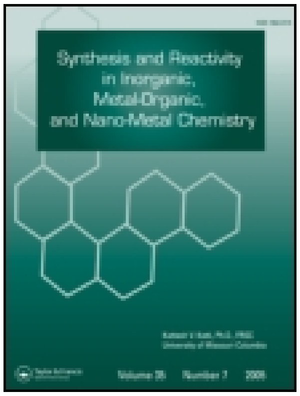

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Cyclobutane and Thiazole Substituted Schiff Base Ligands and Their Cobalt(II), Copper(II), Nickel(II), and Zinc(II) Complexes

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Cyclobutane and Thiazole Substituted Schiff Base Ligands and Their Cobalt(II), Copper(II), Nickel(II), and Zinc(II) Complexes

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ABSTRACT

Two novel bidentate Schiff base ligands containing cyclobutane and 2,4-disubstituted thiazole rings, 4-(1-methyl-1-*p*-xylylcyclobutane-3-yl)-2-(2-hydroxybenzylidenehydrazino)thiazole (L^1H), 4-(1-methyl-1-*p*-xylylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidenehydrazino)thiazole (L^2H), and their mononuclear complexes with a 1:2 metal:ligand ratio have been prepared with acetate salts of Co(II), Cu(II), Ni(II) and Zn(II) in ethanol. The authenticity of the ligands and their complexes have been established by microanalyses, IR, ^1H and ^{13}C NMR spectra, and by

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magnetic susceptibility measurements. The thermal properties of all complexes have been studied by TGA and DSC techniques. All the complexes were found to be mononuclear.

Key Words: Cyclobutane; Thiazole; Schiff base; Complexes.

INTRODUCTION

As a part of our research program concerning the chelating behaviour of 2,4-disubstituted thiazoles, we have examined previously the coordination properties of some 2,4-disubstituted thiazoles in several transition metal complexes.[1–4] Metal complexes of some 2,4-disubstituted thiazoles derivatives have been found in some instances to have enhanced or modified their activity in comparison to the uncomplexed ligand. Thiosemicarbazones, cyclobutanes, thiazoles and Schiff bases are of great importance for the preparation of various pharmaceuticals and are used in many other areas of chemistry as starting materials. Schiff bases derived from salicylaldehydes are well known polydentate ligands.[5] It has been a suggestion shown that Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have strong anticancer activity.[6] Some thiazole derivatives containing the tetralin moiety have been synthesized and used in biological activity studies.[7] Recently, there has been considerable interest

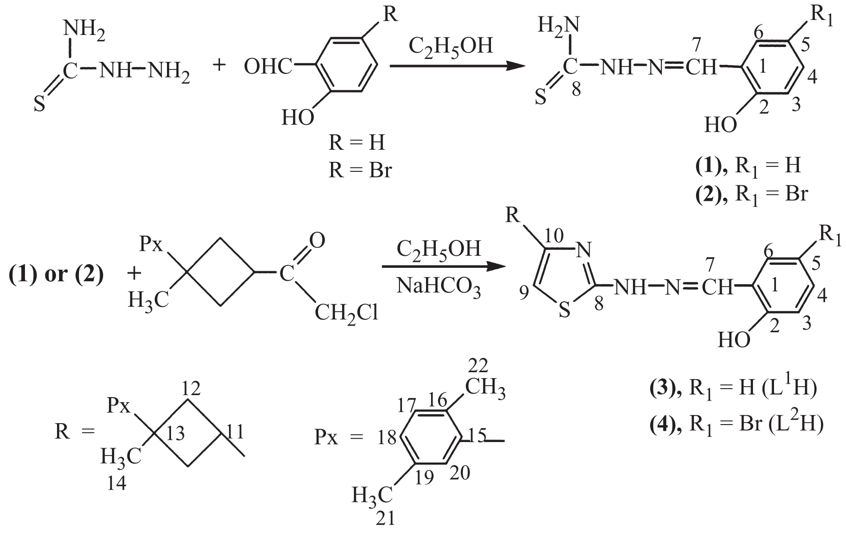

Figure 1. Synthesis of the ligands.

in the chemistry of Schiff base compounds containing thiosemicarbazones and their metal complexes due to their biological activities[8] and non-linear optical properties.[9] Research has concentrated on different properties of poly-substituted cyclobutane derivatives for years.[10] On the other hand, our group has been heavily engaged in the synthesis of novel 1,1,3-trisubstituted cyclobutane thiazoles and their Schiff base derivatives.[11] These compounds, containing cyclobutane, thiazole and Schiff base functions in their molecules, seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful ligands.

Since these ligands have not been reported in the literature, this paper deals with their preparation (Figure 1) and characterization, as well as their complexes with cobalt(II), copper(II), nickel(II), and zinc(II) acetates.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligands

Synthetic pathways for the preparation of the ligands are shown in Figure 1. Two of the starting substances, 1-(2-hydroxybenzylidene) thiosemicarbazide (**1**) and 1-(2-hydroxy-5-bromobenzylidene) thiosemicarbazide (**2**) were synthesized by condensation of thiosemicarbazide, and salicylaldehyde or 5-bromosalicylaldehyde in absolute ethanol at 60–70 °C. The new ligands, 4-(1-methyl-1-*p*-xylylcyclobutane-3-yl)-2-(2-hydroxybenzylidenehydrazino)thiazole (**3**), and 4-(1-methyl-1-*p*-xylylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidenehydrazino)-thiazole (**4**) were then prepared by a one-step reaction of 1-methyl-1-*p*-xylyl-3-(2-chloro-1-oxoethyl)cyclobutane, which was prepared according to the previously published procedure,[12] with (**1**) or (**2**). The compounds are very soluble in $CHCl_3$, Me_2CO, DMSO and DMF and partially soluble in organic solvents such as EtOH and MeOH. Furthermore, hot solutions of the ligands were used for the preparation of the complexes. The synthetic process for the formation of the ligands is shown in Figure 1. It is necessary to say that these ligands are the product of difficult, tedious and time-consuming organic syntheses.

The elemental analysis results (Table 1) of (**3**), (**4**) and their metal derivatives were found to agree with their proposed constitutions. The characterization of (**1**) and (**2**) has been published elsewhere.[1] The most important infrared spectral bands of the ligands and their complexes are provided in Table 2. In the IR spectrum of (**3**) and (**4**), stretching vibrations for NH_2 and C=S were not observed, but there are new peaks at 1600 and 2978–2927 cm^{-1} for C=N (thiazole) and aliphatics, respectively.

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Table 1. Analytical and physical data of the compounds.

Compound	F.W. (g·mol^{-1})	Color	M.p. (°C)	Yield (%)	Elemental analyses % calc. (found)			
					C	H	N	S
L^{1}H (**3**)	391.54	Yellow	168	75	70.56	6.44	10.73	8.19
$C_{23}H_{25}N_3OS$					(71.14)	(5.89)	(10.84)	(8.29)
(L^1)$_2$Co	840.00	Light brown	306	83	65.78	5.76	10.01	7.63
$C_{46}H_{48}CoN_6O_2S_2$					(65.96)	(5.90)	(9.93)	(7.15)
[(L^1)$_2$Cu]$_2$	1689.22	Brown	> 320	67	65.42	5.73	9.95	7.59
$C_{92}H_{96}Cu_2N_{12}O_4S_4$					(65.96)	(5.54)	(9.46)	(7.05)
(L^1)$_2$Ni	839.72	Dark yellow	309	76	65.79	5.76	10.01	7.64
$C_{46}H_{48}NiN_6O_2S_2$					(65.37)	(5.90)	(9.90)	(7.37)
(L^1)$_2$Zn	846.43	Yellow	297	71	65.27	5.72	9.93	7.58
$C_{46}H_{48}ZnN_6O_2S_2$					(65.04)	(5.84)	(9.88)	(7.78)
(L^{2}H) (**4**)	470.43	Yellow	168	74	58.72	5.14	8.93	6.82
$C_{23}H_{24}BrN_3OS$					(58.66)	(4.93)	(8.84)	(6.69)
(L^2)$_2$Co	997.77	Light brown	306	66	55.37	4.65	8.42	6.43
$C_{46}H_{46}Br_2CoN_6O_2S_2$					(55.85)	(4.71)	(8.13)	(6.41)
[(L^2)$_2$Cu]$_2$	2004.76	Dark green	> 320	76	55.12	4.63	8.38	6.40
$C_{92}H_{92}Br_4Cu_2N_{12}O_4S_4$					(55.29)	(4.52)	(7.91)	(6.45)
(L^2)$_2$Ni	997.53	Dark yellow	309	69	55.39	4.65	8.42	6.43
$C_{46}H_{46}Br_2NiN_6O_2S_2$					(55.66)	(4.73)	(8.24)	(6.59)
(L^2)$_2$Zn	1004.23	Yellow	297	63	55.02	4.62	8.37	6.39
$C_{46}H_{46}Br_2ZnN_6O_2S_2$					(55.33)	(4.81)	(8.23)	(6.46)

Table 2. Infrared spectral data (cm^{-1}) of the ligands and their complexes.[a]

Compound	ν(O–H)	ν(C–O)	ν(C=N) Azomethine	ν(C=N) Thiazole	ν(N–H)	ν(C–S–C)	μ_{eff} (B.M.)
L^1H (**3**)	3182 s	1286 s	1619 vs	1558 s	3113 s	637 m	–
$(L^1)_2Co$	–	1292 m	1606 vs	1558 s	3113 s	637 m	4.15
$[(L^1)_2Cu]_2$	–	1292 m	1606 vs	1558 s	3113 s	637 m	0.49
$(L^1)_2Ni$	–	1303 m	1606 vs	1558 s	3113 s	637 m	3.81
$(L^1)_2Zn$	–	1303 m	1606 vs	1558 s	3113 s	637 m	dia
L^2H (**4**)	3275 s	1151 s	1625 vs	1529 s	3121 s	656 m	–
$(L^2)_2Co$	–	1176 m	1606 vs	1529 s	3121 s	656 m	4.13
$[(L^1)_2Cu]_2$	–	1182 m	1609 vs	1529 s	3121 s	656 m	0.96
$(L^2)_2Ni$	–	1176 m	1611 vs	1529 s	3121 s	656 m	3.80
$(L^2)_2Zn$	–	1176 m	1605 vs	1529 s	3121 s	656 m	dia

[a] m: medium, s: strong, vs: very strong.

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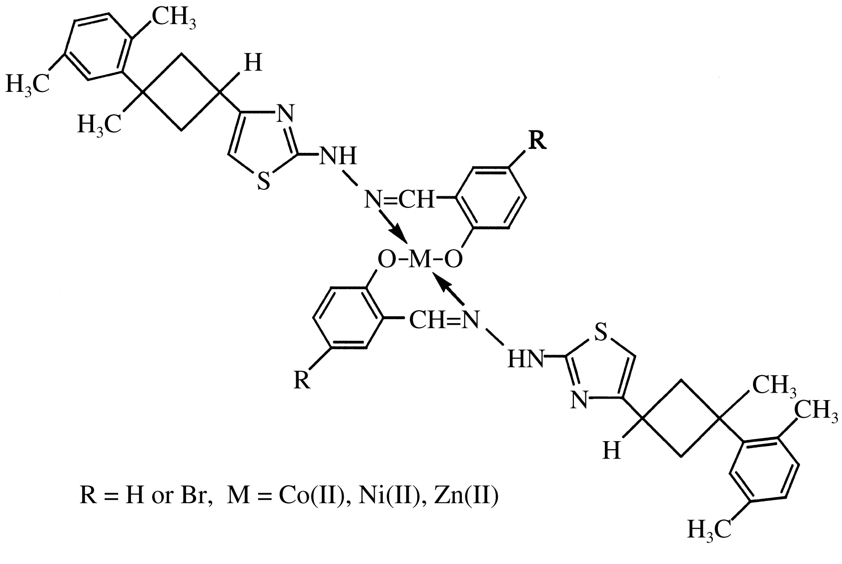
Observation of the absence of C=O, C–Cl, C=S and NH_2 absorptions in the IR spectra of the ligands L^1H and L^2H, and existing characteristic peaks indicate the formation of the expected compounds.

The strong and sharp band observed at 3113 and 3131 cm^{-1} for the ligands, respectively, can be attributed to –NH– group vibrations. Both ligands exhibit a broad, medium-intensity band in the 2700–2560 cm^{-1} range which is assigned to the intramolecular H-bonding vibrations (O–H···N). As is known, this situation is common for aromatic azomethine compounds containing *o*-OH groups.[13] The azomethine group vibration of the free ligands occurs at 1619 and 1625 cm^{-1}, respectively. In the free ligands, the band at 3182 and 3275 cm^{-1} can be attributed to the phenolic (O–H) group vibration,[13] respectively, for L^1H and L^2H. Characteristic bands for C–O of the ligands are observed at 1286 and 1140 cm^{-1}, respectively. The aliphatic group vibrations indicating that the compounds contain cyclobutane are in the 2978–2927 cm^{-1} range for both ligands. The C=N group vibrations in the thiazole ring are observed at 1558 cm^{-1} for L^1H and 1529 cm^{-1} for L^2H. Another group, C–S–C, which may be affected by the complexation, exhibits bands at 637 and 656 cm^{-1} for the ligands L^1H and L^2H, respectively.

The ^1H and ^{13}C NMR spectra of the ligands were recorded in $CDCl_3$. The ^1H NMR and ^{13}C NMR assignments are given in detail in the Experimental section. It is important to emphasize that the ^1H NMR resonance of the O–H group at 10.75–11.45 and 8.60–9.80 ppm for the L^1H and L^2H ligands, respectively, as broad singlet, is due to the presence of intramolecular hydrogen bonding.[14] These two broad singlets also contain the –NH– signals of the molecules. The ^1H NMR signal observed for the protons of C–OH and –NH– disappeared upon addition of D_2O to the solution. The singlet proton resonances in the ^1H NMR spectra of these ligands at 8.12 and 8.06 ppm have been assigned to the azomethine group protons. The aromatic ring resonances are observed at 6.80–7.31 and 6.77–7.00 ppm as multiplets for the ligands L^1H and L^2H, respectively. The detailed ^1H NMR spectral data of the ligands are given in the Experimental section, and a more detailed spectral investigation of a similar cyclobutane compound can be found in the literature.[4] The ^{13}C NMR spectral data of the ligands confirm the ^1H NMR spectral results.

Metal Complexes of L^1H and L^2H Ligands

Mononuclear complexes were obtained by the reactions of the ligands with Co(II), Cu(II), Ni(II) and Zn(II) acetates. In general, the reactions of the ligands L^1H, L^2H, with the metal acetates were rapid and gave good yields of the complexes corresponding to the general formula $M(L)_2$; they are stable at room temperature and soluble in Me_2CO, DMF, DMSO and $CHCl_3$. In every complex compound, one metal ion is coordinated to two azomethine nitrogen atoms and two oxygen atoms of two ligand molecules (Figure 2). The IR spectra of all mononuclear complexes, the copper complexes are dimers (Fig. 3), are very similar to those of their ligands except for the disappearance of the OH stretching frequency and the shift of the azomethine stretching of the ligands. The azomethine stretching vibration of the ligands are shifted to the lower frequency of 1606 cm^{-1} for all of the metal complexes of the ligand L^1H. A similar situation was observed for the L^2H ligand complexes; their azomethine vibrations are at 1604 cm^{-1}. At the same time, the C–O stretching vibrations of the ligands are also shift to higher frequencies at 1292, 1292, 1303 and 1303 cm^{-1}, respectively, for L^1H and 1176, 1182, 1176 and 1176 cm^{-1} for L^2H for the above metal ion complexes. These results indicate the high effectiveness of two functional groups of the ligands by complexation with metal salts. Despite their presence in the ligands and the possibility of complexation by the C=N group and sulfur atoms in the thiazole ring, the unchanged band positions for these groups in the IR spectra of the complexes indicate that the thiazole ring does not complex with the metal. In the complexes, the bands in the 556–491 and 457–428 cm^{-1} range can



R = H or Br, M = Co(II), Ni(II), Zn(II)

Figure 2. Suggested structure of the complexes.

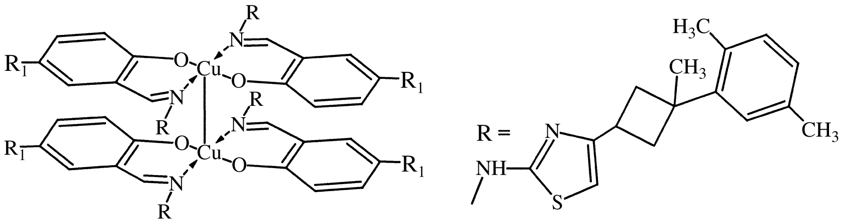


Figure 3. Suggested structure of the Cu(II) complexes.

be attributed to the ν(M–N) and ν(M–O) modes for the L^1H complexes, and the 584–497 and 482–434 cm^{-1} range for ν(M–N) and ν(M–O) modes for the L^2H complexes.

The metal contents were determined by FAAS, and the TGA curves were studied in the temperature range 20–900 °C. The weight losses in the TGA and the metal contents as determined by FAAS of the complexes have been found to be approximately the same as the percentages calculated stoichiometrically from their chemical formulas given in Table 1. All of these complexes undergo complete decomposition to the corresponding metal oxides, CuO, Co_3O_4, NiO or ZnO.

As is known, magnetic susceptibility measurements provide information regarding the structure of the complexes. The magnetic moments of the complexes were measured at room temperature. The cobalt(II), copper(II) and nickel(II) complexes of both ligands are paramagnetic and their magnetic susceptibilities are 4.15, 0.49 and 3.81 B.M., respectively, for the L^1H complexes and 4.13, 0.96 and 3.80, respectively, for the L^2H complexes. The zinc(II) complexes of the present ligands are diamagnetic. These data indicate two unpaired electrons for Ni(II) and three for Co(II). The magnetic moments of the Co(II) complexes of both ligands at room temperature fall in the range of 4 to 5 B.M., which is characteristic for mononuclear, high-spin, tetrahedral Co(II) complexes. The magnetic moment values of the Ni(II) complexes of the ligands are also consistent with a tetrahedral geometry.[15]

Cu(II) complexes exhibit a wide range of geometries, often with low symmetry and in most geometries the electronic spectra exhibit a very broad band with a maximum, which contains all the expected transitions. On the other hand, the copper complexes of the present ligands have unexpected magnetic moments, 0.49 and 0.96 B.M. (nearly diamagnetic), respectively, for the ligands L^1H and L^2H. This means that the copper complexes have a dimeric structure. Clearly the single unpaired electron on the copper atoms interacts, or ‘‘couples’’, antiferromagnetically, to produce a low-lying singlet (diamagnetic).[16] For all of these complexes, the elemental analysis results are in good agreement with the proposed structure. On the basis of the spectral and magnetic data, the cobalt, nickel and zinc complexes have tetrahedral geometry, while the copper complexes are in a square-planar structure.

As mentioned in the Introduction, our group has been heavily engaged in the synthesis of novel 1,1,3-trisubstituted cyclobutanethiazoles and their Schiff base derivatives. Many more thiazole derivatives, containing substituted cyclobutane, were synthesized, characterized in detail and used for the complexation with some transition metal salts. The effect of functional groups, such as benzene and mesitylene, on the complexes have no effect. These functional groups are very far from the pendants taking part in the complexation. On the other hand, in the case of *p*-xylene as a functional group in the molecule, the copper complexes showed low magnetic moments. This situation may be interpreted as a structural effect of *p*-xylene-bearing molecules on the complexes. But it is very difficult to explain the reason for this effect.

EXPERIMENTAL

Thiosemicarbazide, 2-hydroxybenzaldehyde, 2-hydroxy-5-bromobenzaldehyde and metal acetates were purchased from Merck (pure) and were used without further purification. 1-Methyl-1-*p*-xylyl-3-(2-chloro-1-oxoethyl)-cyclobutane was prepared according to a known procedure[12] and was purified by column chromatography prior to use. Solvents were of analytical grade and purified by standard methods where necessary.

Physical Measurements

Elemental analysis were performed on a LECO CHNSO-932 auto elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Gemini 200 MHz at 50.34 MHz or JEOL FX-90Q spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20 °C) using $Hg[Co(SCN)_2]$ as calibrant. Melting points were determined on a Gallekamp melting point apparatus and checked by differential scanning calorimetry (DSC) and are uncorrected. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance. Metal contents of the complexes were determined by an Ati Unicam (model 929) atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in concentrated HCl and subsequent dilution with 0.01 M HCl.

Synthesis of the Ligands (3) and (4)

To a suspension of 1-(2-hydroxybenzylidene) thiosemicarbazide (1.95 g, 10 mmol), or 1-(2-hydroxy-5-bromobenzylidene)thiosemicarbizide (2.74 g, 10 mmol), in absolute ethanol (30 mL), a solution of 1-methyl-1-*p*-xylyl-3(2-chloro-1-oxoethyl)cyclobutane (2.505 g, 10 mmol) in absolute ethanol (20 mL) was added dropwise at *ca*. 30–40 °C with continuous stirring and monitoring the reaction with IR. Excess of $NaHCO_3$ was added to the reaction mixture in order to neutralize the liberated HCl. After completing the addition of the α-haloketone, the temperature of the mixture was raised to 50–55 °C. Monitoring the presence of the carbonyl group of 1-methyl-1-*p*-xylyl-3-(2-chloro-1-oxoethyl)cyclobutane is easily done by IR and thus it is very easy to determine when the reaction is complete. The solution was then made alkaline (if necessary) with an aqueous solution of NH_3 (5%) and the yellow solids of L^1H and L^2H separated. The precipitate was filtered, washed with aqueous NH_3 solution several times, dried in air and crystallized from ethanol, dried and stored in a desiccator over $CaCl_2$.

Characteristic ^1H NMR peaks for L^1H, ($CDCl_3$, TMS, δ ppm): 6.80 – 7.31 (m, 7H, Ar–H), 1.47 (s, 3H, CH_3), 2.19 (s, 3H, *ortho*-CH_3 of *p*-xylyl), 2.29 (s, 3H, *meta* CH_3 of *p*-xylyl), 2.55 (d, 4H, J = 9 Hz, $-CH_2-$ of cyclobutane), 3.54 (q, 1H, J = 7 Hz, >CH–), 6.07 (s, 1H, =CH–S), 8.12 (s, 1H, N=CH), 10.75–11.45 (broad singlet, 2H, –NH– plus –OH, D_2O-exchangeable); Characteristic ^{13}C NMR peaks for L^1H, ($CDCl_3$, TMS, δ ppm): 120.05 (C_1), 159.83 (C_2), 118.86 (C_3), 133.17 (C_4), 121.51 (C_5), 132.26 (C_6), 150.82 (C_7), 171.02 (C_8), 101.73 (C_9) 153.39 (C_{10}), 32.14 (C_{11}), 41.86 (C_{12}), 43.06 (C_{13}), 29.52 (C_{14}), 149.83 (C_{15}), 133.26 (C_{16}), 132.96 (C_{17}), 128.22 (C_{18}), 137.29 (C_{19}), 129.81 (C_{20}), 21.49 (C_{21}), 22.99 (C_{22}) ppm.

Characteristic ^1H NMR peaks for L^2H, ($CDCl_3$, TMS, δ ppm): 6.77–7.00 (m, 3H, Ar–H) and 7.24–7.36 (m, 3H, Ar–H), 1.45 (s, 3H, CH_3), 2.18 (s, 3H, *ortho*-CH_3 of *p*-xylene), 2.28 (s, 3H, *meta* CH_3 of *p*-xylene), 2.52 (d, J = 9 Hz, 4H, $-CH_2-$), 3.48 (q, 1H, J = 7 Hz, >CH–), 6.02 (s, 1H, =CH–S), 8.06 (s, 1H, N=CH), 8.60–9.80 (br, 2H, –NH– plus –OH, D_2O-exchangeable); Characteristic ^{13}C NMR peaks for L^2H, ($CDCl_3$, TMS, δ ppm): 121.82 (C_1), 158.84 (C_2), 120.73 (C_3), 133.64 (C_4), 113.12 (C_5), 133.45 (C_6), 148.69 (C_7), 171.40 (C_8), 101.53 (C_9), 152.18 (C_{10}), 31.88 (C_{11}), 41.89 (C_{12}), 42.98 (C_{13}), 29.45 (C_{14}), 150.43 (C_{15}), 135.41 (C_{16}), 133.21 (C_{17}), 128.14 (C_{18}), 137.30 (C_{19}), 128.67 (C_{20}), 21.50 (C_{21}), 23.00 (C_{22}).

Synthesis of the Complexes

The ligand L^1H (0.1955 g, 0.50 mmol), or L^2H (0.235 g, 0.50 mmol) was dissolved in absolute ethanol (15–20 mL). A solution of 0.25 mmol of the metal salt [$Co(AcO)_2 \cdot 4H_2O$ (0.0623 g), $Cu(AcO)_2 \cdot H_2O$ (0.0499 g), $Ni(AcO)_2 \cdot 4H_2O$ (0.0623 g) $Zn(AcO)_2 \cdot 2H_2O$ (0.0549 g)] in ethanol (10 mL) was added drop-wise with continuous stirring. In the case of the cobalt(II) complexes, a slow stream of nitrogen was passed through the solution. Every mixture was refluxed for 1 hour and then left to stand overnight at room temperature. The complexes, precipitated as micro-crystals, were filtered, washed with cold ethanol and water several times and dried in vacuum at 60 °C (over P_4O_{10}) and stored in a desiccator over $CaCl_2$. Yields, melting points, elemental analysis results and characteristic IR bands (NaCl cell) are given in Tables 1 and 2. The ^1H NMR spectra of the Zn(II) complexes of the ligands showed the same resonances as those of L^1H and L^2H except for the absence of the OH proton resonance and a small shift was observed for the azomethine proton resonance.

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