DOI:10.7598/cst2018.1476
ISSN:2278-3458

Chemical Science Transactions
2018, **7(2),** 290-296

RESEARCH ARTICLE

Synthesis and Characterization of Complexes of Some Transition Metals with Two Bifunctional Thiourea Derivatives

ZOHRA SOLTANI[1], AHMED THENIA[1], MOHAMMED BOUCHEKARA[1], INAS EL HASSAN[2], HANNA EL-NAKAT[3], FAWAZ EL OMAR[2] and AHMAD ALLOUCH[2]

[1]Laboratory of Process Engineering and Solutions Chemistry, Faculty of Sciences and Technologies, University Mustapha Stambouli of Mascara, Algeria

[2]Laboratory of Applied Chemistry (LAC), Faculty of Sciences III, Lebanese University, P.O. Box 826, Tripoli, Lebanon

[3]Department of Chemistry, Faculty of Sciences, University of Balamand, P.O. Box 100, Tripoli, Lebanon

aallouch@ul.edu.lb

Received 2 November 2017 / Accepted 23 November 2017

Abstract: Synthesis and characterization of complexes of Fe(II), Ni(II), Zn(II), Hg(II) and Cu(II) with two thiourea derivatives such as *N*-(2-methylphenyl), *N*'-(2,3-dimethylphenyl)thiourea (H_2L_1) and *N*-(2-methylphenyl), *N*'-(2-chlorophenyl) thiourea (H_2L_2) have been studied. Their structures were confirmed by IR spectroscopy. The ligands H_2L_1 and H_2L_2 used were prepared according to the procedure reported in the literature

Keywords: Synthesis, Thiourea complexes, Transition metals

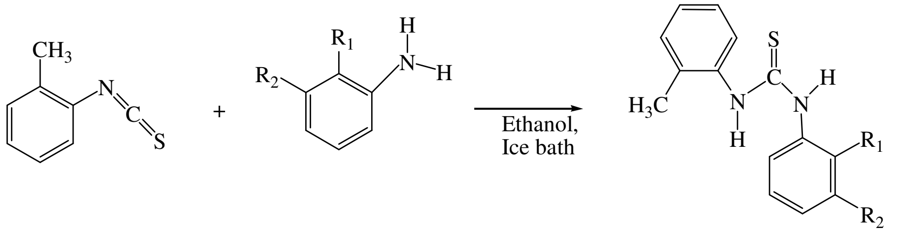
Introduction

Fe, Ni, Zn, Hg and Cu are essential elements for biological systems when present in minor quantities. On the other hand, these metal ions play an important role in mineral chemistry and their heavy use in industrial production is one of the major causes of environmental pollution. In both cases, it is absolutely essential to understand the role of these metal ions in biological systems by carrying out the structural studies of biological compounds and to examine their metal complexes.

Bifunctional chiral thioureas, derivatives of *N*-(2-methylphenyl)-*N*'-(2-methylphenyl) thiourea are active traps of the heavy metals. In fact, they are employed as inhibitors for metals corrosion in aqueous aggressive environments[1]. They play also an important role in the field of asymmetric organocatalysis[2], such as the cyanosilylation of ketones[3], Michael additions[4], Baylis-Hillman reactions[5] and hydrophosphonylation of imines[6]. In addition, they show a broad spectrum of biological activities such as antibacterial, antiviral, anticancer and anticonvulsion[7-9]. Their success is based upon their rigid, semi planar structures which provide sites for a number of important substitutions. As well, the presence of one or several heteroatoms permits interactions, of electrostatic type (hydrogen-bond, Vander Waals-bond…)[10].

The donor hetero atoms (O, N and S) of the thiourea derivatives have several modes of coordination. The ligands and their metal complexes display a wide range of biological activities, including antibacterial, antifungal, anti-tuberculosis, antithyroid, anthelmintic, rodenticides, insecticides, herbicides, and plant growth regulating properties[11].

In the present study, we report the synthesis and characterization of complexes of Fe(II), Ni(II), Zn(II), Hg(II) and Cu(II) with two thiourea derivatives: *N*-(2-methylphenyl), *N*'-(2,3-dimethylphenyl)thiourea (H_2L_1) and *N*-(2-methylphenyl), *N*'-(2-chlorophenyl) thiourea (H_2L_2). Their structures were confirmed by IR spectroscopy. The ligands H_2L_1 and H_2L_2 used were prepared according to the procedure reported in the literature[12] as shown in Scheme 1.



H_2L_1: $R_1 = CH_3$, $R_2 = CH_3$

H_2L_2: $R_1 = Cl$, $R_2 = H$

Scheme 1. Synthesis of *N*-(2-methylphenyl), *N*'-(2,3-dimethylphenyl) thiourea (H_2L_1) and *N*-(2-methylphenyl), *N*'-(2-chlorophenyl) thiourea (H_2L_2) ligands

The synthesis of the complexes between ligands (H_2L_1 and H_2L_2) and metals is performed[13-16] according to the Scheme 2. The synthesis is based on a reaction between an acid (electrons acceptor) M(II) / and a base (electrons donor) Ligand.

$$MCl_2.xH_2O \quad + \quad nL \quad \longrightarrow \quad M(L)_n.2Cl \qquad (n = 2,3,4)$$

M = Fe ; x = 4 ; T = 0°C
M = Ni ; x = 0 ; reflux for 1 hour
M = Zn ; x = 0 ; room Temp.
M = Hg ; x = 0 ; room Temp.
M = Cu ; x = 2 ; room Temp.

Scheme 2. Preparation of the complexes

Experimental

All chemicals were purchased from Sigma-Aldrich Chemical Company. Solvents were of the highest grade of purity commercially available and were used without further purification. The ligands H_2L_1 and H_2L_2 used were prepared according to the procedure reported in the literature[12] as shown in Scheme 1. Their purities were verified by chromatography with silica gel using benzene as a mobile phase and their structures were confirmed by IR and ^{1}H NMR spectroscopy. All the complexes synthesized were identified by their FT-IR spectra, recorded on a FT-IR-4200 type **A** spectroscopy between 4000-400 cm^{-1}. Water was purified by triple distillation.

Preparation of metal complexes of *N*-(2-methylphenyl), *N'*-(2,3-dimethylphenyl) thiourea (H_2L_1)

Synthesis of complex of H_2L_1/Fe (II)

The complex was prepared by the procedure described in the literature[13]. To a solution of $FeCl_2.4H_2O$ (199 mg in 20 mL of ethanol, 1 mmol), a solution of H_2L_1 (540 mg in 20 mL of CH_2Cl_2, 2 mmol) was added. The medium was kept stirred in ice bath for 30 min. After evaporation at room temperature, the complex, H_2L_1/Fe(II), obtained as brown precipitate, was collected by filtration, washed with cold ethanol and dried *in vacuum*. The H_2L_1/Fe(II) complex was obtained in 80% yield and in high purity (M.P. = 217 °C).

Synthesis of complex of H_2L_1/Ni(II)

The complex was prepared by the procedure described in the literature[14]. To a solution of $NiCl_2$ (130 mg in 20 mL of *n*-BuOH, 1 mmol), a solution of H_2L_1 (540 mg in 20 mL of CH_2Cl_2, 2 mmol) was added. The mixture was stirred and refluxed for 1 hour. After evaporation in heat bath at 60 °C, the product obtained, as oil solution, was dissolved in 4 mL of acetone. After evaporation of acetone, a precipitate was obtained, washed with cold CH_2Cl_2. By crystallization with diethyl ether, a white precipitate, H_2L_1/Ni(II), was collected. The H_2L_1/Ni(II) complex was obtained in 70% yield and in high purity (M.P. = 223 °C).

Synthesis of complex of H_2L_1/Zn(II)

The synthesis of the complex is performed according to the method described in the litterature[14,15]. To a solution of $ZnCl_2$ (136 mg in 10 mL of MeOH, 1 mmol) a solution of H_2L_1 (540 mg in 20 mL of CH_2Cl_2, 2 mmol) was added. The mixture was stirred and refluxed for few minutes. After crystallization by slow evaporation of the solvent, the white precipitate obtained was washed with cold water. The H_2L_1/Zn(II) complex was obtained in 73% yield and in high purity (M.P. = 192 °C).

Synthesis of complex of H_2L_1/Hg(II)

According to the method described in the literature[15], a solution of H_2L_1 (540 mg in 20 mL of CH_2Cl_2, 2 mmol) was added to a solution of $HgCl_2$ (136 mg in 15 mL of MeOH, 0.5 mmol). The mixture was stirred and refluxed for a few minutes. After crystallization, by slow evaporation of the solvent, the white precipitate obtained was washed with cold ethanol and dried in vacuum. The H_2L_1/Hg(II) complex was obtained in 33% yield and in high purity (M.P. = 220 °C).

Synthesis of complex of H_2L_1/Cu(II)

According to the method described in the literature[16], to form this complex, a solution of H_2L_1 (540 mg in 20 mL of CH_2Cl_2, 2 mmol) was added to a hot solution of $CuCl_2.2H_2O$ (170.5 mg in 15 mL of EtOH, 1 mmol). The mixture was stirred for 30 minutes. After crystallization by slow evaporation of the solvent, the blue precipitate obtained was washed with cold water, then with ethanol and later dried *in vacuum*. The H_2L_1/Cu(II) complex was obtained in 71% yield and in high purity (M.P. = 228 °C).

Preparation of metal complexes of N-(2-methylphenyl),N'-(2-chlorophenyl) thiourea (H_2L_2)

Fe(II), Ni(II), Zn(II), Hg(II) and Cu(II) complexes of H_2L_2 were prepared following the same procedures described for the complexes of H_2L_1, but carrying out minor appropriate modifications as described below:

Synthesis of complex of H_2L_2/Fe(II)

The complex was prepared by the procedure described with H_2L_1 by using 553 mg (2 mmol) of H_2L_2. The dried complex was grey in color; it was obtained in 66% yield and in high purity (M.P. = 218 °C).

Synthesis of complex of H_2L_2/Ni(II)

The reaction is performed as described above with H_2L_1 by using 130 mg of $NiCl_2$ (1 mmol). A yellow orange complex of H_2L_2/Ni(II) was obtained in 62% yield and in high purity (M.P. = 212 °C).

Synthesis of complex of H_2L_2/Zn(II)

The complex was prepared by the following the same procedure described for the synthesis of H_2L_1/Zn(II) by using 553 mg of H_2L_2 (2 mmol) instead of 540 mg of H_2L_1. A white precipitate complex of H_2L_2/Zn(II) was obtained in 66% yield and in high purity (M.P. = 195 °C).

Synthesis of complex of H_2L_2/Hg(II)

The same procedure described for the preparation of the complex H_2L_1/Hg(II) was implemented for preparing the complex H_2L_2/Hg(II) by using 553 mg of H_2L_2 (2 mmol) instead of 540 mg of H_2L_1. A white precipitate complex of H_2L_2/Hg(II) was obtained in 29% yield and in high purity (M.P. = 225 °C).

Synthesis of complex of H_2L_2/Cu(II)

The complex was prepared by the procedure described for the synthesis of H_2L_1/Cu(II) whereby 553 mg of H_2L_2 (2 mmol) was used in place of 540 mg of H_2L_1. The blue precipitate of H_2L_2/Cu(II) complex was obtained in 55% yield and in high purity (M.P. = 210 °C.)

Results and Discussion

The major infrared bands of Ligands H_2L_1 and H_2L_2 and their complexes are presented in Tables 1 and 2 respectively. The IR spectra of the complexes show a large number of bands which occur at various intensities in IR spectra due to the polarity of the double bond and the electron donating groups at the ortho-position of the substituent on the aromatic[17]. Of these, the focus is on the characteristic infrared bands, needed to verify the complexation objective of this study, that are assigned to the bonds between the metals and the ligands.

Thiourea is potentially capable of forming coordination bonds by both sulfur and nitrogen, even if the basicity of the ligand is extremely low[18]. The shift of the ν (N–H) band from 3333 cm^{-1}) before complexation towards a higher frequency regions (up to 3364 cm^{-1} in Table 1 and 3443 cm^{-1} in Table 2) after complexation, in addition to the constant decrease of ν(C=S) + ν(C–N) vibrations from 766 cm^{-1} before complexation to 753 cm^{-1} in Table 1 and even 753 cm^{-1} in Table 2 are indicatives of metal to ligand π-electron interactions[19-21], and that the coordination occurs through the S atom of the C=S group[22,23]. These result are obtained for Fe(II), Ni(II), Zn(II) and Cu(II).

Unlike the above metals, the L-Hg complexation shows a different IR behavior. The absorption band ν(N–H) at 3333 cm^{-1} for the free ligand is significant reduced to reach 3290 cm^{-1} in Table 1 and 3299 cm^{-1} in Table 2, as well, the absorption bands ν(C=S) + ν(C–N) was observed to undergo minor reduction indicating that the Hg(II) binds by the nitrogen atom[24,25].

Table 1. Infrared data of the ligand H_2L_1 and its complexes, FT-IR (KBr) cm^{-1}

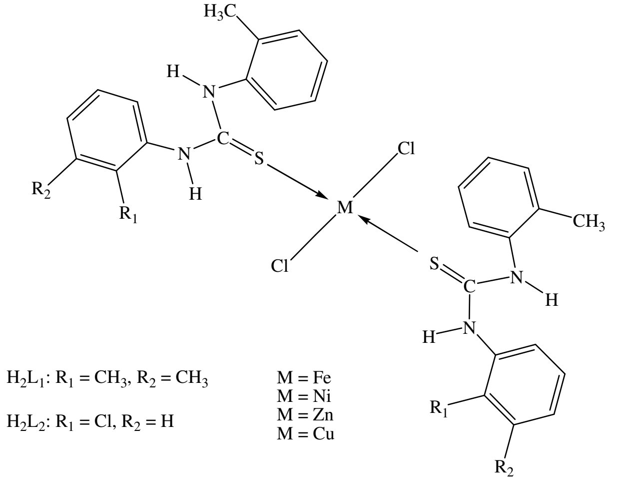
H_2L_1	H_2L_1/ Fe(II)	H_2L_1/ Ni(II)	H_2L_1/ Zn(II)	H_2L_1/ Hg(II)	H_2L_1/ Cu(II)	Assignements
3333 S	3344	3334	3344	3290	3364	ν (N–H)
3136	3119	3136	3119	3022	3139	ν (Ar–H)
2946 m	2941	2946	2941	2923	2958	ν (C–H)
1629	1627			1639	1647	ν (C=C)
1532 w	1531	1531		1564	1537	ν (C–N) + δ (N–H)
1487 S	1494	1488	1494	1457	1492	ν (N–C–N) + ν (C=S)
1342				1377		ν (C=S) + δ (N–C–S)
1274 S	1342	1273	1259	1291	1278	ν (C=S) + δ (N–C–N)
1026			1052			ν (N–C–N) + ν (C=S)
766 w	763		753	764	763	ν (C=S) + ν (C–N)
717		716				ν (C=S) + ν (C–N)

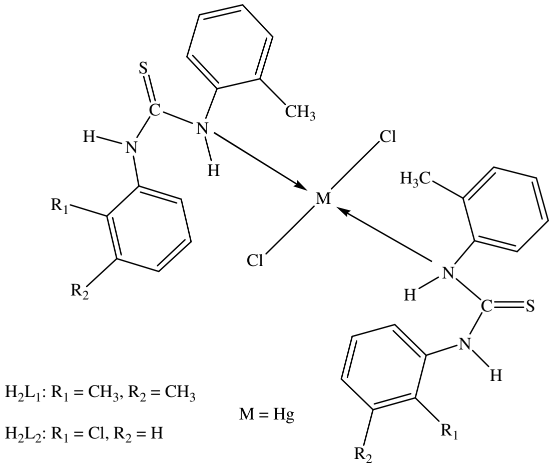
Only characteristic peaks are labeled as:S: Strong; m: middle; w: weak

Table 2. Infrared data of the ligand H_2L_2 and its complexes, FT-IR (KBr) cm^{-1}

H_2L_2	H_2L_2/ Fe(II)	H_2L_2/ Ni(II)	H_2L_2/ Zn(II)	H_2L_2/ Hg(II)	H_2L_2/ Cu(II)	Assignements
3333 S	3344	3334	3343	3299	3443	ν(N–H)
3135	3136	3118	3115	3160	3131	ν(Ar–H)
2946 m	2951	2941	2941	2965	2946	ν(C–H)
1633	1632	1628		1640	1629	ν(C=C) Ar
1532 w	1533	1583	1531	1540	1552	ν(C–N) + δ (N–H)
1487 S	1492	1491	1490	1504	1474	ν(N–C–N) + ν(C=S)
1380			1435			ν(C=S) + δ (N–C–S)
1274 S	1290			1289	1292	ν(C=S) + δ (N–C–S)
766 w	718		753	765	752	ν(C=S) + ν(C–N)

The above results lead us to propose structures as shown in Scheme 3 (n = 2).





Scheme 3. A possible mechanism for the complexes ligand/M(II) with n = 2

Conclusion

Thiourea derivatives have caught attention both at the theoretical and the practical levels. Thiourea and its derivatives have found application in biological activities, in trapping transition and heavy metals and have demonstrated its potential in both fields of coordination chemistry and environmental sustainability. In this regard, the synthesis of thiourea derivatives has become, in itself, an aim and the application of such new derivatives has become a perspective potential to look forward to. Accordingly, this study has fulfilled its objective through the synthesis and the characterization of five complexes with two thiourea derivatives: *N*-(2-methylphenyl), *N*'-(2,3-dimethylphenyl) thiourea (H_2L_1) and *N*-(2-methylphenyl), *N*'-(2-chlorophenyl) thiourea (H_2L_2). These compounds possess two aryl-bisubstutated thioamide groups, which can react as potential monodentate ligands forming stable complexes, insoluble or poorly soluble in water, with transition metals: Fe(II), Zn(II), Ni(II), Hg(II) and Cu(II).

The application part of the objective still needs to be addressed through carrying out comparative studies of the biological activity and the therapeutic properties of the free thiourea derivatives and their complexes with the above metals to confirm the importance of these two derivatives.

IR spectroscopy continues to present itself as a powerful and a reliable characterization technique. The interpretation of the obtained IR results has been verified by comparison with similar studies reported in the literature. The results obtained verified the complexion capacity of the ligands towards transition metals.

The heteroatoms N and S present different coordination types M-N or M-S. In the case of Fe(II), Zn(II), Ni(II) and Cu(II), the coordination is found to be done by the sulfur atom S. For Hg(II), the coordination is carried out by the nitrogen atom (N). This shows that the coordination nature depends on the electronic structure, the steric effect of the ligands and the nature of the metal cation. The results of this work confirm the two possible modes of coordination N and S.

References

1. (a) Robson R, *J Chem Soc., Dalton Trans.*, 2000, 3735-3744; DOI:10.1039/B003591M (b) Atrees M S, Metwally E, Demerdash M and Salem H,

J Rad Res Appl Sci., 2016, **9(3),** 207-216; DOI:10.1016/j.jrras.2015.02.004 (c) Alodan M and Smyrl W, *Electrochim Acta*, 1998, **44(2-3),** 299-309; DOI:10.1016/S0013-4686(98)00060-7

2. Dalko P I and Moisan L, *Angew Chem., Int*., 2004, **43(39),** 5138-5175; DOI:10.1002/anie.200400650
3. Fuerst D E and Jacobsen E N, *J Am Chem Soc*., 2005, **127(25**), 8964-8965; DOI:10.1021/ja052511x
4. (a) Hoashi Y, Yabuta T, Yuan P, Miyabe H and Takemoto Y, *Tetrahedron*, 2006, **62(2-3),** 365-374; DOI:10.1016/j.tet.2005.08.109 (b) Hoashi Y, Okino T and Takemoto Y, *Angew Chem., Int Ed*., 2005, **44(26**), 4032-4035; DOI:10.1002/anie.200500459 (c) Okino T, Hoashi Y, Furukawa T, Xuenong X and Takemoto Y J, *Am Chem Soc*., 2005, **127(1**), 119-125; DOI:10.1021/ja044370p
5. (a) Wang J, Li H, Yu X, Zu L and Wang W, *Org Lett*., 2005, **7(19**), 4293-4296; DOI:10.1021/ol051822+ (b) Sohtome Y, Tanatani A, Hashimoto Y and Nagasawa K, *Tetrahedron Lett*., 2004, **45(43),** 5589-5592; DOI:10.1016/j.tetlet.2011.08.051
6. Joly G D, Jacobsen E N J, *Am Chem Soc*., 2004, **126(13**), 4102-4103; DOI:10.1021/ja0494398
7. Henderson W, Kemmitt R D W, Mason S, Moore M R, Fawcett J and Russell D R, *J Chem Soc., Dalton Trans*., 1992, **1**, 59-66; DOI:10.1039/DT9920000059
8. Eweis M, Elkholy S S and Elsabee M Z, *J Biol Macromol*., 2006, **38(1),** 1-8; DOI:10.1016/j.ijbiomac.2005.12.009
9. Ugur D, Florke U, Kulcu N and Arslan H, *Acta Cryst E*., 2003, **59,** 1345-1346.
10. Steele M R, Monti C, Gennari C, Piarulli U, Andreoli F, Vanthuyne N and Roussel C, *Tetrahedron: Asymmetry*, 2006, **17(6),** 999-1006; DOI:10.1016/j.tetasy.2006.03.008
11. Li Z, Liu Z, Liao Q X L, Wei Z B, Long L S and Jiang Y B, *Com Ren Chimie*, 2008, **11(1-2),** 67-72; DOI:10.1016/j.crci.2007.06.009
12. Bellec N, Lorcy D and Robert A, *Synthesis,* 1998, **10,** 1442-1446; DOI:10.1055/s-1998-2183
13. Lobana T S, S´anchez A, Casas J S, *J Chem Soc, Dalton Trans*., 1997, **22**, 4289-4300; DOI:10.1039/A703726K
14. El-Bahy G M S, El-Sayed B A and Shabana A A, *Vibrational Spectroscopy*, 2003, **31(1**), 101-107; DOI:10.1016/S0924-2031(02)00099-1
15. Gosavi R K and Rao C N R, *J Inorg Nucl Chem*., 1967, **29(8),** 1937-1945; DOI:10.1016/0022-1902(67)80453-6
16. Jensen K A and Nielsen P H, *Acta Chem Scand*., 1966, **20,** 597-629; DOI:10.3891/acta.chem.scand.20-0597
17. Yahyazadeh A and Ghasemi Z, *Eur Chem Bull*., 2013, **2(8**), 573-575; DOI:10.17628/ECB.2013.2.573
18. Stewart J E, *J Chem Phys*., 1957, **26**, 248-254.
19. Kashyap B C, Taneja A D and Banerji S M, *J Inorg Nucl Chem*., 1975, **37(2),** 612-615; DOI:10.1016/0022-1902(75)80397-6
20. Kashyap B C, Taneja A D and Banerji S M, *J Inorg Nucl Chem*., 1975, **37(6),** 1542-1544; DOI:10.1016/0022-1902(75)80813-X
21. Tucker I, Singh R P and Zacharias P S, *Indian J Chem*., 1979, **18A**, 60-61.
22. Satpathy K C, Mishra H P and Patel B N, *Indian J Chem*., 1992, **22A**, 338.
23. Andrea S, Tscheatschal F, Dietze F and Philip T, *J Prakt Chem*., 1991, **333,** 501.
24. Mishra L and Pandey A K, *Polyhedron,* 1992, **11,** 4243-4251.
25. Chavan M C, Deshpande V D and Vaida P V, *Asian J Chem*., 1992, **4(2**), 246-250.