

Magnetic And Thermal Properties of Mixed-Metal Complex (Cu-Co) With N-O Donor Ligand

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ABSTRACT

A Schiff base derived from 2,4-dihydroxybenzaldehyde and 1,8-diaminooctane reacted with copper (II) acetate to form $[\text{Cu}(\text{CH}_3\text{COO})_2]\cdot\text{H}_2\text{O}$ (1), with cobalt(II) acetate to form $[\text{Co}(\text{CH}_3\text{COO})_2]\cdot 4\text{H}_2\text{O}$ (2) and lastly with an equimolar mixture of copper(II) acetate and cobalt(II) acetate to form a mixed-metal complex (3) with the formula $[\text{CoCu}(\text{CH}_3\text{COO})_2(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4)(\text{H}_2\text{O})]$. The ligand and the complexes were characterized by ¹H-NMR, elemental analysis, FTIR, UV-Vis spectroscopy and magnetic measurements. TGA indicates that the complexes was thermally stable up to 268 °C and the room-temperature effective magnetic moment were 1.89 B.M (1), 6.13 B.M (2) and 4.9 B.M (3) respectively, indicating that all complexes were paramagnetic.

Keyword Mixed-Metal complex, Schiff base, Magnetic properties, Thermal Properties.

1. INTRODUCTION

Salicyldiimine Schiff bases metal complexes magnetic properties has been an exciting field of research in the materials science discipline. The multiplicity of variety in applications of the Schiff base ligand make it a very popular ligand selection besides having considerable stability and uncomplicated synthesis pathway[1]. A wide variety of magnetic phenomenon have been reported for transition metal complexes ranging from ferromagnetic, antiferromagnetic, ferrimagnetic, spin-crossover and spin canting. The study of magnetism on mixed-metal complexes involving Cu and Co were less explored due to the nature of low-spin cobalt(III) being diamagnetic. Cu(II) and Co(II) complexes are well suited for magnetic evaluation however cobalt(II) tend to be harder to stabilize in the presence of N-donor ligand. Nevertheless, there has been cobalt(II) complexes with magnetic behaviour recently reported[2]. Most of the recent works reported were on same metal dinuclear complexes or mixed ligands metal complexes with magnetic properties[3]. Thus there is a need to study the effect of having a mixed-metal centres on a metal complex magnetic behaviour especially between Cu-Co dinuclear complex as it is rarely being reported[4].

In this present study, we have successfully synthesized a mixed-metal Cu(II) and Co(II) complexes along with individual Cu(II) and Co(II) complexes respectively with N-O donor ligand for comparison. The complexes has been fully characterized by elemental and spectral analyses. The magnetic study property of each complex has also been well investigated.

2. MATERIALS AND METHODS

2.1 Materials

All reagents were purchased from commercial sources and used without further purification. FTIR spectra were recorded over a range of region $4000\text{--}450\text{ cm}^{-1}$ on a Perkin-Elmer Frontier FT-IR spectrometer equipped with a diamond-attenuated total reflectance attachment. The elemental analyses (carbon, hydrogen and nitrogen) data were obtained from Series II CHNS/O analyser 2400 of Perkin Elmer. The electronic spectra were recorded on Shimadzu UV-Vis-NIR 3600 spectrophotometer, using 1 cm quartz cells. Solid state spectra were obtained using the reflectance attachment of the same instrument and employing BaSO_4 as a standard. The Thermogravimetric analysis (TGA) were recorded from $50\text{--}900\text{ }^\circ\text{C}$ on Pyris Diamond /DTA Perkin Elmer instrument with scan rate of $20\text{ }^\circ\text{C min}^{-1}$ under constant nitrogen gas flow of 20 ml min^{-1} , while the magnetic moment were determined using a Sherwood Scientific magnetic susceptibility balance at room temperature. 2,2'-[Octane-1,8-diylbis(nitrilomethylidene)]diphenol ($\text{H}_2\text{L1}$) ligand was synthesised and characterised as previously reported [5].

2.2 Synthesis of metal complexes

2.2.1 $[\text{Cu}(\text{L1})_2]\cdot\text{H}_2\text{O}$ (1)

A mixture of 1,8-diaminooctane (0.3139 g; 2.18 mmol), 2-hydroxybenzaldehyde (0.50 g; 4.10 mmol) in ethanol (200 mL), and a few drop glacial acetic acid (catalyst) was refluxed for 1 hour. Copper(II) acetate monohydrate (0.8369 g; 4.20 mmol) was dissolved in a small amount of hot ethanol, and the solution was added portionwise and the hot reaction mixture, which was then refluxed for another 3 hours. The khaki-green powder formed was filtered off from the hot reaction and dried in an oven overnight. The yield was 0.8883 g (69.9%).

2.2.2 $[\text{Co}_2(\text{CH}_3\text{COO})_2(\text{L1})_2]\cdot 2\text{H}_2\text{O}$ (2)

The complex was similarly synthesized as for copper complex (Section 2.2.1), using 1,8-diaminooctane (0.3129 g; 2.17 mmol), 2-hydroxybenzaldehyde (0.5 mL; 4.10 mmol) and cobalt(II) acetate tetrahydrate (1.0533 g; 4.23 mmol). The product was a brown powder, and its yield was 0.7340 g (56.2%).

2.2.3 $[\text{CuCo}(\text{CH}_3\text{COO})_2(\text{HL1})_2(\text{H}_2\text{O})]$ (3)

The complex was similarly synthesized as for copper complex (Section 2.2.1), using 1,8-diaminooctane (0.3177 g; 2.1 mmol) and 2-hydroxybenzaldehyde (0.5126 g; 4.2 mmol), copper(II) acetate monohydrate (0.4280 g; 2.1 mmol) and cobalt(II) acetate tetrahydrate (0.5277 g; 2.1 mmol). The product was a dark brown powder, and its yield was 0.7590 g (75.2%).

3. RESULTS AND DISCUSSIONS

3.1 Structural deduction

All complexes were synthesised using one-pot reaction from the reaction of $\text{H}_2\text{N}(\text{CH}_2)_8\text{NH}_2$ and 2-hydroxybenzaldehyde with $[\text{Cu}(\text{CH}_3\text{COO})_2]\cdot\text{H}_2\text{O}$ to form (1), with $[\text{Co}(\text{CH}_3\text{COO})_2]\cdot 4\text{H}_2\text{O}$ to form (2), while with $[\text{Cu}(\text{CH}_3\text{COO})_2]\cdot\text{H}_2\text{O}$ and $[\text{Co}(\text{CH}_3\text{COO})_2]\cdot 4\text{H}_2\text{O}$ to form (3) in ethanol. The products were khaki green powder (1 and 3) and dark brown powder (2), respectively.

The structure of metal complexes were deduced from combined results of the elemental analyses, FTIR and UV-visible spectroscopies.

The results from the elemental analyses of complexes were in good agreement with the proposed chemical formula $\text{Cu}_2\text{C}_{44}\text{H}_{54}\text{N}_4\text{O}_5$ (846.02 g mol^{-1}) (1), $\text{Co}_2\text{C}_{26}\text{H}_{36}\text{N}_2\text{O}_8$ (622.44 g mol^{-1}) (2) and $\text{CuCoC}_{48}\text{H}_{62}\text{N}_4\text{O}_9$ (961.51 g mol^{-1}) (3). The result suggest that 1 are formed in 1:1 (L:M) ration, while 2 and 3 were formed in 1:2 (L:M) ratio.

The IR spectra of the metal complexes were recorded and compared with data reported for ligand $\text{H}_2\text{L1}$ [5]. The IR spectral of $\text{H}_2\text{L1}$ shows a strong peak of $\text{C}=\text{N}$ at 1630 cm^{-1} and for metal complexes at $(1596, 1620)\text{ cm}^{-1}$. The $\text{C}=\text{N}$ peak for metal complexes were shifted to a lower wavenumber compared to $\text{H}_2\text{L1}$ indicating coordination of the azomethine nitrogen to Cu(II) atom [6]. The spectra in metal complexes also shows the disappearances of OH stretching which indicating coordination of O to metal ions. The band at $(1536, 1538)\text{ cm}^{-1}$ and $(1442, 1446)\text{ cm}^{-1}$ were attributed to COO_{asym} , and COO_{sym} , respectively. The difference value (Δ) were $(94, 92)\text{ cm}^{-1}$, suggesting a chelating binding mode for COO - ligand.

Table 1 Physical properties and analytical data of complexes

Complex	Yield (%)	Elemental Analysis % Found (Calc.)			λ_{\max} (nm)
		C	H	N	
1	70	62.5 (62.5)	6.0 (6.4)	6.8 (6.6)	678
2	56	49.3 (50.2)	5.5 (5.8)	4.8 (4.5)	608
3	75	60.0 (60.0)	6.2 (6.5)	5.7 (5.8)	640, 461

Table 2 IR spectral data of metal complexes

Complex	ν (-OH)	ν (-CH ₂)	ν (HC=N)	ν (-COO)	Reference
H ₂ L1	-	2919, 2849	1630	-	[5]
1	-	2921, 2851	1620	-	This work
2	3246	2921, 2853	1596	1536, 1442	This work
3	3377	2921, 2851	1620	1538, 1446	This work

The UV-visible spectrum of complex 1 was recorded in THF. The spectrum shows a broad d-d band at 679 nm ($\epsilon_{\max} = 75 \text{ M}^{-1} \text{ cm}^{-1}$) and a weak shoulder at 385 nm ($\epsilon_{\max} = 25 \text{ M}^{-1} \text{ cm}^{-1}$). These suggest a square pyramidal Cu(II) centre in the complex [7-8]. For complex 2, its UV-visible spectrum was recorded in chloroform. The spectrum shows a d-d band at 608 nm ($\epsilon_{\max} = 153 \text{ M}^{-1} \text{ cm}^{-1}$) and MLCT band at 364 nm ($\epsilon_{\max} = 2509 \text{ M}^{-1} \text{ cm}^{-1}$). The position of the d-d peak was similar to tetrahedral Co(II) complexes reported in the literature. An example is [Co(L)₂], where L = 3-methoxysalicylidene-p-aminoacetophenoneoxime ($\lambda_{\max} = 669 \text{ nm}$) [9-10]. Finally, for complex 3, its UV-visible spectrum was recorded in chloroform, shows d-d bands at 640 nm ($\epsilon_{\max} = 153 \text{ M}^{-1} \text{ cm}^{-1}$) and 461 nm ($\epsilon_{\max} = 545 \text{ M}^{-1} \text{ cm}^{-1}$), and MLCT bands at 369 nm ($\epsilon_{\max} = 5749 \text{ M}^{-1} \text{ cm}^{-1}$) and 307 nm ($\epsilon_{\max} = 5446 \text{ M}^{-1} \text{ cm}^{-1}$). These suggest a tetrahedral geometry at each Cu(II) and Co(II) centre for this complex.

Combining the above results, the proposed structural formula for Complex 1 is [Cu(L1)]₂.H₂O, Complex 2 is [Co₂(CH₃COO)₂(L1)].2H₂O and Complex 3 is [CuCo(CH₃COO)₂(HL1)₂(H₂O)]. The dimeric structure is similar with [Cu(Sal-5)]₂ reported by Nathan et al. [11-12], but differs from [Cu₂(L)(CH₃COO)₂].2H₂O (L was dianionic Schiff base formed from H₂N(CH₂)₉NH₂ and 2-HOC₆H₄CHO), reported by Abdullah et al. [13]. Hence, unlike the corresponding Cu(II) complex, complex 2 and 3 were dinuclear complexes with two CH₃COO⁻ and one L¹⁻ ions coordinated to Co(II) ion and/or Cu(II) ion.

3.2 Magnetic properties

Table 3 Magnetic moment values of metal complexes

Complex	Magnetic moment (B.M)
1	1.89
2	6.13
3	4.13

Its effective magnetic moment (μ_{eff}) was 1.89 BM at 298 K. The effective magnetic moment (μ_{eff}) value was calculated using the formula: $\mu_{\text{eff}} = 2.83[T(\chi_{\text{m}}^{\text{corr}} - N\alpha)]^{1/2}$. Table 2 shows μ_{eff} for complex 1 was 1.89 BM at 298 K. The calculated value is higher than expected spin-only value of 1.73 BM for a mononuclear Cu(II) complex ($S = 1/2$), indicating ferromagnetic interaction between Cu(II) centre [14]. For complex 2, its μ_{eff} value, was 6.13 BM at 298 K. This value is comparable to [Co₂(L)Cl₂(H₂O)₂], where L = 3-hydroxy-N-phenyl-but-2-enamidine ($\mu_{\text{eff}} = 5.97 \text{ BM}$ at room temperature), which also have two tetrahedral Co(II) centres [15]. Lastly for complex 3, its μ_{eff} value, was 4.13 B.M. This is lower than the expected value 5.60 B.M for 4 unpaired electron (1 unpaired electron from Cu(II) and 3 unpaired electron from Co(II)), suggesting a weak ferromagnetic interaction between Cu(II) and Co(II) centers.

3.3 Thermal properties

Complex 1 was thermally stable up to 268 °C. Its TGA trace shows an initial weight loss of 76.5% from about 268 °C to 900 °C, assigned to the decomposition of $L1^{2-}$ ion (calculated, 82.9%). The experimental value was lower than the expected value as the trace did not plateau out at temperatures above 900 °C due to incomplete decomposition of the organic ligand. Also, it is inferred that the lattice H_2O has evaporated before the thermal analysis was recorded since the trace does not show an initial loss below its decomposition temperature.

For complex 2, its TGA trace shows an initial weight loss of 4.8% from about 50 °C to 225 °C due to evaporation of lattice H_2O (calculated, 5.8%). The next weight loss of 72.0% from 247 °C to 623 °C is assigned to decomposition of $L1^{2-}$ and CH_3COO^- ions (calculated, 75.3%). The amount of residue at temperatures above 637 °C was 23.2%, which is in a good agreement with the calculated value of 24.1 %, assuming pure CoO [16-17]. Hence, Complex 2 was thermally stable up to 247 °C.

For complex 3, its TGA trace shows an initial weight loss of 1.8% from about 142 °C to 222 °C due to the evaporation of coordinated H_2O (calculated, 1.9%). The next weight loss of 79.3% from 222 °C to 676 °C is assigned to decomposition of two $HL1^-$ and two CH_3COO^- ions (calculated, 86.4%). The amount of residue at temperatures above 676 °C was 18.9%, which is in a good agreement with the calculated value of 16.1%, assuming pure CuO and CoO . Accordingly, the decomposition temperature for Complex 3 was 142 °C.

4. CONCLUSIONS

All complexes were paramagnetic. Complex 1 was dimeric while complex 2 and 3 were dinuclear. All complexes were thermally stable (142 °C. -268°C).

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