II) complex ions and two cobalt(II) complex ions were modeled to determine their thermodynamic stability as shown in Fig. 1. The optimization and frequency calculation of both the Cu(II) complexes and Co(II) complexes were performed using both semi-empirical method (PM3) and DFT (B3LYP/6-31G*) DFT levels of calculations based on the preliminary stability study. Semi-emperical method (PM3) was considered along with DFT since PM3 have been successfully used either alone or with other theoretical methods for structural analysis of Cu(II) complexes[15-20]. Density functional theory (DFT) calculations were performed with the hybrid B3LYP exchange and correlation functional[21,22] and 6-31G(d) basis set. All calculations carried out both at PM3 and DFT levels are without symmetry restriction.
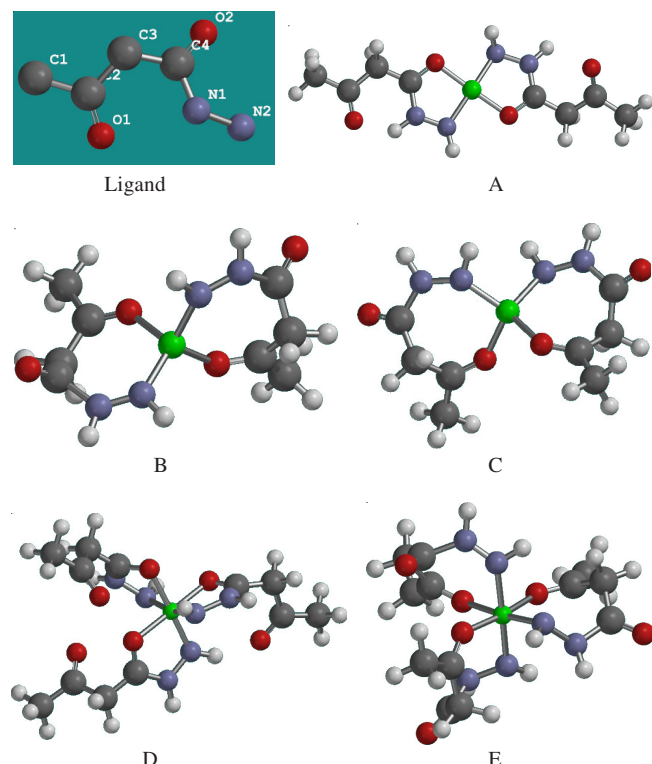

Fig. 1. Optimized structures of the ligand and complex ions: (A) = Cu(II) complex ion (square planar), (B) = Cu(II) complex ion (*trans-*), (C) = Cu(II) complex ion (*cis-*), (D) = Co(II) complex ion (octahedral) and (E) = Co(II) complex ion (bend octahedral)

RESULTS AND DISCUSSION

The formation of acetoacetic acid hydrazide proceeded generally in appreciable yields as shown in the following equations:

$$CH_3COCH_2COOR' + H_2NNH_2 \rightarrow CH_3COCH_2CONHNH_2 + R'OH$$
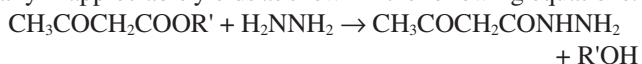
The reaction of the metal salts and the ligand to form complexes can be represented as:

$$MX_2 \cdot xH_2O + 2CH_3COCH_2CONHNH_2 \rightarrow M[CH_3COCH_2CONHNH_2]_2 + xH_2O$$
$$M = Co$$
$$MX_2 \cdot xH_2O + 2CH_3COCH_2CONHNH_2 \rightarrow M[CH_3COCH_2CONHNH_2]_2 + xH_2O$$
$$M = Cu$$

The analytical data for the ligand and complexes are presented in Table-1. The complexes were obtained in different shades of colours ranging from purple to green. The complexes obtained as solids display very poor solubility in protic and non-coordinating solvents; hence the single crystals X-ray diffraction studies of any of the compounds could not be studied.

Infrared spectra of ligand and complexes: The infrared spectra bands (Table-2) were assigned by critically comparing the spectra of the free ligand with those of the complexes. There are three major vibrations that have been used successfully to infer coordination of ligands to the metal in the spectra of complexes of hydrazides. These are the carbonyl stretching frequency $[\nu_s(C=O)]$ or the 'amide 1', the in-plane bending deformation and stretching frequency for cyanate $[\delta(N\text{-}H) + \nu_s(C\text{-}N)]$ or the 'amide II' and the amino stretching vibrations $\nu_s(NH_2)$. In the spectra of the acetoacetic acid hydrazide the absorption band observed at 1612 cm^{-1} is assigned to the $\nu(C=O)$, the carbonyl stretching mode called "amide 1". The band was also observed at 1614 and 1704 cm^{-1} from DFT and PM3 quantum mechanical calculations. These vibrations experienced a bathochromic shift on coordination to the Co(II) metal to 1570-1566 cm^{-1}. In the modeled Cobalt(II) complex ion the 'amide 1' band was observed between 1672-1600 and 1598-1552 cm^{-1} for PM3 and DFT calculations, respectively. The similar band for the Cu(II) complexes were experimentally observed between 1566-1563 cm^{-1}; 1645-1642 cm^{-1} for PM3 and 1584-1545 cm^{-1} for DFT calculations.

The "amide II" band was observed at 1544 cm^{-1} in the acetoacetic hydrazide ligand. This band was found at 1620 cm^{-1} for PM3 and 1540 cm^{-1} for DFT calculations, respectively. This band also experienced bathochromic shift on coordination to the metal between 1556-1507 and 1542-1507 cm^{-1} for the Co(II) and Cu(II) complexes studied, respectively[23-26]. The calculated 'amide II' for both the Co(II) and Cu(II) complexes were at 1608-1598 cm^{-1} for PM3 and 1535-1525 cm^{-1} for DFT, respectively.

This $\nu(N\text{-}H)$ stretching frequency of the amino observed at 3539 cm^{-1} on coordination was lowered to between 3345-3199 cm^{-1} for the Co(II) complexes while for the Cu(II) complexes the bands were observed between 3357-3278 cm^{-1}. The observed values are consistent with previous studies[23-26]. The calculated values of $\nu(N\text{-}H)$ for the Co(II) and Cu(II) complexes appear at 3383-3196 and 3427-3264 cm^{-1} for PM3 and 3456-3257 and 3498-3321 cm^{-1} for DFT, respectively. Although the vibrational frequencies calculated at DFT are closer to the experimentally determined values especially for amide I and amide II, the PM3 calculated IR followed quantitatively the same trend as the experimentally observed ones (Table-2). In addition, only the IR data calculated for Cu(II) and Co(II) complex ions involving the O2 and N2 atoms of

TABLE-1
ANALYTICAL DATA OF LIGAND AND Co(II) AND Cu(II) COMPLEXES

Compound	Colour	Yield (%)	μ_{eff} (BM)	m.p. (ºC)	Metal observed (calcd.) (%)			
					M	C	H	N
AAAH	White	63	–	217-219	–	41.22 (41.37)	6.86 (6.94)	23.68 (24.13)
Co[AAAH]$_3$(OAc)$_2$	Purple	61	5.24	194	11.07 (11.22)	36.42 (36.58)	5.68 (5.76)	16.22 (16.00)
Co[AAAH]$_3$Cl$_2$	Purple	76	5.23	162	12.39 (12.32)	30.62 (30.13)	4.89 (5.06)	17.55 (17.57)
Co[AAAH]$_3$SO$_4$	Purple	60	5.17	192	11.37 (11.71)	28.88 (28.63)	4.80 (4.81)	16.50 (16.70)
Co[AAAH]$_3$(NO$_3$)$_2$	Purple	60	5.54	210	11.05 (11.09)	27.33 (27.13)	4.55 (4.55)	21.00 (21.09)
Cu[AAAH]$_2$(OAc)$_2$	Dirty-green	55	1.54	146	15.00 (15.35)	34.62 (34.83)	4.57 (5.36)	13.65 (13.54)
Cu[AAAH]$_2$Cl$_2$	Dirty-green	75	1.76	154	17.61 (17.32)	26.49 (26.20)	4.69 (4.40)	15.41 (15.28)
Cu[AAAH]$_2$SO$_4$	Dirty-green	68	1.79	142	15.93 (16.22)	24.23 (24.53)	4.28 (4.12)	13.95 (14.30)
Cu[AAAH]$_2$(NO$_3$)$_2$	Dirty-green	53	1.77	178	15.33 (15.14)	22.69 (22.89)	3.74 (3.84)	20.00 (20.02)

TABLE-2
RELEVANT EXPERIMENTAL AND CALCULATED INFRARED SPECTRAL
BANDS (cm^{-1}) OF LIGAND AND Co(II) AND Cu(II) COMPLEXES (cm^{-1})

Compound		Amide I	Amide II	ν(N-H)	ν(C=O)	ν(C-H)
AAAH		1612(m)	1544(w)	3539(w)	1782(m)	2939(w)
Co(AAAH)$_3$Cl$_2$		1570(s)	1514(w)	3333(w)	1724(s)	2913(w)
Co(AAAH)$_3$(OAc)$_2$		1570(s)	1514(w)	3290(w)	1708(m)	2919(w)
Co(AAAH)$_3$SO$_4$		1570(s)	1556(w)	3199(w)	1712(s)	2925(w)
Co(AAAH)$_3$(NO$_3$)$_2$		1566(m)	1507(w)	3345(w)	1700(s)	2900(w)
Cu(AAAH)$_2$Cl$_2$		1563(m)	1542(s)	3247(m)	1697(m)	2913(w)
Cu(AAAH)$_2$(OAc)$_2$		1563(m)	1542(w)	3357(w)	1731(m)	2913(w)
Cu(AAAH)$_2$SO$_4$		1563(m)	–	3278(w)	1703(m)	2960(w)
Cu(AAAH)$_2$(NO$_3$)$_2$		1566(m)	1507(m)	3345(w)	1700(w)	–
AAAH	PM3	1704	1620	3385, 3350, 3350	1964	3089, 3080, 2944
	DFT	1614	1540	3467, 3365, 3235	1778	3256, 3167, 3051
Co(AAAH)$_3$$^{2+}$	PM3	1672, 1610, 1600	1608, 1601, 1598	3383, 3377, 3326, 3312, 3196	1960, 1939, 1931	3063, 3013, 3008, 2933, 2931
	DFT	1598, 1557, 1552	1535, 1532, 1525	3456, 3426, 3367, 3257	1742, 1740, 1732	3256, 3241, 3172, 2998
Cu(AAAH)$_2$$^{2+}$	PM3	1642, 1645	1586, 1508	3427, 3422, 3264	1959, 1932	3070, 3069, 3065, 2913, 2964, 2913
	DFT	1584, 1560	1532, 1523	3498, 3364, 3321	1739, 1736	3257, 3232, 2968, 2962

the ligand formed coordinate bonds with the metal ions (*i.e.*, complex A and complex D) which, are also in agreement with the experimental observations.

Structural features: The formation of both Cu(II) and Co(II) complex ions involving the O2 and N2 atoms of the ligand are thermodynamically and energetically favoured in forming coordinate bonds with the metal ions (*i.e.*, complexes A and D) over those involving O1 and N2 atoms of the ligand (*i.e.*, complexes B, C and E) as shown in Table-3. This is also in agreement with the experimentally predicted structures from spectroscopic data. Therefore, the selected geometric parameters of the most thermodynamically stable Cu(II) and Co(II) complex ions calculated at both semi-empirical (PM3) and DFT levels are displayed in Table-4.

The structural parameters calculated at semi-empirical (PM3) were quite different from those obtained at DFT. For instance, Cu-O1 (Cu-N1) bond lengths are 1.830 Å (1.847 Å) and 1.842 Å (1.845 Å) for PM3 and DFT, respectively. The Co-O1 (Co-N1) bond lengths are 1.915 Å (1.926 Å) and 1.860 Å (1.857 Å) for PM3 and DFT, respectively. Also, the bond angles calculated at PM3 are slightly different from those calculated at DFT level (Table-4). Generally, both PM3 and DFT methods showed that M-O and M-N calculated for Cu(II) complex ion are shorter than that of Co(II) complex ion. However, based on the infrared data that showed close correlation between experimentally observed values and DFT calculations, the structural data calculated at DFT are expected to be closer to the experimental values than that of PM3.

TABLE-3
CALCULATED RELATIVE ENERGIES (REL. E), HOMO, LUMO AND DIPOLE
MOMENT AT SEMI-EMPIRICAL (PM3) AND B3LYP/6-31G* LEVELS

	Cu(II) complex ions			Co(II) complex ions	
	Sq-planar	*Trans*	*Cis*	Nor. Octah.	Bend Octah.
Rel. E	0.00 (0.00)*	122.06 (165.54)	87.34 (114.20)	0.00 (0.00)	179.02 (270.77)
H (eV)	-12.80 (-16.06)	-12.82 (-16.10)	-12.31 (-16.82)	-12.46 (-15.98)	-12.53 (-15.06)
L (eV)	-7.57 (-9.13)	-7.68 (-9.53)	-7.09 (-8.83)	-7.44 (-9.58)	-7.56 (-9.76)
Δ(H-L) eV	5.23 (6.93)	5.14 (6.57)	5.22 (7.99)	5.02 (6.40)	4.97 (5.30)
D.M (debye)	3.54 (4.98)	6.67 (9.24)	3.21 (3.65)	3.55 (4.97)	7.32 (10.19)
*PM3 values in bracket. Relative energies (Rel. E), HOMO (H), LUMO (L) and dipole moment (DM).					

TABLE-4
SELECTED GEOMETRICAL PARAMETERS OF MOST STABLE Cu(II)
AND Co(II) COMPLEX IONS CALCULATED AT PM3 AND B3LYP/6-31G* LEVELS

Cu(II) complex ion			Co(II) complex ion		
Bond length (Å)	PM3	DFT	Bond length (Å)	PM3	DFT
Cu-O1	1.830	1.842	Co-O1	1.915	1.926
Cu-O2	1.851	1.855	Co-O2	1.922	1.967
Cu-N1	1.847	1.845	Co-O3	1.917	1.922
Cu-N2	1.840	1.843	Co-N1	1.860	1.857
Bond angle (Å)			Co-N2	1.852	1.865
O1-Cu-O2	175.75	176.80	Co-N3	1.820	1.821
O1-Cu-N1	89.84	86.07	Bond angle (Å)		
O1-Cu-N2	90.88	92.34	O1-Co-O2	88.09	89.98
O2-Cu-N1	91.22	90.89	O1-Co-O3	179.66	177.35
O2-Cu-N2	88.50	89.65	O1-Co-N1	86.97	87.05
N1-Cu-N2	173.91	172.87	O1-Co-N2	88.08	89.22
–	–	–	O1-Co-N3	93.27	92.95
–	–	–	O2-Co-N1	83.78	86.11
–	–	–	O2-Co-N2	83.56	82.90
–	–	–	O2-Co-N3	178.47	177.66
–	–	–	O3-Co-N1	93.14	91.26
–	–	–	O3-Co-N2	91.74	90.65
–	–	–	O3-Co-N3	87.04	89.03
–	–	–	N1-Co-N2	166.55	170.42
–	–	–	N1-Co-N3	95.59	92.09
–	–	–	N2-Co-N3	97.70	100.22

The Frontier molecular orbitals for the complex (A) and (D) computed at the DFT level are shown in Fig. 2. The HOMO and the LUMO of Cu(AAAH)$_2$$^{2+}$ ion are mainly localized on carbonyl and amide II regions of the ligand, respectively, while both the HOMO and LUMO of the Co(AAAH)$_3$$^{2+}$ ion localized around the central metal ions (Fig. 2). The Mulliken atomic charges for copper, cobalt, oxygen and nitrogen atoms are displayed in Table-5. The Mulliken charges of copper and cobalt atoms are -0.429 and -0.226, respectively. In both Cu(AAAH)$_2$$^{2+}$ and Co(AAAH)$_3$$^{2+}$ ions, lower values of Mulliken charges on nitrogen and oxygen atoms that are directly bonded to the central metal ion was observed. This was an evident that charges are transferred from ligand to the central metal ion during complex formation.
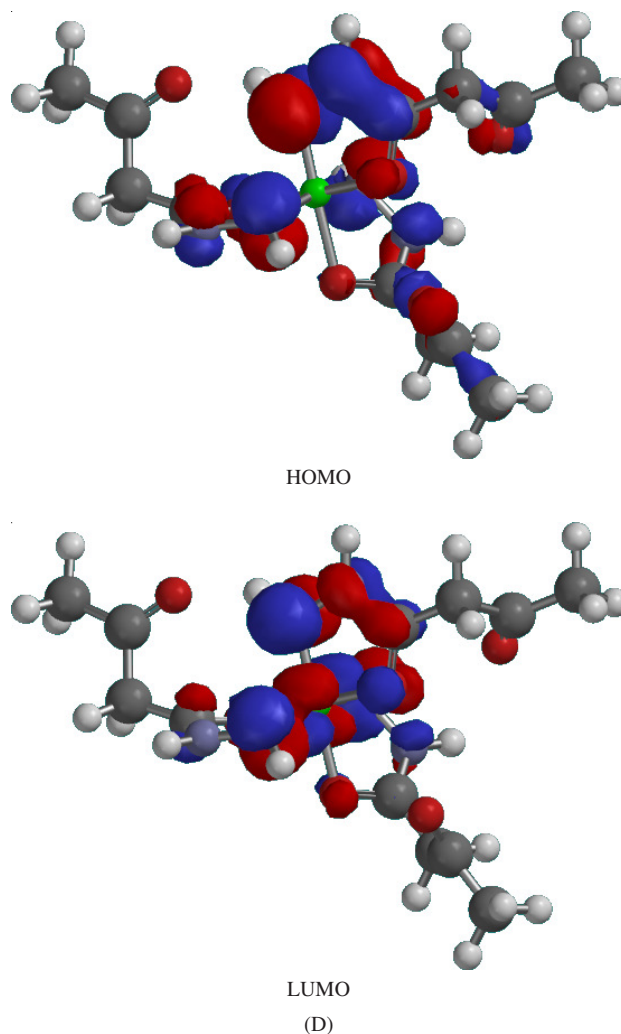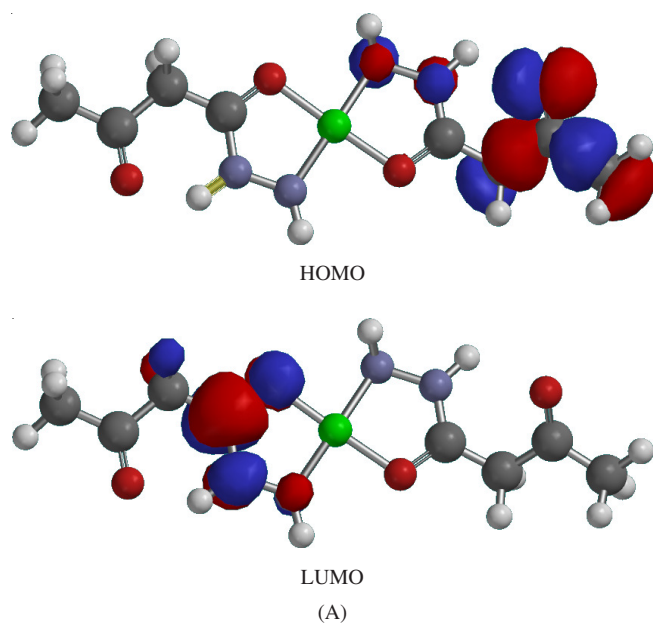
HOMO

HOMO

(A)

LUMO

LUMO

(D)

Fig. 2.   Frontier molecular orbital: HOMO and LUMO of the Cu(AAAH)$_2$$^{2+}$
(A) and Co(AAAH)$_3$$^{2+}$ (D) ions

TABLE-5
MULLIKEN CHARGES OF THE COMPLEX A AND D IONS

Atom	Complex A	Complex D
N1	0.246	0.024
*N2	0.029	0.156
N3	0240	0.146
*N4	0.150	0.042
N5	–	0.171
*N6	–	0.131
*O1	-0.004	-0.235
*O2	-0.069	-0.257
*O3	–	-0.139
aO4	-0.348	-0.385
aO5	-0.371	-0.310
aO6	–	-0.345
M	-0.429	-0.226

*Atoms bonded to metal ion, acarbonyl oxygen atom.

Electronic spectra: The electronic reflectance spectra of the ligand and complexes are presented in Table-6. In the ultraviolet spectra of the acetoacetic acid hydrazide, the $n \rightarrow \pi^*$ transition observed at 51,282 cm^{-1} attributed to the excitation of a nitrogen lone pair of electron to the antibonding σ^* orbital of the amino group was shifted to 48,077-51,020 cm^{-1} in the spectra of the complexes. The $\pi \rightarrow \pi^*$ transition in the carbonyl group observed at 37,175 cm^{-1} in the ligand also experienced bathochromic shifts to *ca.* 36,496 cm^{-1} upon complexation in all the compounds. An additional band observed in the ultraviolet spectra of the complexes between 31,646-33,223 cm^{-1} was attributed to $\pi \rightarrow \pi^*$ transition. The charge transfer transitions were observed at 23,256-29,497 cm^{-1} in the complexes[12,13,23-26].

In the visible spectra of octahedral cobalt(II) complexes, three electronic transitions; $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ which is represented by ν_1, ν_2 and ν_3, respectively[27]. The experimentally observed transitions are Co[AAAH]$_3$(OAc)$_2$ with transitions at 9,434 and 20,284 cm^{-1} was assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$, respectively. The Co[AAAH]$_3$Cl$_2$, Co[AAAH]$_3$(NO$_3$)$_2$ and Co[AAAH]$_3$SO$_4$ complexes had only one observable $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions at the absorption peaks 17,241, 18,767 and 20,408 cm^{-1}, respectively.

The electronic reflectance spectra of the copper(II) complexes displays broad bands at 13,699-16,155 cm^{-1}. These bands observed in the spectra of the Cu(II) complexes are assignable to $^2T_2 \rightarrow {}^2E$ transitions which is consistent with a square planar geometry[28].

Magnetic moment: The Co(II) complexes studied display effective magnetic moments (μ_{eff}) between 5.17-5.54 BM. Cobalt(II) complexes in octahedral environments have observed magnetic moments around 4.8-5.2 BM at room temperature[29], which favourably compare with those of the acetoacetate complexes studied. The copper(II) complexes display the effective magnetic moments (μ_{eff}) in the range 1.76-1.79 BM except Cu[AAAH]$_2$(OAc)$_2$ with 1.54 BM. Most of the copper(II) complexes agrees with the spin-only value ($\mu_{s.o}$) of 1.73 BM. In the Cu[AAAH]$_2$(OAc)$_2$ complex, a reduction in the (μ_{eff}) to 1.54 BM from the spin-only value of 1.73 BM observed can be attributed to strong Cu-Cu interactions in the crystal lattice of the compound[29].

The experimental data thus obtained are consistent with the following structures of the complexes (Fig. 3).

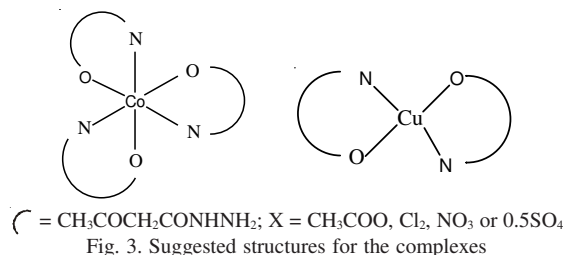⌒ = CH$_3$COCH$_2$CONHNH$_2$; X = CH$_3$COO, Cl$_2$, NO$_3$ or 0.5SO$_4$
Fig. 3. Suggested structures for the complexes

Conclusion

The elemental and spectroscopic studies revealed that the cobalt(II) ions are in an octahedral environment while the copper(II) metal complexes adopt a square planar geometry. This is further supported by the room temperature magnetic susceptibility measurements and the quantum chemical studies employed using semi-empirical PM3 and density functional theory (DFT) methods. The DFT method appears to compare favourably well with spectra interpretations obtained from the experimental work while the PM3 though slightly different also point to the same trend observed with DFT in both the spectral and structural features obtained.

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TABLE-6
ELECTRONIC SPECTRAL TRANSITIONS FOR THE LIGAND AND COMPLEXES (cm^{-1})

Compound	d-d	CT	Intra ligand transitions
AAAH	–	–	51,282; 37,175
Co(AAAH)$_3$(OAc)$_2$	20,284; 9,434	29,497; 27,855	50,251; 47,393; 36,496; 31,646
Co(AAAH)$_3$Cl$_2$	17,241	–	–
Co(AAAH)$_3$SO$_4$	20,408	–	51,020; 47,393; 31,646
Co(AAAH)$_3$(NO$_3$)$_2$	18,767	28,653	48,077; 45,455; 31,646
Cu(AAAH)$_2$(OAc)$_2$	15,060	–	48,077; 38,168; 36,496
Cu(AAAH)$_2$Cl$_2$	13,699	–	–
Cu(AAAH)$_2$SO$_4$	14,286	–	–
Cu(AAAH)$_2$(NO$_3$)$_2$	16,155	23,256	50,251; 36,496; 33,223

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