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Iman T. Ahmed^a

^a Chemistry Department, El-Minia University, El-Minia, Egypt

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Synthesis and Spectroscopic Characterization of Some Divalent Metal Complexes Derived from 1,4-Dibenzoylthiosemicarbazide and *N*-[2-(3-Benzoylthioureido)ethyl]benzamide

Iman T. Ahmed

Chemistry Department, El-Minia University, El-Minia, Egypt

The binary metal complexes $[M(II)-L^1 \text{ or } L^2]$, where $M(II) = Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II)$ and $UO_2(II)$; $L^1 = 1,4\text{-dibenzoylthiosemicarbazide}$; and $L^2 = N\text{-}[2\text{-(3-benzoylthioureido)ethyl}]\text{benzamide}$; were prepared and characterized by elemental analysis, thermogravimetric analysis, molar conductance, and electronic spectroscopies (IR, 1H -, and $^{13}C\text{-NMR}$) in addition to mass spectra.

Keywords 1,4-Dibenzoylthiosemicarbazide; binary metal complexes; *N*-[2-(3-benzoylthioureido)ethyl]benzamide

Many of the metal complexes with sulphur compounds containing NS and NSO donor atoms, such as thiosemicarbazides, dithiocarbamates, and their oxidation products have been found to exhibit fungicidal, bactericidal, antiviral, and antitubercular activities.^{1–8} Owing to their pharmacological activity, thiosemicarbazides are very important compounds in biological chemistry and medicine because they possess some degree of cytotoxic activity.⁹ Thus the metal complexes containing sulphur-donor ligands are continuing to attract the interest of scientists. So far, the coordination of thiosemicarbazides with transition metals has been explored more thoroughly than their coordination with nontransition metals. They also can act in a bidentate and/or tetradentate manner. Different stereochemistries were proposed on the bases of spectral and analytical data.¹⁰

A survey of the literature reveals that transition-metal complexes of 4-allyl- and aromatic thiosemicarbazide derivatives,^{10–12} *N*-benzoyl-*N'*-(pyrid-2-yl)thiocarbamide,¹³ 1-oxalylbis(4-phenylthiosemicarbazide),¹⁴ 1-(3-hydroxy-2-naphthyl)-4-phenyl-3-thiosemicarbazide,¹⁵ 1-cinna-

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Address correspondence to Iman T. Ahmed, El-Minia University, Chemistry Department, Faculty of Science, El-Minia 61519, Egypt. E-mail: h.imanth124@yahoo.com

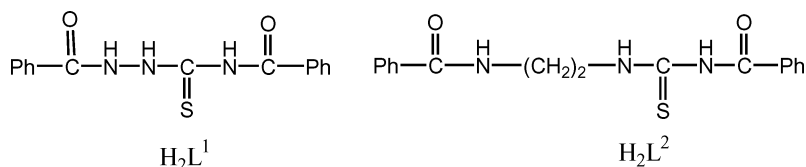


FIGURE 1 The structure of ligands.

moyl-4-phenyl-3-thiosemicarbazide,¹⁶ and 1-acetyl-4-phenyl-3-thiosemicarbazide¹⁷ as well as thiosemicarbazone derivatives^{18,19} were reported.

However, no studies have been made on binary systems containing divalent metal ions as well as 1,4-dibenzoylthiosemicarbazide (L^1) or *N*-[2-(3-benzoylthioureido)-ethyl]benzamide (L^2). Motivated by these facts and pursuing our research in the field of the synthesis of binary and ternary metal complexes,^{20–25} we report here the results of our recent investigations on the reaction of 1,4-dibenzoylthiosemicarbazide (H_2L^1) as well as *N*-[2-(3-benzoylthioureido)ethyl]benzamide (H_2L^2) (Figure 1) with some divalent metal ions: Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), and $\text{UO}_2(\text{II})$. The prepared complexes were characterized by elemental analysis, thermogravimetric analysis, molar conductance, and electronic spectroscopies (IR, ^1H -, and ^{13}C NMR) in addition to mass spectra.

EXPERIMENTAL

Apparatus

Melting points have been determined in open glass capillaries on a Gallen Kamp melting points apparatus and are uncorrected. The C, H, N, and S contents of the prepared binary complexes were determined by the Microanalytical Unit at Cairo University. Molar Conductances of DMSO solutions of the synthesized binary complexes were measured at 25°C using a model 31 YSI conductivity bridge with a conductivity cell constant = 0.10 m^{-1} . Thermogravimetric (TG) analysis were performed automatically using a DuPont 9000 thermal analyzer with a computer at a heating rate of 10°C min^{-1} in a dynamic air atmosphere. Infrared spectra were recorded in the 4000–200 cm^{-1} range on FT-IR 1650 (Perkin Elmer) spectrophotometer using KBr pellets. A Bruker WM 300 instrument was used to determine ^1H NMR (300.13 MHz) and ^{13}C NMR (65.47 MHz) spectra. Mass spectra were obtained with a Varian MAT 311 doubly focusing instrument. Electronic spectra of freshly prepared solutions of the complexes in DMSO were monitored

at 25°C in the 300–1000 nm range by an Unicam Scanning UV-Vis spectrophotometer model UVA 1000E with an accuracy of ± 1 nm using matched silica cells of 1.0 cm path length. The spectrophotometer and its accessories were controlled by software under Windows to provide advanced operational facilities.

Materials and Complexes

The nitrate metal salts ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{UO}_2 \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) that were used were BDH analytical grade products.

Synthesis of N-[2-(3-Benzoylthioureido)ethyl]benzamide (H_2L^2)

To a stirred solution of ethylene diamine (10 mmol) in 30 mL of dimethylformamide, benzoylisothiocyanate (16.3 g, 10 mmol) was added dropwise at r.t. Stirring at r.t. was continued for 3 h and the mixture was set aside overnight, then added to 300 mL of ice water. A white precipitate was formed, which was recrystallized from ethanol to give colorless crystals from H_2L^2 .

1,4-Dibenzoylthiosemicarbazide (H_2L^1)

M.p. 172–174°C (lit. 173–176),²⁶ IR (KBr): $\nu = 3213$ (NH), 1674, 1643 (CO), 1600 (Ar–C=C) and 1354 cm^{-1} (C=S),²⁷ ^1H NMR (DMSO- d_6): $\delta_{\text{H}} = 7.52\text{--}7.99$ (m, 10H, Ar–H), 11.13 (s, br, 1H, $^2\text{NHCS}$), 11.77 (s, br, 1H, PhCON ^1H), 12.39 (s, br, 1H, CSN $^4\text{HCOPh}$), ^{13}C NMR, $\delta_{\text{C}} = 126.90$, 127.60, 129.00, 129.60, 130.05, 130.14, 132.02, 132.11 and 132.31 (all Ar–C), 164.78 and 168.06 (CO), 180.83 (C=S), Ms, m/z (%) 299 (M^+ , 13), 266 (16), 223 (18), 195 (18), 105 (100), 77 (72), 51 (18).

N-[2-(3-Benzoylthioureido)ethyl]benzamide (H_2L^2)

M.p 178–180°C; yield (22.265 g, 68%), (Found, C, 62.48; H, 5.11; N, 12.71; S, 9.92, Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{SO}_2$ (327.40): C, 62.37; H, 5.23; N, 12.83; S, 9.79), IR (KBr): $\nu = 3336$, 3285, 3223 (NH), 3060 (Ar–CH), 2931 (Al–CH), 1664, 1645 (CO), 1600 (Ar–C=C), 1350 cm^{-1} (C=S), ^1H NMR (DMSO- d_6): $\delta_{\text{H}} = 3.77\text{--}3.83$ (m, 2H, CH_2), 4.04–4.10 (m, 2H, CH_2), 7.12 (br, s, $^2\text{NHCS}$), 7.38–7.51, 7.58–7.84 (m, 10H, Ar–H), 9.11 (br, s, 1H, $^1\text{NHCOPh}$), 11.03 (br, s, 1H, CSN $^4\text{HCOPh}$), ^{13}C NMR (DMSO- d_6): $\delta_{\text{C}} = 40.35$, 43.50 (2CH_2), 126.90, 127.10, 127.78, 128.50, 129.14, 131.88, 133.90 and 134.20 (all Ar–C), 166.82 and 168.00 (CO), 181.30

(C=S), Ms, m/z (%) 327 (12), 206 (8), 180 (18), 147 (25), 134 (27), 105 (100), 77 (54), 51 (16).

Synthesis of the Binary Metal Complexes

The complexes $[M(L^1)(H_2O)_2]H_2O$ or $[M(L^2)(H_2O)_4]H_2O$, $M=Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Pb(II)$, $Cd(II)$, and $UO_2(II)$ were synthesized according to the following procedure: The nitrate metal salt (5.00 mmol) dissolved in a minimum quantity of water was added slowly to an EtOH (10 mL) solution of 5.00 mmol of the ligand (H_2L^1 or H_2L^2) with stirring. The binary mixture was refluxed for 5 h, and then was evaporated to a small volume and left to cool. The binary complexes, were precipitated, collected by filtration, washed thoroughly with water and EtOH, and dried in *vacuo* over P_4O_{10} .

1H NMR, ^{13}C NMR, and Mass Spectral Data of Binary Metal Complexes

$[Ni(L^1)(H_2O)_2]H_2O$ complex 1H NMR (DMSO- d_6) δ_H = 7.46–7.71, 7.87–8.21 (m, 10H, Ar–H), 11.78 (br, s, 1H, NH); ^{13}C NMR (DMSO- d_6): δ_C = 126.86, 128.29, 128.74, 129.00, 129.30, 129.45, 131.58, 132.86 (Ar–C), 158.20 and 159.80 (N=CS and N=CO), 165.27 (CO); Ms, m/z (%): 282 $[M^+-(NiO+3H_2O)$, 44], 177 (26), 149 (22), 105 (100), 77 (81), 51 (41).

$[Zn(L^2)(H_2O)_4]H_2O$ complex: 1H NMR (DMSO- d_6): δ_H = 3.91–3.98 (m, 2H, CH_2), 4.10–4.16 (m, 2H, CH_2), 7.39–7.93 (m, 10H, Ar–H), 9.59 (br, s, 1H, NH); ^{13}C NMR (DMSO- d_6) δ_C = 43.94, 46.12, 127.11, 127.53, 128.12, 128.76, 129.88, 131.51, 134.11, 134.67 (Ar–C), 157.86 and 158.62 (N=CS and N=CO), 166.12 (CO); Ms, m/z (%) 310 $[(M^+-ZnO+5H_2O)$, 16], 190 (26), 105 (96), 77 (100), 51 (52).

RESULTS AND DISCUSSION

The analytical data given in Table I for the isolated binary complexes are consistent with the general molecular formula $[M(L^1) \text{ or } (L^2)(H_2O)_n]H_2O$, $M=Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Pb(II)$, $Cd(II)$ and $UO_2(II)$, $L^1=1,4$ -dibenzoylthiosemicarbazide, $L^2=N$ -[2-(3-benzoylthioureido)ethyl]benzamide, where $n=2$ for complexes containing ligand L^1 , and $n=4$ for complexes containing ligand L^2 (Figure 2). The formation of the binary metal complexes can be represented by Eq. (1):

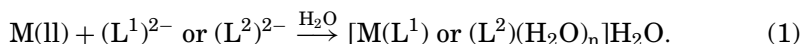


TABLE I Microanalytical Data and Physical Properties of the Different Synthesized Binary Complexes^a

Complex (empirical formula)	M. Wt.	Color	M.p. (°C)	Yield(g) %	Found(calcd.)(%)			
					C	H	N	S
[Co(L ¹)(H ₂ O) ₂].H ₂ O	410.31	Gray	320–322	(0.984)	44.10	4.29	10.11	7.96
C ₁₅ H ₁₇ CoN ₃ SO ₅				48	(43.91)	(4.18)	(10.24)	(7.81)
[Ni(L ¹)(H ₂ O) ₂].H ₂ O	410.07	Palc green	> 360	(1.066)	43.84	4.10	10.41	7.66
C ₁₅ H ₁₇ N ₃ NiSO ₅				52	(43.93)	(4.18)	(10.25)	(7.82)
[Cu(L ¹)(H ₂ O) ₂].H ₂ O	414.88	Brown	250–252	(1.265)	43.31	3.98	9.97	7.87
C ₁₅ H ₁₇ CuN ₃ SO ₅				61	(43.43)	(4.13)	(10.13)	(7.73)
[Zn(L ¹)(H ₂ O) ₂].H ₂ O	416.77	Yellow	300–302	(1.229)	43.10	4.23	10.22	7.85
C ₁₅ H ₁₇ ZnN ₃ SO ₅				59	(43.23)	(4.11)	(10.08)	(7.69)
[Cd(L ¹)(H ₂ O) ₂].H ₂ O	463.79	Yellow	226–228	(1.136)	38.96	3.52	8.95	7.10
C ₁₅ H ₁₇ CdN ₃ SO ₅				49	(38.85)	(3.69)	(9.06)	(6.91)
[Pb(L ¹)(H ₂ O) ₂].H ₂ O	457.80	Pale brown	212–214	(1.052)	39.47	3.88	9.27	6.86
C ₁₅ H ₁₇ PbN ₃ SO ₅				46	(39.35)	(3.74)	(9.18)	(7.00)
[UO ₂ (L ¹)(H ₂ O) ₂].H ₂ O	621.41	Orange	295–297	(1.678)	29.10	2.84	6.62	5.24
C ₁₅ H ₁₇ N ₃ UO ₂ SO ₅				54	(28.99)	(2.76)	(6.76)	(5.16)
[Co(L ²)(H ₂ O) ₄].H ₂ O	474.40	Pale violet	330–332	(1.303)	42.91	5.47	8.71	6.88
C ₁₇ H ₂₅ CoN ₃ SO ₇				55	(43.04)	(5.31)	(8.86)	(6.76)
[Ni(L ²)(H ₂ O) ₄].H ₂ O	474.16	Pale green	> 360	(1.563)	43.22	5.21	8.94	6.63
C ₁₇ H ₂₅ N ₃ NiSO ₇				66	(43.06)	(5.31)	(8.86)	(6.76)
[Cu(L ²)(H ₂ O) ₄].H ₂ O	479.01	Blue	226–228	(1.531)	42.55	5.41	8.92	6.54
C ₁₇ H ₂₅ CuN ₃ SO ₇				64	(42.63)	(5.26)	(8.77)	(6.70)
[Zn(L ²)(H ₂ O) ₄].H ₂ O	480.85	Yellow	302–304	(2.351)	42.61	5.18	8.90	6.81
C ₁₇ H ₂₅ ZnN ₃ SO ₇				48	(42.46)	(5.24)	(8.74)	(6.67)
[Cd(L ²)(H ₂ O) ₄].H ₂ O	527.87	Yellow	> 360	(1.186)	38.59	4.88	8.11	5.95
C ₁₇ H ₂₅ CdN ₃ SO ₇				45	(38.68)	(4.77)	(7.96)	(6.13)
[Pb(L ²)(H ₂ O) ₄].H ₂ O	521.88	Gray	284–287	(1.277)	39.29	4.76	7.93	6.27
C ₁₇ H ₂₅ N ₃ PbSO ₇				49	(39.13)	(4.83)	(8.05)	(6.14)
[UO ₂ (L ²)(H ₂ O) ₄].H ₂ O	685.49	Orange	300–303	(1.711)	29.87	3.57	6.31	4.57
C ₁₇ H ₂₅ N ₃ UO ₂ SO ₇				50	(29.79)	(3.68)	(6.13)	(4.68)

^aL¹ and L² represent 1,4-dibenzoylthiosemicarbazide and *N*-[2-(3-benzoylthioureido)ethyl]benzamide, respectively.

The measured molar conductances Λ_m of the DMSO solutions of the isolated binary complexes given in Table I are found to be in the range of 11–19 Ohm⁻¹ cm⁻¹ mol⁻¹ L indicating the non-electrolytic nature of the complexes.²⁸

Thermographic Analysis

TG analysis of the different synthesized binary complexes have been carried out to obtain diagnostic structural evidence for the suggested molecular formula. Generally, the TG curves show two successive mass

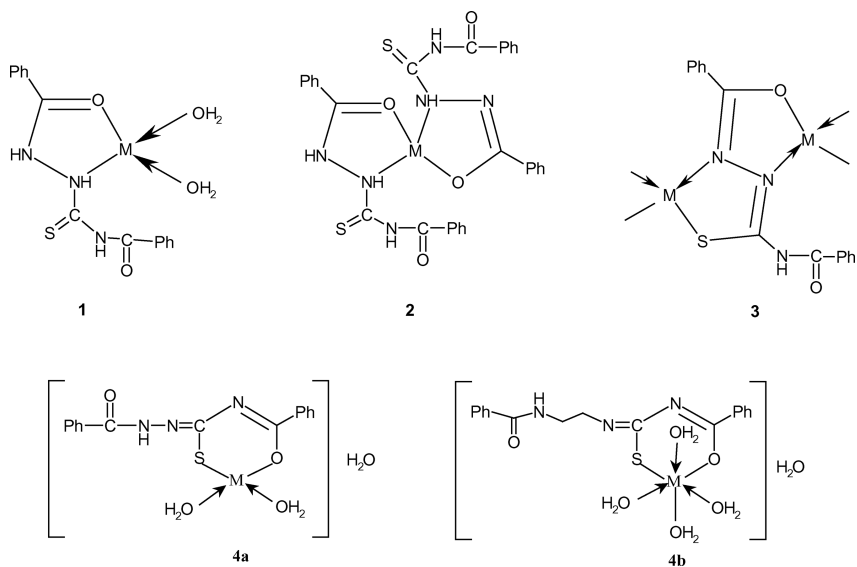


FIGURE 2 Suggested structures of synthesized binary metal complexes $M=\text{Co(II)}$, Ni(II) , Cu(II) , Zn(II) , Pb(II) , Cd(II) , and $\text{UO}_2(\text{II})$. (a) for 1,4-dibenzoylthiosemicarbazide; (b) for *N*-[2-(3-benzoylthioureido)ethyl]benzamide.

loss steps over the temperature range 50–300°C the overall mass loss is consistent with the removal of two H_2O molecules, where the low-temperature mass loss 50–150°C corresponds to the removal of one hydrated H_2O molecule and the other mass loss at 200–300°C is due to the removal of two coordinated H_2O molecules for complexes containing the L^1 ligand and four coordinated H_2O molecules for complexes containing the L^2 ligand (Figure 2). This is in accordance with the suggested structural formula as well as the microanalytical data and infrared spectra cited in Tables I and II, respectively.

IR Spectra

The most important IR assignment of the binary complexes as well as the bonding sites have been determined by a careful comparison of both the IR spectra of the ligands L^1 and L^2 and their metal complexes (Table II). The major changes in the spectra of the complexes as compared to that of the ligands are as follows:

1. A broad band appeared in the 3550–3500 cm^{-1} range for the binary complexes, which most likely is attributed to the stretching vibration of the H_2O molecule. Also a strong band appeared in the range of

TABLE II The Infrared Bands (cm^{-1}) of the Binary Complexes^a

Complex	ν_{OH}	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{N-N}}$	$\nu_{\text{rock, H}_2\text{O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-S}}$
$[\text{Co}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3500	3380	1655	1590	1160	1055	915	490	335
$[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3520	3340	1645	1590	1150	1040	890	486	308
$[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3530	3420	1655	1580	1140	1060	895	466	314
$[\text{Zn}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3550	3410	1650	1585	1155	1040	890	490	325
$[\text{Cd}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3510	3360	1655	1575	1155	1060	900	450	340
$[\text{Pb}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3530	3410	1655	1600	1145	1045	910	474	326
$[\text{UO}_2(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3520	3360	1640	1585	1130	1040	905	466	335
$[\text{Co}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3530	3350	1645	1600	1150	1030	890	480	343
$[\text{Ni}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3510	3420	1655	1600	1130	1050	895	482	336
$[\text{Cu}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3515	3360	1645	1575	1130	1050	890	484	310
$[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3530	3350	1645	1600	1150	1030	915	480	343
$[\text{Cd}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3500	3330	1650	1590	1140	1060	910	466	314
$[\text{Pb}(\text{L}^2)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	3530	3320	1645	1600	1160	1040	900	486	328
$[\text{UO}_2(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$	3510	3410	1650	1600	1130	1050	890	482	336

^a L^1 and L^2 represent 1,4-dibenzoylthiosemicarbazide and *N*-[2-(3-benzoylthioureido)-ethyl]-benzamide, respectively.

$915\text{--}890\text{ cm}^{-1}$ in the IR spectra of the complexes, which is assigned to the rocking vibration mode of the coordinated H_2O molecule.²⁹

- The IR spectra of the complexes also showed a broad band at the range $3420\text{--}3320$ assigned to $\nu(\text{NH})$.
- The two strong bands at $1655\text{--}1640\text{ cm}^{-1}$ and $1600\text{--}1575\text{ cm}^{-1}$ are attributed to the stretching vibrations of the carbonyl group of benzoyl and C=N moieties, respectively. The bands due to C=S stretching vibrations of ligands L^1 and L^2 are not present in the spectra of complexes.
- On the other hand, the far IR spectra of metal complexes exhibited new bands in the $490\text{--}450$ and $343\text{--}308\text{ cm}^{-1}$ ranges, which may be ascribed to $\nu(\text{M-O})$ and $\nu(\text{M-S})$,¹⁷ respectively. Furthermore, the $\nu(\text{N-N})$ is shifted to a higher wavenumber¹⁷ and a new band appeared in the region of $1160\text{--}1130$ due to $\nu(\text{C-O})$.

¹H NMR and ¹³C NMR Spectra of Binary Complexes

The ¹H NMR spectrum of the $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ binary complex showed only one broad singlet for the PhCONH group at position 11.78 ppm in addition to aromatic protons, which resonate at $7.46\text{--}8.21\text{ ppm}$. The presence of two multiplets in the ranges $\delta_{\text{H}} = 3.91\text{--}3.98$ and $4.10\text{--}4.16$ in the ¹H NMR spectrum of $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$ complex are assigned to two methylene groups. Again, in the ¹H NMR spectrum

of $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$ complex a broad singlet at $\delta_{\text{H}} = 9.59$ ppm is due to PhCONH group. The disappearance of the NH signals at $\delta_{\text{H}} = 11.13$ and 12.39 ppm in the ^1H NMR spectrum of the $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ complex and at $\delta_{\text{H}} = 7.12$ as well as 11.03 ppm in the spectrum of $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$ complex indicates that the deprotonation has occurred through both ^2NH and ^4NH groups as shown in structures H_2L^1 and H_2L^2 . The decoupled carbon spectrum (^{13}C NMR) of the $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ complex showed signals at the range of aromatic carbons and at $\delta_{\text{C}} = 158.20$ and 159.80 ($\text{C}=\text{N}$), whereas at $\delta_{\text{C}} = 165.27$ was assigned to one carbonyl group, pointing out that the deprotonation has occurred through both ^2NH and ^4NH groups as shown in structures H_2L^1 and H_2L^2 .

Mass Spectra of Binary Complexes

The molecular formula of complexes are evidenced from elemental analysis (Table I) as well the mass spectra of $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$, and $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$, which gave the molecular ions at $m/z = 282$ (44%) and $m/z = 310$ (16%), for $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ and $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$, respectively. These fragments are attributed to the molecular ions of the complexes after losing the water molecules and the metal oxides. For $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$, the ion peak at 177 results from the elimination of the benzoyl fragment (which appears at $m/z = 105$), whereas the fragment at $m/z = 149$ is due to diazo cleavage.

Electronic Spectra

The electronic absorption spectroscopic data of 10^{-3} mol dm $^{-3}$ dimethylsulfoxide (DMSO) solutions of the various prepared binary complexes are listed in Table III.

Complexes of the 1,4-Dibenzoylthiosemicarbazide (H_2L^1) Ligand

The electronic spectrum of the Co(II) binary complexes display a broad band in the visible region at $\lambda = 530$ nm ($\epsilon = 270$ cm $^{-1}$ mol $^{-1}$ L). This is indicative of a square-planar³⁰ stereochemical configuration of the Co(II) ion, where the recorded broad is assigned to the electron transition from $\text{A}_{1\text{g}}(\text{dz}^2)$ to the empty $\text{B}_{1\text{g}}(\text{dx}^2 - \text{y}^2)$.

The recorded spectra of the Ni(II) complex show an absorption band at 568 nm with $\epsilon = 200$ cm $^{-1}$ mol $^{-1}$ L employing a square-planar structure. This band commonly is assigned to the $^1\text{A}_{1\text{g}} \rightarrow ^1\text{A}_{2\text{g}}$, $^1\text{A}_{1\text{g}} \rightarrow ^1\text{B}_{1\text{g}}$

TABLE III Electronic Absorption Spectral Data of 10^{-3} mol dm $^{-3}$ DMSO Complex Solutions^a

Complexes ^a	λ_{\max} (nm)	ε_{\max} (mol $^{-1}$ cm $^{-1}$ L)	Band assignment
[Co(L ¹)(H ₂ O) ₂]H ₂ O	530	270	A _{1g} (dz ²) → B _{1g} (dx ² - y ²)
[Ni(L ¹)(H ₂ O) ₂]H ₂ O	568	200	¹ A _{1g} → ¹ A _{2g} and ¹ A _{1g} → B _{1g}
[Cu(L ¹)(H ₂ O) ₂]H ₂ O	698	21	² B _{2g} → ² E _{1g} and ² B _{2g} → ² A _{1g}
[UO ₂ (L ¹)(H ₂ O) ₂]H ₂ O	525	12	¹ E _g → 3πh
[Co(L ²)(H ₂ O) ₄]H ₂ O	520	22	⁴ T _{1g} (f) → ⁴ T _{1g} (p)
[Ni(L ²)(H ₂ O) ₄]H ₂ O	606	15	³ A _{2g} (f) → ³ T _{1g} (f)
[Cu(L ²)(H ₂ O) ₄]H ₂ O	670	49	² B _{1g} → ² B _{2g} , ² B _{1g} → ² A _{1g} and ² B _{1g} → ² E _g
[UO ₂ (L ²)(H ₂ O) ₄]H ₂ O	500	13	¹ E _g → 3πh

^aL¹ and L² represent 1, 4-dibenzoylthiosemicarbazide and *N*-[2-(3-benzoylthioureido) ethyl] benzamide, respectively.

transitions. This assignment is based on the fact that a square-planar structure of Ni(II) complex exhibits a strong absorption band between 670 and 400 nm.³⁰

The electronic spectrum of Cu(II) complex shows a broad band with maxima at 698 nm ($\varepsilon = 21$ cm $^{-1}$ mol $^{-1}$ L), which is characteristic of a d-d transition in a square-planar structure of Cu(II) complexes.³¹ This band is due to the combination of ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g} transitions.

Complexes of the *N*-[2-(3-Benzoylthioureido)ethyl]benzamide (H₂L²) Ligand

The synthesized Co(II) complex is characterized by a broad band at 520 nm ($\varepsilon = 22$ cm $^{-1}$ mol $^{-1}$ L). In terms of the previous work, an octahedral structure³⁰ can be suggested for such binary complexes, where the broad band is ascribed to the ⁴T_{1g}(f) → ⁴T_{1g}(p) transitions.

Six-coordinated and octahedral Ni(II) complexes exhibit an absorption spectrum involving 3 allowed transitions in the ranges 1428–770, 909–500, and 526–370 nm of comparatively low intensity.³⁰ Accordingly, an octahedral structure is suggested for the Ni(II) complex, where the observed band at 606 nm ($\varepsilon = 15$ cm $^{-1}$ mol $^{-1}$ L) is assigned to the ³A_{2g}(f) → ³T_{1g}(f) transition.

On the other hand, the visible spectra of Cu(II) complexes are characterized by a broad band at 670 nm of relatively high intensity ($\varepsilon = 49$ cm $^{-1}$ mol $^{-1}$ L) (Table III). This band is consistent with the previously reported absorption band for the tetragonal-distorted structure of six-coordinate Cu(II) complexes, which are usually a green or blue color.^{23,24,30} Therefore, a tetragonal-distorted structure is suggested for

this complex, where the observed band involves the combination of the ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$, and ${}^3B_{1g} \rightarrow {}^2E_g$ transitions.³⁰

All complexes of $UO_2(II)$, in general, containing a ligand L^1 and L^2 display a broad band at 525 and 500 nm, respectively. It can be assigned to the ${}^1E_g \rightarrow 3\pi h$ transition typical of O-U-O symmetric stretching for the first excited state of the UO_2 moiety.³²

Several alternative structures could be suggested for the transition metal complexes derived from dibenzoylthiosemicarbazide (H_2L^1) or *N*-[2-(3-benzoylthioureido)ethyl]benzamide (H_2L^2) as follows:

1. H_2L^1 or H_2L^2 can act with $M(II)$ as a neutral bidentate ligand, coordinating via the 2NH and (C=O) groups to give one five-membered ring as in structure **1** (Figure 2).
2. Also, H_2L^1 or H_2L^2 behave as a mono-negative bidentate ligand via 2NH and the enolic oxygen (=C-OH) and act with $M(II)$ with the displacement of the hydrogen atom from the latter group forming two five-membered rings including the metal atom as in structure **2** (Figure 2).
3. H_2L^1 or H_2L^2 functions as a binegative tetradentate ligand coordinating with $M(II)$ through the enolic oxygen atom and the nitrogen atom of the 2NH group from one end and the thiol sulphur atom and the nitrogen atom of 1NH group on the other end, such as the structure **3** (Figure 2).
4. Finally, H_2L^1 or H_2L^2 act as a binegative bidentate ligand coordinating through the enolic oxygen atom (attached to 4N) and the thiol group (attached to 2N) with the replacement of hydrogen atoms from the enolized carbonyl and thiol group end such as the structures **4a**, **b** (Figure 2).

Summarizing the present results, it can be seen that:

- the elemental analysis (Table I); mass spectroscopy of L^1 and L^2 and their metal complexes were found to agree with their proposed constitutions. Accordingly, the alternative structure of complexes **2**, **3** could be ruled out on the bases of combustion analyses.
- TG-curves show the removal of hydrated and coordinated H_2O molecules for the complexes containing L^1 and L^2 ligands. The presence of coordinated water molecules in the complexes is confirmed by the presence of a new signal in 1H NMR at around 3.50–3.65 ppm, which overlapped with DMSO signals and has been attributed to H_2O protons.³³ Also, a broad band at 3550–3500 cm^{-1} together with new bands at 915–890 cm^{-1} in the IR spectra of complexes may be

assigned to stretching and rocking vibration modes of coordinated water.²⁹

- the disappearance of signals at $\delta_{\text{H}} = 11.13$ and 12.39 ppm in the ^1H -NMR spectrum of the $[\text{Ni}(\text{L}^1)(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ complex and at $\delta_{\text{H}} = 7.12$ as well as 11.03 ppm in the spectrum of the $[\text{Zn}(\text{L}^2)(\text{H}_2\text{O})_4]\text{H}_2\text{O}$ complex indicates that the deprotonation has occurred through both the ^2NH and ^4NH groups, as shown in structures H_2L^1 and H_2L^2 .
- in addition to the aromatic protons, a broad peak observed at $\delta_{\text{H}} = 11.78$ ppm may be assigned to ^1NH protons.³⁴ A low-field shift of this signal may be due to strong coordination of the neighboring atoms with the metal ion.³⁵
- the presence of only one amide group at $\delta_{\text{C}=\text{O}} = 165.27\text{--}166.12$ ppm, new signals at 158.20 ppm ($\text{N}=\text{CS}$) and at 159.80 ppm ($\text{C}=\text{CO}$), as well as the absence of a thioamide function support the absence of the five-membered ring structure **1**.
- the electronic spectral results of these complexes in DMSO solutions suggest a tendency of metal to form a square-planar stereochemical configuration with the L^1 ligand and six-coordinated and octahedral complexes with the L^2 .
- further, the molecular mechanics of the PM3 program³⁶ of **1** and **4a** as examples suggests that the coordination by both the sulfur and the oxygen towards the Ni metal is more stable with respect to the other structure which involved coordination by the NH and oxygen atoms towards the same metal. More indicatively, the six-membered ring formation **4a** is more stable (steric energy = 150 Kcal/mole) compared to the five-member ring **1** (steric energy = 325 Kcal/mol).
- the metal complexes are insoluble in ethanol, methanol, acetonitrile and various solvents, but are soluble in DMSO. All attempts to prepare single crystals of the compounds failed. Thus, no definite structure can be described, but the analytical and spectroscopic data enable us to predict the possible structures as shown in **4a**, **b** (Figure 2).

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