

Synthesis and characterization of new binuclear metal complexes from 2,2'-malonylbis(*N*-phenylhydrazine-1-carbothioamide)

Mona G. Farag, Ehab Abdel-Latif, Mohamed H. Abdel-Rhman, Ola A. El-Gammal

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

CONTACT: Ehab Abdel-Latif: ehabattia00@gmx.net

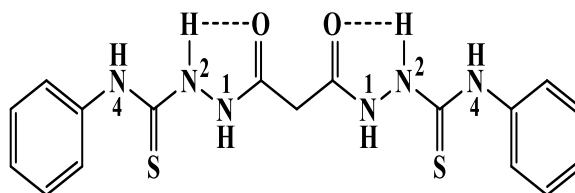
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Abstract: The bimetallic complexes of 2,2'-malonylbis(*N*-phenylhydrazine-1-carbothioamide) have been prepared and characterized via different spectral tools. The ligand can exist in keto-thio keto form and chelated to the metal ion in binate and neutral tetradentate manners as indicated by the infrared spectra. The electronic spectra and magnetic moment measurements showed that the Cu(II) complex has a square planar geometry while the Co(II) and Ni(II) have octahedral structure. The ESR spectrum of the Cu(II) complex confirmed the square planar configuration. Thermal gravimetric analysis (TGA) for the isolated complexes was performed to explain its thermal stability

keywords: Malonohydrazide, Phenyl isothiocyanate, Metal complexes, ESR spectra, TGA

1. Introduction

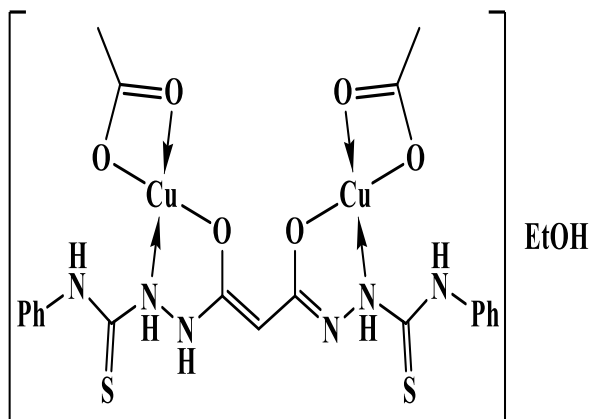
actively. The release of new absorption at 1947 cm^{-1} cleared the formation of intermolecular hydrogen bond between N^2H and carbonyl oxygen [25]. Furthermore, three new bands observed at 1564, 1473, 1268 and 873 cm^{-1} were assigned to the thioamide I, II, III and $\nu(\text{C}=\text{S})$ vibrations [26], respectively (Table 2). All this foundations with the lack of absorptions due to $\nu(\text{OH})$ and $\nu(\text{SH})$ vibrations suggested that the ligand exists in keto-thio keto form (Structure 1). The $^1\text{H-NMR}$ spectrum of the ligand H_4L , in DMSO-d_6 , exhibits three singlet signals at 10.34, 9.82 and 9.62 ppm corresponding to the protons of N^4H , N^2H and N^1H [24, 27], respectively. After addition of D_2O , the obtained spectrum clearly indicate that these three signals were disappeared. Thus, the appearance and disappearance of these signals confirmed the presence of the ligand in keto form. In addition, the doublet signal observed at 7.46 ppm were assigned to the protons at *ortho*-position of the phenyl rings, while the two triplet signals at 7.32 and 7.16 were attributed to those at *meta*- and *para*-positions, respectively [27, 28]. The singlet signal at 3.35 ppm was assigned to methylene group protons.



Structure 1. The suggested form of H_2L

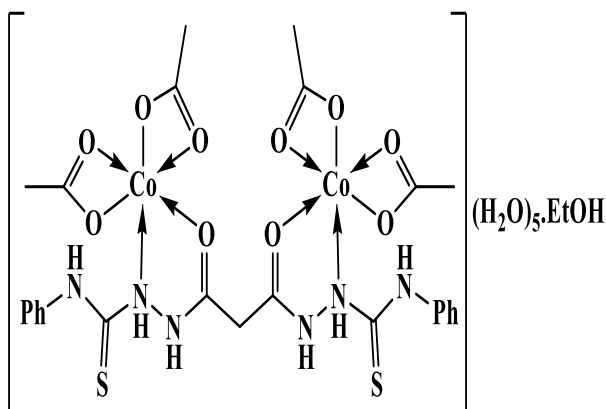
The complexes of Cu(II) and Ni(II) spectral data were quite similar. For instance, the Cu(II) complex exhibited vibrations bands at 3268, 3203 and 3143 cm^{-1} assigned to NH groups [29]. The overlapped bands in the range $1700\text{--}1500\text{ cm}^{-1}$ was resolved by deconvolution analysis and the data displayed bands at 1624, 1603 and 1592 cm^{-1} attributed to the new double bonds $\nu(\text{C}=\text{N})^*$ [30], $\nu(\text{C}=\text{C})_{\text{Alf}}$ [31], and $\nu(\text{C}=\text{C})_{\text{Ph}}$ [31], respectively. The appearance of former two bands endorsed the asymmetric enolization of the ligand. The splitting of the thioamide bands supported the asymmetric enol forms of the ligand (Table 2). The new bands, with respect to ligand spectral data, at 1649 and 1542 cm^{-1} were attributed to the $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ vibrations, respectively, for bidentate acetate ($\Delta\nu \approx 107\text{ cm}^{-1}$) [32, 33]. On contrary, the Ni(II) acetate complex showed the $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ vibration bands with difference 175 cm^{-1} revealing the ionic nature of the

acetate anion [32, 33]. Furthermore, the appearance of two new bands assigned to the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ at 578-582 and 482-468 cm^{-1} [29, 31], respectively, confirmed the enol form of the ligand and its coordination to metal ion in bidentate tetradentate fashion, through the enolized carbonyl oxygen and nitrogen of N^2H atoms (Structure 2).



Structure 2. The suggested structure of $[\text{Cu}_2(\text{H}_2\text{L})(\text{OAc})_2]\text{EtOH}$ complex.

The spectral data of the $\text{Co}(\text{II})$ complex exhibited absorptions at 3261, 3195 and 3147 cm^{-1} attributed to $\nu(\text{NH})$ groups [29]. Additionally, the $\nu(\text{C=O})$ band was shifted to lower wavenumber, 1669 cm^{-1} [23], while the $\nu(\text{C=S})$ bands appeared at 870 cm^{-1} [26], respectively. The $\nu(\text{M-O})$ in addition to $\nu(\text{M-N})$ bands were observed at 584 and 470 cm^{-1} [29, 31], respectively. The complex exhibited two new absorptions at 1613 and 1523 cm^{-1} due to the bidentate acetate vibrations (difference $\approx 90 \text{ cm}^{-1}$) [32, 33]. Hence, the ligand occurred in keto-thione form and the shift in both carbonyl and N^2H vibration bands revealed their participation in coordination as neutral tetradentate (Structure 3).



Structure 3. The suggested structure of $[\text{Co}_2(\text{H}_4\text{L})(\text{OAc})_4](\text{H}_2\text{O})_5.\text{EtOH}$ complex

Table 2. IR absorptions of the ligand and its complexes.

Vibration	H_4L	Complex		
		$\text{Cu}(\text{II})$	$\text{Co}(\text{II})$	$\text{Ni}(\text{II})$
$\nu(\text{OH})_{\text{solvent}}$	-	3454	3417	3430
$\nu(\text{N}^4\text{H})$	3315	3268	3261	(3270)
$\nu(\text{N}^2\text{H})$	3243, 3205	3203	3195	(3204)
$\nu(\text{N}^1\text{H})$	3147	3143	3147	(3129)
$\nu(\text{CH})_{\text{Ph}}$	3047	3027	3060	3056
$\nu(\text{CH}_2)$	2969	2971	2975	2935
$\nu(\text{OAc})$	-	(1649),(1542)	(1613), (1523)	(1657), (1483)
$\nu(\text{C=O})$	1675	-	(1669)	-
$\nu(\text{C=N})^*$	-	(1624)	-	(1649)
$\nu(\text{C=C})_{\text{Ph}}$	1604	(1603)	(1597)	(1598)
Thioamide I	1564	(1563), (1530)	(1554)	(1572), (1541)
Thioamide II	1473	1456, 1417	(1493), (1458)	(1449)
Thioamide III	1268	1257, 1220	1222	1261, 1228
$\nu(\text{N-N})$	1181	1155, 1128	1159	1155, 1122
$\nu(\text{C-O})$	1073	1067, 1047	1074, 1039	1074, 1025
$\nu(\text{C=S})$	872	885	870	887
$\rho(\text{NH})$	748	778, 752	754	781, 750
$\nu(\text{M-O})$	-	578	584	582, 532
$\nu(\text{M-N})$	-	482, 443	470	468

Values between brackets obtained from deconvolution analysis

3.3. Electronic spectra and magnetic moments

The ligand's electronic spectrum, in DMF, displayed bands at 34250 and 32895 cm^{-1} indorsed to $\pi \rightarrow \pi^*$ transition of phenyl rings and both of C=O and C=S groups [27], respectively. Moreover, the shoulder observed at 25640 cm^{-1} due to $n \rightarrow \pi^*$ transition of thione and keto groups [27], respectively. The $[\text{Cu}_2(\text{H}_2\text{L})(\text{OAc})_2]\text{EtOH}$ complex recorded in DMF displayed a wide band at 34250 cm^{-1} with a shoulder at 32050 cm^{-1} ascribed to $\pi \rightarrow \pi^*$ transition of phenyl rings in addition to carbonyl and thiocarbonyl groups [27], respectively. The new shoulder at 23700 cm^{-1} was assigned LMCT [34, 35] while it was observed at 20920 cm^{-1} in Nujol mull. Furthermore, the two new bands at 14580 and 13090 cm^{-1} , in DMF, and at 14245 and 12990 cm^{-1} , in Nujol, and were attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transitions of the square planar structure around $\text{Cu}(\text{II})$ ions [34, 35] (Fig. 1). Also, the complex showed subnormal magnetic moment value, 1.43 B.M., which indicated $\text{Cu}(\text{II})$ - $\text{Cu}(\text{II})$ interaction [35]. The $\text{Co}(\text{II})$

complex in DMF exhibited bands at 18795-19050 and 15480-15750 cm^{-1} endorsed to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{P})$ (ν_2) transitions, respectively, of octahedral configuration around the metal ions [34]. Moreover, the Nujol spectrum presented the d-d and the LMCT bands at more or less the same wavenumber confirming the suggested octahedral configuration of the complex [29, 30] (Table 3). The spectral data were employed to estimate the ν_1 , B and 10Dq, and were 7375, 847, 8470 cm^{-1} that confirming the proposed structure [24, 34]. The Co(II) complex exhibited magnetic moment values 5.49 B.M., with small deviation from standard values of octahedral geometry, 4.3-5.2 B.M., which may attributed to the presence of metal-metal interaction [36]

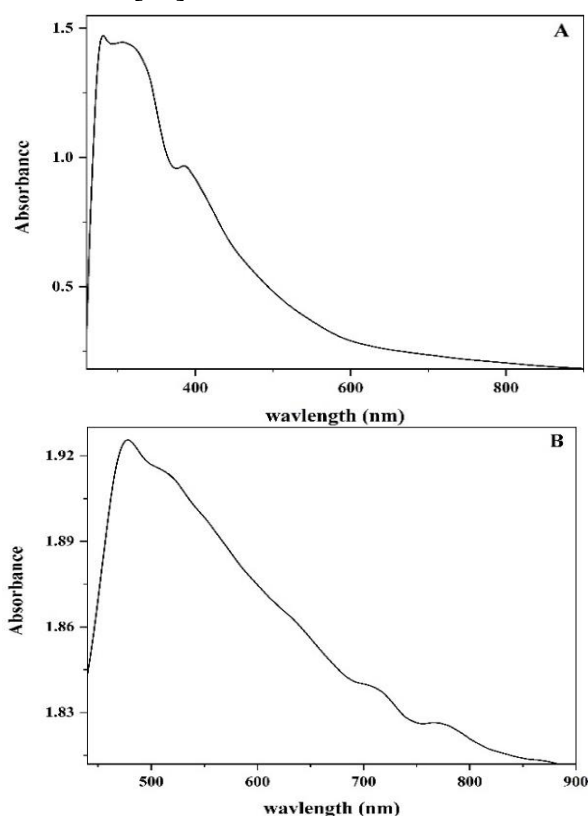


Fig 1. Electronic spectra of Cu(II) complex in DMF (A) and Nujol mull (B). Finally, the Ni(II) complex, in DMF, displayed band at 34245 with a shoulder observed at 31645 cm^{-1} ascribed to $\pi \rightarrow \pi^*$ of the phenyl rings and the keto-thione groups [27], respectively. In addition, the band displayed at 28410 cm^{-1} with a shoulders at 24750 cm^{-1} were assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) [34] and $n \rightarrow \pi^*$ of the keto-thione groups [27], respectively. The bands at 17125 and 13625 cm^{-1} were due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2), and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1)

transitions of octahedral Ni(II) [34]. The spectrum in Nujol exhibited the d-d and LMCT transitions at more or less the same wavenumber confirming the suggested octahedral structure [29, 30] (Table 3). Using the values of ν_2 and ν_1 transitions, the ligand field parameters, B and 10Dq, of the d^8 -system and ν_3 were estimated. The obtained data were B = 931, 10Dq = 13630 and $\nu_3 = 28550 \text{ cm}^{-1}$, confirming octahedral structure [24, 34]. Furthermore, the magnetic moment value was found 2.77 B.M., respectively, showing small deviation from the standard values of the octahedral geometry (2.9-3.3 BM) [34] which may attributed to the presence of metal-metal interaction

3.4. ESR spectra of Cu(II) complex

The Cu(II) complexes that have either octahedral, square pyramidal or square planar geometries showed $d_{x^2-y^2}$ ground state with ${}^2\text{B}_{1g}$ ground term. In ESR spectra, when the g-tensors are $g_{\parallel} > g_{\perp} > 2.0023$, the ${}^2\text{B}_{1g}$ is the ground state, while ${}^2\text{A}_{1g}$ ground state is proposed when $g_{\perp} > g_{\parallel} > 2.0023$ [37]. The solid-state ESR spectrum of $[\text{Cu}_2(\text{H}_2\text{L})(\text{OAc})_2]\text{EtOH}$ complexes exhibited g-tensor values at $g_{\parallel} = 2.121$ and $g_{\perp} = 2.070$, respectively (Fig. 2), and thus its ground state is $d_{x^2-y^2}$, corresponding to octahedral or square planar geometry [38]. Moreover, the covalent character of metal-ligand bonds were suggested as g_{\parallel} was less than 2.3 [39]. The axial symmetry parameter, G, describe the metal-metal interaction occurred in solid state where $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$. A small interaction is suggested when $G > 4$, while significant one is proposed when $G < 4$. The obtained G value, 1.75, signifying considerable interaction [40]

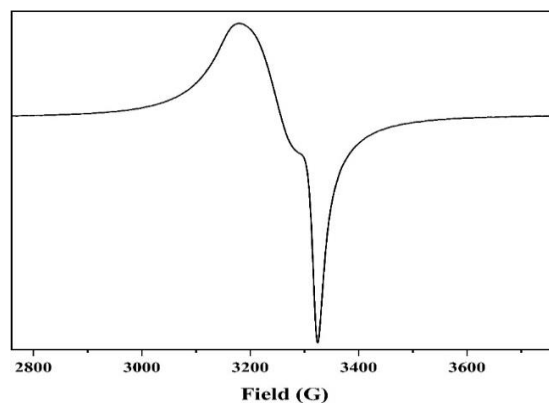


Fig2. ESR spectra of $[\text{Cu}_2(\text{H}_2\text{L})(\text{OAc})_2]\text{EtOH}$ (B) complexes

3.5. Thermal analyses

To illuminate thermal stability of the complexes, thermogravimetric analysis (TGA) was carried out. The TG curve of the ligand showed four consecutive decomposition stages. The first stage was observed at 40-247 °C with weight loss 37.92% corresponding to loss of two phenyl rings (38.31%). The second step started from 248 to 367 °C matching to loss of two HCNS fragments (Found 29.09; Calcd. 29.36%). The other two stages were extended over 367-650 °C leading to a residue at 650 °C of C₃H₂ (Found 9.63; Calcd. 9.45%) (Table 4).

The TG curve of [Cu₂(H₂L)(OAc)₂]EtOH displayed a decomposing stage at midpoint 90 °C, corresponds to ethanol molecule loss (Found 6.70; Calcd. 6.60 %). The next stage, 145-445 °C, was ascribed to the acetate ions and Ph₂NH fragment loss (Found 41.00; Calcd.

41.50 %). The third step started from 445 to 515 °C and corresponding to complete degradation of the ligand resulting in Cu₂C₄O₂S₂ residue (Found 38.78; Calcd. 39.21 %).

The [Co₂(H₄L)(OAc)₄](H₂O)₅.EtOH diagram showed only two decomposition steps till 575 °C. The first started from 35 °C to 155 °C and attributed to the loss of water and ethanol molecules (Found 15.85; Calcd. 15.25 %). The next stage observed at 156-575 °C region and assigned to loss of the acetate ions and two phenyl rings (Found 43.23; Calcd. 43.73%) leaving a residue of Co₂C₅H₈N₆O₂S₂ (Found 40.95; Calcd. 41.02%). Finally, the Ni(II) complex exhibited thermal stability till 290 °C where only one decomposition step were observed in 290-520 °C leaving a residue of Ni₂C₃H₄N₄O₂ (Found 25.28; Calcd. 25.88%)

Table 3. Electronic transition bands and magnetic moment of isolated metal complexes.

Compound	Bands (cm ⁻¹), transition	μ _{eff} (B.M.)
H ₄ L	34250 (π→π*) _{Ph} ; 32895 (π→π*) _{C-S&C=O} ; 25640 (n→π*) _{C-S&C=O}	-
[Cu ₂ (H ₂ L)(OAc) ₂]EtOH	34250 (π→π*) _{Ph} ; 32050 (π→π*) _{C-S&C=O} ; 26315 (n→π*) _{C-S&C=O} ; 23700 (20920) (LMCT); 14580 (14245) ² B _{1g} → ² E _g ; 13090 (12990) ² B _{1g} → ² A _{1g}	1.43
[Co ₂ (H ₄ L)(OAc) ₄](H ₂ O) ₅ .EtOH	34250 (π→π*) _{Ph} ; 31645 (π→π*) _{C-S&C=O} ; 25640 (n→π*) _{C-S&C=O} ; 23255 (19920) (LMCT); 19050 (17010) ⁴ T _{1g} (F)→ ⁴ T _{1g} (P) (ν ₃); 15750 (15480) ⁴ T _{1g} (F)→ ⁴ A _{2g} (P) (ν ₂)	5.49
[Ni ₂ (H ₂ L)(EtOH) ₆ (H ₂ O) ₂](OAc) ₂	34245 (π→π*) _{Ph} ; 31645 (π→π*) _{C-S&C=O} ; 27175 (π→π*) _{C=N*} ; 24750 (20835) (n→π*) _{C-S&C=O} ; 19685 (18520) (LMCT); 28410 ³ A _{2g} (F)→ ³ T _{1g} (P) (ν ₃); 17125 (15105) ³ A _{2g} (F)→ ³ T _{1g} (F) (ν ₂); 13625 (13795) ³ A _{2g} (F)→ ³ T _{2g} (F) (ν ₁)	2.77

The values placed in italic between brackets recorded in Nujol mull (Table 4)

Table 4. Thermal gravimetric analyses data of the ligand and its metal complexes

	Temp. range (°C)	Wt. loss % Found (Calcd.)	Fragment loss
H ₄ L	40-247	37.92 (38.31)	Ph ₂
	247-367	29.09 (29.36)	(HCNS) ₂
	367-535	10.62 (11.19)	N ₃ H ₃
	535-650	12.74 (11.68)	HNO ₂
	residue	9.63 (9.45)	C ₃ H ₂
[Cu ₂ (H ₂ L)(OAc) ₂]EtOH	35-145	6.70 (6.60)	EtOH
	145-445	41.00 (41.50)	(OAc) ₂ + Ph ₂ NH
	445-515	13.19 (12.59)	CH ₃ N ₅
	residue	38.78 (39.20)	Cu ₂ C ₄ O ₂ S ₂
[Co ₂ (H ₄ L)(OAc) ₄](H ₂ O) ₅ .EtOH	35-155	15.85 (15.25)	(H ₂ O) ₅ + EtOH
	156-575	43.23 (43.73)	(OAc) ₄ + Ph ₂
	Residue	40.95 (41.02)	Co ₂ C ₅ H ₈ N ₆ O ₂ S ₂
[Ni ₂ (H ₂ L)(EtOH) ₆ (H ₂ O) ₂](OAc) ₂	290-520	74.72 (74.12)	(EtOH) ₆ + (H ₂ O) ₂ + (OAc) ₂ + Ph ₂ N ₂ H ₂ C ₂ S ₂
	Residue	25.28 (25.88)	Ni ₂ C ₃ H ₄ N ₄ O ₂

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