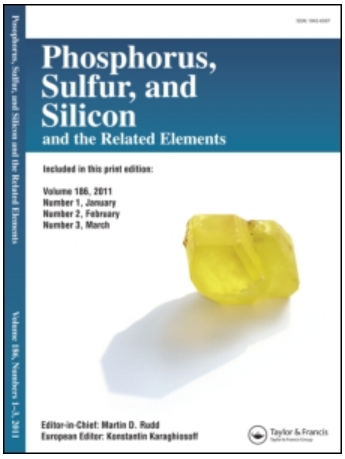


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SPECTRAL AND THERMAL CHARACTERIZATION OF DIVALENT TRANSITION METAL COMPLEXES WITH SOME TRIAZOLYLTHIOUREA DERIVATIVES

Hassan M. A. Salman[a]
[a] Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt

To cite this Article Salman, Hassan M. A.(2001) 'SPECTRAL AND THERMAL CHARACTERIZATION OF DIVALENT TRANSITION METAL COMPLEXES WITH SOME TRIAZOLYLTHIOUREA DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 173: 1, 193 — 209
To link to this Article: DOI: 10.1080/10426500108045269
URL: http://dx.doi.org/10.1080/10426500108045269

Phosphorus, Sulfur and Silicon, 2001, Vol. 173, pp. 193-209
Reprints available directly from the publisher
Photocopying permitted by license only

SPECTRAL AND THERMAL CHARACTERIZATION OF DIVALENT TRANSITION METAL COMPLEXES WITH SOME TRIAZOLYLTHIOUREA DERIVATIVES

HASSAN M.A. SALMAN*

Department of Chemistry, Faculty of Science, South Valley University, Qena 83523, Egypt

(Received November 11, 1999; In final form December 10, 2000)

The complexes of Co(II), Ni(II), Cu(II) and Cd(II) with N-ethyl, N′-(3-triazolyl)thiourea (L1), N-phenyl, N′-(3-triazolyl)thiourea (L2), and N-benzoyl, N′-(3-triazolyl)thiourea (L3) have been prepared. The structure of the complexes has been determined on the basis of elemental and thermal analyses, electronic spectra, IR spectral data as well as molar conductance measurements. Thiourea derivatives used were found to act as neutral bidentate ligands in the case of L1 and L2, while L3 acts as a neutral tridentate ligand. The complexes were found to be in a distorted octahedral or tetrahedral configuration.

Keywords: Transition metals; Complexes; Thiourea; Electronic spectra; IR spectra; Thermal analysis

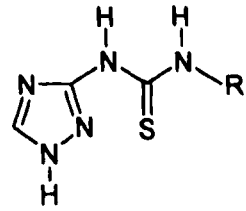
INTRODUCTION

Thiourea has proved to be an important reagent in many fields. It may be preferably used in silver recovery from photographic fixing baths [1] where the impregnation of thiourea to supporting material will release sulfide ions which react, in alkaline medium, with silver ions to produce black silver sulfide.

On the other hand, metal complexes contaning thiourea derivatives as ligands have found many applications. For example, catalysts for the

* Corresponding Author.

reduction of vat dyes [2], preparation of organometallic non-linear optical materials [3], extractive spectrophotometric determination of metal ions [4,5], plant virucides for voltammetric and polarographic determination of trace amounts of metal ions [6,7] and for determination of free bilirubin in blood or urine [8]. However, the literature contains only a few references [9,10] concerning metal complexes of thiourea derivatives having the benzoyl moiety as one substituent and an alkyl group as the other. Little is reported concerning thiourea derivatives involving a heterocyclic ring as one of the substituents [11–14]. No studies of metal complexes on thiourea derivatives involving both triazolyl and/or alkyl (aryl and benzoyl) moieties as substitutions on the same substrate are reported. It is thought, therefore, that it would be of interest to describe the divalent metal complexes of some triazolylthiourea derivatives. The thiourea derivatives used in the present investigation have the following structure:



Where,

R = CH_2CH_3; N-ethyl, N′-(3-triazolyl)thiourea (L1).
= phenyl; N-phenyl,N′-(3-triazolyl)thiourea (L2).
= benzoyl, N-benzoyl, N′-(3-triazolyl)thiourea (L3).

EXPERIMENTAL

Solvents and organic materials used in the present study were AR grade (BDH or Merck products). General purpose metal salts $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and anhydrous $CdCl_2$ were used.

Preparation of the organic ligands

3-amino-1,2,4-triazole (o.1 mole) was mixed with an equimolar amount of the appropriate isothiocyanate (ethylisothiocyanate (L1), phenylisothiocy-

anate (L2) and benzoylisothiocyanate (L3) in dry benzene (200 ml). The reaction mixture was refluxed, with stirring for one 1hr, and cooled to room temperature where a solid was separated. This was filtered, washed with dry benzene and recrystallized from absolute ethanol. The purity of the ligands was checked by IR spectra (cf. Table II) and elemental analysis. Results of elemental analyses were as follows:

L1 ($C_5H_9N_5S$) calculated % C 35.07, H 5.30, N 40.90, S 18.72;

Found % C 35.43, H 5.25, N 40.84, S 18.64;
m.p. 140–42 °C.

L2 ($C_9H_9N_5S$) calculated % C 49.30, H 4.14, N 31.94, S 14.62;

Found % C 49.64, H 4.10, N 31.85, S14.56;
m.p. 215–17 °C.

L3 ($C_{10}H_9N_5OS$) calculated % C 48.57, H 3.76; N 28.32, S 12.97;

Found % C 48.76, H 3.62; N 28.38, S 12.89;
m.p. 266 °C.

Synthesis of the solid complexes

The solid complexes were prepared by mixing together a hot ethanolic solution of the respective metal (II) salt (in 30 ml) and the ligand (in 25 ml) in appropriate molar ratio (i.e. 1:1 or 1:2 metal-ligand). All the complexes, which precipitated immediately or in stirring the reaction mixture for 15 min, were digested on a water bath for 30 min, cooled to room temperature whereby solid complexes were separated in a microcrystalline form. The solid complexes were filtered off, washed with ethanol and dried in *vacuo* over P_4O_8. The prepared complexes were analyzed for the C, H, N, S and Cl content. The data are given in Table I. All complexes were insoluble in water, sparingly soluble in common organic solvents but were soluble in DMF and DMSO.

Physical measurements

Electronic spectra were recorded on a Shimadzu 2401 PC spectrophotometer using 1cm matched quartz cell, FT-IR spectra (4000–200 cm^{-1}) were preformed on a Nicolet FT-IR 560 using the KBr disc technique. Conduc-

tivity measurements was carried out using a LF Digi conductance bridge. Thermal analysis experiments including thermogravimetry (TGA) and derivative therogravimetric analysis (DTG) were preformed using a Shimadzu Stand-Alone thermal analyzer (TGA-50H), Japan. The heating rate was 10°C/min in a dynamic atmosphere (40ml/min) of nitrogen. Spectral and conductivity measurements were carried at room temperature.

RESULTS AND DISCUSSION

The structures of the studied complexes were evaluated from their elemental analysis, molar conductance, spectroscopic (IR, UV-visible) and thermoanalytical data.

The analytical data, melting point, colour and molar conductance values of the prepared complexes are assembled in Table I.

Molar conductance values of 10^{-3} M DMF solutions of the different complexes lie in the range 8.60–58.20 Ohm^{-1} cm^2 mol^{-1}, except for the complexes Cu-L3 and Cd-L3 where their conductance values were 74.40 and 70.20, respectively. Since, it has been reported [15] that the reasonable range of 1:1 electrolytes in DMF is 65–90 Ohm^{-1} cm^2 mol^{-1}. Accordingly, solutions of the former complexes are non-electrolytes while the latter one are 1:1 electrolytes.

It is evident from elemental analysis, molar conductance values (cf. Table I) and thermal analysis given hereafter, that the divalent metal ion used form 1:1 and 1:2 (metal-ligand) complexes with ligands L1 and L2 (Cu gave only 1:1 complex with L1) having the following formulae:

$[MLCl_2].2H_2O$, $[M(L)_2Cl_2].2H_2O$ where L = L1 or L2, M = Co or Ni, $[CuLCl_2.2H_2O].H_2O$ where L= L1 or L2, $[Cu(L2)_2Cl_2]$ and $[CdLCl_2]$ where L= L1 or L2. Ligand L3, however, form only 1:1 complexes having the formulae:

$[ML3Cl_2.H_2O].nH_2O$ where M= Co or Ni and n = 2 or 4, respectively, $[CuL3Cl.2H_2O]Cl.2H_2O$ and [CdL3Cl]Cl.

All complexes are fairly stable at room temperature and can be stored for a long period.

TABLE I Analytical data, melting points, colour and molar conductance values of metal complexes of L1, L2 and L3

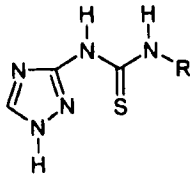
No.	Complex	M p.°C	Colour	Analysis (%) Calcd / Found				
				C	H	N	S	Cl
	Complexes of L1							
	$[Co(C_5H_9N_5S)Cl_2].2H_2O$	280[b]	Greenish black	17.79	2.69	20.77	9.51	21.06
				17.88	2.61	20.72	9.38	20.92
	$[Co(C_5H_9N_5S)_2Cl_2].2H_2O$	250[b]	Greenish black	23.61	3.57	27.56	12.62	13.96
				23.74	3.52	27.50	12.46	13.79
	$[Ni\ (C_5H_9N_5S)Cl_2].2H_2O$	>300	Bluish grey	17.81	2.69	20.78	9.51	21.07
				17.91	2.64	20.64	9.42	20.94
	$[Ni(C_5H_9N_5S)_2Cl_2].2H_2O$	>300	Grey	23.62	3.57	27.56	12.62	13.97
				23.85	3.49	27.44	12.56	13.87
	$[Cu(C_5H_9N_5S)Cl_2.2H_2O].H_2O$	230	Dark green	16.68	2.52	19.46	8.91	19.73
				16.83	2.47	19.40	8.82	19.83
	$[Cd(C_5H_9N_5S)Cl_2]$	250	White	16.92	2.56	19.75	9.04	20.02
				17.12	2.53	19.65	8.94	20.00
	Complexes of L2							
	$[Co(C_9H_9N_5S)Cl_2].2H_2O$	>300	Dark brown	28.04	2.36	18.18	8.32	18.43
				28.23	2.32	17.94	8.30	18.47
	$[Co(C_9H_9N_5S)_2Cl_2].2H_2O$	>300	Dark brown	35.75	3.00	23.17	10.61	11.75
				35.90	2.94	23.01	10.56	11.93
	$[Ni(C_9H_9N_5S)Cl_2].2H_2O$	>300	Pale Blue	28.06	2.36	18.20	8.33	8.45
				28.13	2.30	17.95	8.13	8.40
	$[Ni(C_9H_9N_5S)_2Cl_2].2H_2O$	>300	Blue	35.76	3.00	23.18	10.61	11.75

No.	Complex	M p.°C	Colour	Analysis (%) Calcd / Found				
				C	H	N	S	Cl
				35.83	2.95	22.97	10.60	11.56
	$[Cu(C_9H_9N_5S)Cl_2.2H_2O].H_2O$	240[b]	Dark green	26.49	2.23	17.17	7.86	17.41
				26.69	2.19	17.00	7.68	17.38
	$[Cu(C_9H_9N_5S)_2Cl_2]$	200–3	Dark green	37.70	3.17	24.45	11.19	12.39
				37.85	3.00	24.41	11.07	12.20
	$[Cd(C_9H_9N_5S)Cl_2]$	>300	White	26.82	2.25	17.40	7.96	17.63
				26.94	2.21	17.28	7.85	17.52
	Complexes of L3							
	$[Co(C_{10}H_9N_5OS)Cl_2.\ H_2O].2H_2O$	>300	Grey	27.84	2.10	16.24	7.44	16.47
				28.18	1.98	16.19	7.37	16.40
	$[Ni(C_{10}H_9N_5OS)Cl_2.H_2O].4H_2O$	250[b]	Pale yellow	25.70	1.94	15.00	6.87	15.21
				25.80	1.90	14.88	6.82	15.05
	$[Cu(C_{10}H_9N_5OS)Cl.2H_2O]Cl.2H_2O$	290	Green	26.45	2.00	15.44	7.07	15.65
				26.63	2.02	15.33	7.00	15.53
	$[Cd(C_{10}H_9N_5OS)Cl]Cl$	>300	White	27.87	2.11	16.26	7.45	16.49
				28.02	2.10	16.15	7.32	16.34

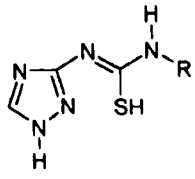
$^{-1}$ cm^2 mol^{-1}.
posed.
le in DMF.

IR Spectra of the ligand and their metal complexes

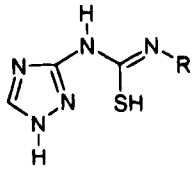
The IR spectra of the thiourea derivatives, in general, are quite complicated where many absorption bands resulted from mixed vibrations [12, 16–19]. On the other hand, the ligands used (L1 and L2) can exist in the ketothione (I) and thiol (II) and (III) tautomeric forms such as:



(I)



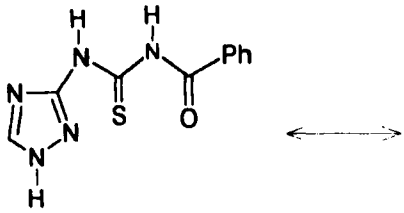
(II)



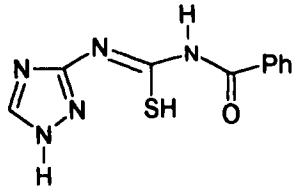
(III)

Where, R = CH_2CH_3, L1; R = ph, L2.

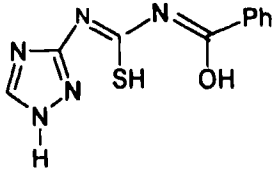
Whereas ligand L3 can exist in the following tautomeric forms:



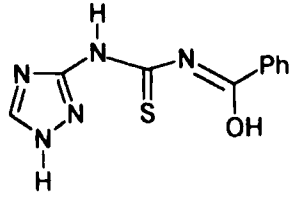
Ketothione (a)



Ketothiol (b)



Enolthiol (d)



Enolthione (c)

However, the IR spectra provide ample evidence in favour of the existence of both the free ligands and the complexed ligands in the ketothione (I) in case of L1 and L2 and ketothione (a) in case of L3. In the high frequency region, the spectra of all the free ligands lack any absorption band neither near 3500 cm^{-1} nor around 2500 cm^{-1}. Only a structured band due to υNH + υCH (aliphatic in case of L1 and aromatic in case of L2 and L3) appeared in the range 3405–3075 cm^{-1}. This rules out any possibility of finding -OH or -SH stretching vibration. Also, a strong band due to C=O (in case of L3) has appeared at 1705 cm^{-1} and a well recognized band in the region 795–747 cm^{-1} due to C=S [12] in all the free ligands under investigation.

In the IR spectra of the complexes of L3, the carbonyl stretching vibration was found to acquire a marked shift towards lower frequency (cf. Table II). This behavior indicates a decrease in the bond order of the C=O group as a result of coordination of the oxygen atom to the metal ion.

The cyclic C=N band stretching vibration, occurred at 1570, 1574, and 1601 cm^{-1} in the free ligands L1, L2 and L3, respectively. It was found to acquire an appreciable shift towards higher frequency in the IR spectra of the complexes due to metal to ligand π-electron interaction [20]. The band appeared at 1510, 1520 and 1519 cm^{-1} in the spectra of the free ligands L1, L2 and L3, respectively, which is attributed to NCN vibration [21] is shifted also to higher frequencies in the spectra of of the complexes. This could be due to the increased double bond character of the C-N bond because of the coordination of the sulfur atom to the metal ion. The C=S band is located at lower frequency in the spectra of the complexes relative to its position in the spectra of all the free ligands. This behavior can be considered as convincing evidence for the coordination of the ketothione form (structure (I) in case of L1 and L2 and structure (a) in case of L3) to metal ion [22]. Furthermore, the increase in frequency of υ(NCN + C-S) band upon complexation is in agreement with electronic shift HN-C=S → M due to the coordination of the ligand through its thiocarbonyl sulfur atom [23].

The cyclic N-N stretching vibration occurred at 983, 978 and 920 cm^{-1} in the spectra of the free ligands L1, L2 and L3, respectively, has been considerably weakened and shifted towards lower values (cf. Table II) in the complexes. This may be attributed to electronic donation of N2 of triazole ring to the metal ion [24]. This is expected to produce a weakness in the N-N bond.

TABLE II Relevant IR spectra of the ligands and their metal complexes

Free Ligands	*Complexes*				*Assignments*
	Co(II)	*Ni(II)*	*Cu(II)*	*Cd(II)*	
L1					
3400–3075	3390–3152	3386–3153	3409–3158	3343–3151	υNH
1605	1600	1600	1605	1608	δNH
1570	1548	1544	1558	1548	υC=N Triazole ring
1510	1526	1519	1508	1548	υNCN
1389	1420	1420	1432	1413	(υNCN + υC–S)
983	975	970	970	972	υN-N ring
747	728	744	712	727	υC=S
L2					
3390–3138	3390–3134	3391-3138	3461–3130	3512–3149	υNH
1600	1601	1603	1593	1604	δNH
1574	1580	1590	1590	1577	υC=N triazole ring
1520	1537	1557	1546	1548	υNCN
1390	1406	1414	1415	1398	(υNCN + υC–S)
978	964	968	970	965	υN–N ring
778	758	757	755	769	υC=S
L3					
3405-3291	3403-3290	3399–3285	3402–3275	3414–3288	υNH
1705	1692	1693	1698	1688	υC=O
1663	1659	1657	1659	1655	δNH
1601	1599	1599	1600	1599	υC=N
1519	1555	1559	1556	1549	υNCN
1388	1411	1410	1413	1410	(υNC + υC–S)
920	900	902	900	905	υN-N ring
795	787	788	786	788	υC=S

Based on the foregoing discussion, we can conclude that the ligands L1 and L2 behave as neutral bidentate donors and bonding sites are the thione sulfur and N2 atom of the triazole ring. Ligand L3, on the other hand, behaves as a neutral tridentates donor and the bonding sites are the thione sulfur, the carbonyl oxygen and the N2 atom of the triazole ring.

In the complexes 5, 11, 14, 15 and 16, the presence of coordinated water molecules has been confirmed [25] by the appearance of three bands in the range 704–735, 433–466 and 360–375 cm^{-1} which can be assigned to the rocking, wagging and MO stretching modes, respectively.

On the other hand, in the complexes 1–4 and 7–10, the above vibrational stretching modes of corresponding coordinated water molecules do not appear and therefore, could be ascribed as hydration water molecules.

Electronic spectra

The electronic spectra of DMF solutions of the isolated solid complexes have been measured in the wavelength range 250–800 nm. The obtained υ_{max} and ε_{max} values are given in Table III. The complexes displayed one strong band with υ_{max} in the range 32,362–37,174 cm^{-1} due to intraligand electronic transition, mainly π-π^* transition. The bands having υ_{max} in the range 20,052–27,777 cm^{-1} are attributable to a ligand to metal charge transfer (LMCT), mainly S $\rightarrow$ M. These bands, based on the energy and the relative intensity considerations [26], are divisible to two main types, namely $\pi S \rightarrow M$ and $\sigma S \rightarrow M$ [27, 28] charge transfer. The CT bands of relatively lower energy are assigned to $\pi S \rightarrow M$ and those relatively higher energy are due to $\sigma S \rightarrow M$ charge transfer.

All complex solutions, except those of Cd (II), displayed a low intensity band in the low energy region due to d-d electronic transition. 1:1 Co (II) complexes displayed a weak band in the range 14,948–15,360 cm^{-1}. This band is assignable to $^4A_2 \rightarrow {}^4T_1(F)$ transition of tetrahedral Co(II) complexes [26]. However, 1:2 Co(II) complexes displayed a band in the range 15,292- 15,385 cm^{-1}. This band is due to d-d electronic transition within the Co(II) chelates and lies in the range reported [26] for six-coordinated Co(II) complexes. The position of this band suggestive for a distorted octahedral geometry around Co(II) ion. Therefore, this band can be assigned to transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.

The $[NiL2Cl_2].2H_2O$ complex comprised a band at 16,584 cm^{-1}. This band may be ascribed as $^4A_2 \rightarrow {}^4T_1(P)$ transition of tetrahedral Ni(II). The $[Ni(L2)_2Cl_2].2H_2O$ and the $[NiL3Cl_2.H_2O].4H_2O$ complexes showed a band at 17,391 and 17,857 cm^{-1}, respectively. This is assigned for $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (F) of six-coordinated Ni(II) [29]. The six-coordinated Cu(II) complexes (12, 13 and 17) displayed a broad band similar to that reported [30] for the distorted octahedral Cu(II) complexes.

TABLE III Electronic spectra data of DMF solutions of the different metal complexes

Complex No.	*Complex*	*Intraligand band*		*LMCT band*		*d-d band*	
		$\upsilon_{max}{}^a$	$(\varepsilon_{max})^b$	$\upsilon_{max}{}^a$	$(\varepsilon_{max})^b$	$\upsilon_{max}{}^a$	$(\varepsilon_{max})^b$
1	Co(L1)	36,496	(5,000)	22,472sh	(301)	16,475 14,970	(279) (319)
2	$Co(L1)_2$	37,174	(5,000)	22,573sh	(597)	16,503 15,385	(432) (446)
5	Cu(L1)	36,496	(4,820)	27,933	(837)	15,267	(55)
6	Cd(L1)	36,496	(3,860)	23,419	(103)	-----	-----
7	Co(L2)	32,787	(4,040)	21,052sh	(1,338)	16,779 15,360	(738) (558)
8	$Co(L2)_2$	34,843	(3,970)	20,833sh	(1,120)	16,793 15,291	(605) (459)
9	Ni(L2)	32,362	(3,790)	22,222	(207)	16,584	(95)
10	$Ni(L2)_2$	32,787	(4,040)	21,276	(259)	17,391	(147)
11	Cu(L2)	32,787	(3,920)	27,777sh	(594)	17,857	(90)
12	$Cu(L2)_2$	32,787	(3,970)	27,777sh	(932)	17,857	(143)
13	Cd(L2)	35,336	(3,820)	24,390	(113)	-------	-----
14	Co(L3)	36,765	(3,402)	22,988sh	(191)	16,502 14,948	(118) (125)
15	Ni(L3)	35,842	(3,703)	25,000sh	(331)	17,857	(103)
16	Cu(L3)	36,364	(3,703)	24,390sh	(150)	17,241 14,706 12,578	(21) (27) (33)
17	Cd(L3)	36,630	(3,641)	23,809sh	(32)	-----	-----

a. υ_{max}, cm^{-1}.
b. ε_{max} in $cm^2\ mol^{-1}$.

TABLE IV TGA data for the different metal complexes

No.	Complex	Weight loss %		Temp. range °C (T_{max} °C)		Change
		Calc.	Found			
	$[Co(L1)Cl_2].2H_2O$	10.68	9.68	25–141	(80)	Loss of two hydration H_2O molecules
		25.86	25.27	141–398	(296)	Loss of one CH_3CH_2NCS molecule
	$[Co(L1)_2Cl_2].2H_2O$	7.08	6.65	38–168	(75)	Loss of two hydration H_2O molecules
		34.28	29.70	168–399	(267)	Loss of two CH_3CH_2NCS molecules
	$[Ni(L1)Cl_2].2H_2O$	10.68	8.58	32–119	(82)	Loss of two hydration H_2O molecules
		25.86	26.51	119–395	(306)	Loss of one CH_3CH_2NCS molecule
	$[Ni(L1)_2Cl_2].2H_2O$	7.08	7.22	32–118	(81)	Loss of two hydration H_2O molecules
		34.29	30.84	118–399	(291)	Loss of two CH_3CH_2NCS molecules
	$[Cu(L1)Cl_2.2H_2O].H_2O$	5.00	6.19	32–230	(223)	Loss of one hydration H_2O molecules
		10.00	9.66	230–260	(246)	Loss of two coordinated H_2O molecules
	$[Cd(L1)Cl_2]$	-----	1.13	26–208	(202)	Decomposition of ligand
		-----	1.07	208–258	(238)	Decomposition of ligand
	$[Co(L2)Cl_2].2H_2O$	9.35	9.12	25–150	(82)	Loss of two hydration H_2O molecules
		26.77	30.92	150–398	(272)	Loss of one benzonitrile molecule
	$[Co(L2)_2Cl_2].2H_2O$	5.95	5.64	32–147	(80)	Loss of two hydration H_2O molecules
		34.07	33.88	147–395	(242)	Loss of two benzonitrile molecules

$[Ni(L2)Cl_2]2H_2O$	9.36	10.83	35–156	(85)	Loss of two hydration H_2O molecules
	26.78	25.19	156–386	(288)	Loss of one benzonitrile molecule
$[Ni(L2)_2Cl_2].2H_2O$	5.95	5.41	38–145	(83)	Loss of two hydration H_2O molecules
	34.13	35.39	145–266	(221)	Loss of two benzonitrile molecules
$[Cu(L2)Cl_2.2H_2O].H_2O$	4.41	3.61	25–145	(73)	Loss of one hydration H_2O molecule
	8.83	9.27	145–312	(200)	Loss of two coordinated H_2O molecules
$[Cu(L2)_2Cl_2]$	-----	1.40	26–238	(203)	Decomposition of ligand
	-----	0.58	238–295	(243)	Decomposition of ligand
$[Cd(L2)Cl_2]$	37.74	39.99	241–398	(259)	Loss of one phenylthiourea molecule
$[Co(L3)Cl_2.H_2O].2H_2O$	12.26	11.94	30–240	(236)	Loss of three H_2O molecules
	-----	16.78	240–397	-----	Decomposition of ligand
$[Ni(L3)Cl_2.H_2O].4H_2O$	19.27	20.32	31–257	(247)	Loss of five H_2O molecules
	-----	12.73	257–385	-----	Decomposition of ligand
$[Cu(L3)Cl.2H_2O]Cl.2H_2O$	15.89	15.92	31–245	(243)	Loss of four H_2O molecules
	35.98	20.94	245–296	(274)	Loss of one Benzoylisothiocyanate
		12.17	296–361	(348)	molecule or decomposition of ligand.
[Cd(L3)Cl]Cl	-----	21.60	24–289	(284)	Decomposition of ligand.
	-----	27.05	289–383	(318)	Decomposition of ligand.

perature of maximum rate of weight loss.

Thermal analysis

Thermogravimetric analysis (TGA) has been performed to the prepared complexes to verify the amount of water molecules that exist in such complexes as well as the way by which they are attached. The calculated and experimental percentage weight losses, along with the corresponding changes, the temperature range and T_{max} (temperature of maximum rate of weight loss) are given in Table IV. The water content in these complexes was consistent with the proposed formula according to the elemental analysis.

The Co(II) and Ni(II) complexes containing both L1 and L2 displayed two successive weight loss steps (cf. Table IV). The first step, in each case, was equivalent to the loss of two hydration water molecules. The second step, however, was equivalent to the loss of one or two ethylisothiocyanate molecules (in case of L1 complexes) depending on the stoichiometry of the complex i.e. one molecule for 1:1 complex and two molecules for 1:2 complex. On the other hand, the complexes containing L2, the weight loss in this step agreed with the loss of one or two benzonitrile molecules depending on the stoichiometry of the complex.

The $[CuL1Cl_2.2H_2O].H_2O$ and $[CuL2Cl_2.2H_2O].H_2O$ complexes displayed two weight loss steps. The first step is due to the loss of one hydration water molecule while the second step is due to the loss of two coordinated water molecules. The calculated weight loss was in accordance with the actual results (cf. Table IV). The TG of $[Cu(L2)_2Cl_2]$ showed no weight loss up to the melting point (200–3 °C). This is in harmony with the molecular formula given in Table I and indicates that this complex does not contain water molecules. TG of $[CuL3Cl.2H_2O]Cl.2H_2O$ displayed three weight loss steps which are accompanied by 15.92, 20.94 and 12.17 % weight loss, respectively. The first at a temperature range 31–245 °C (T_{max} = 243 °C) is due to the loss of four water molecules (the calculated weight loss is 15.89 %). The second and third steps, which appeared between 245–296 and 296–361 °C, are slow with a total weight loss amounting to 34.11 %. These two steps could be attributed to either the loss of one benzoylisothiocyanate molecule (the calculated weight loss equals 35.98 %) or decomposition of the ligand.

TG of Co(II) complex containing L3 displayed two weight loss steps, which are associated with 11.94 and 16.78 % weight loss. The first step represents the loss of three water molecules (between 30–240 °C, T_{max} at

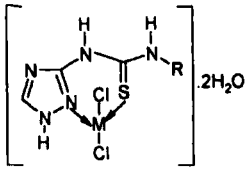
236 °C and weight loss 12.26 %). The second step is due to decomposition of the ligand (between 240–397°C). TG of $[NiL3Cl_2.H_2O].4H_2O$ showed two weight loss steps. The first is due to the loss of five water molecules (31–257 °C, T_{max} = 247 °C). The weight loss (20.32 %) is in accordance with the theoretical calculations (19.27 %). The second step may represents the decomposition of the ligand (257–385 °C).

TG of the two Cd(II) complexes containing both L1 and L3 displayed, in each case, two weight loss steps at relatively high temperature (T_{max} varied between 202–318 °C). These two steps in each complex are due to decomposition of the ligand and indicate that both complexes are anhydrous. On the other hand, TG of $[CdL2Cl_2]$ complex showed a slow weight loss step at relatively high temperature (241–398 °C, T_{max} at 259 °C) associated with 39.99 % weight loss. This step may corresponds to the loss of one phenylthiourea molecule (the calculated weight loss is 37.74 %). This is consistent with the molecular formula (see Table I) and indicates that complex does not contain water molecule i.e. anhydrous.

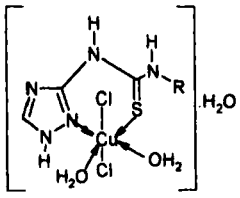
Finally, form the IR results and the above discussions, the following structures are proposed for the various complexes.

References

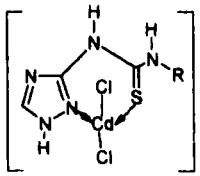
[1] G. Pollakowski and J.A. Keiler, Ger. (East) DD238, 276 (1986), Chem. Abstr. 106 (1987) 130944d.
[2] N.N. Proskina, M.I. Stolbyrya, G.E. Krichevskii, N.E. Bulusheva, T.N. Fioletova, Zoltan Farkas and I.N. Safonova, USSR SU, 1,198 08 (Cl. CO7F15/06) 15, Dec. (1985) Chem. Abstr. 106 (1987) 39227m.
[3] Guangcai Xing, Minhua Jaing, Zongshu Shao and Dong Xu, Zhongguo Jiguang, 14 (1987) 302.
[4] E. Kavlentis, Microchem. J., 36 (1987) 306.
[5] Eva A. Terpinski, Analyst (London), 113 (1988) 1473.
[6] V.N. Kiryushov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser Khim. Nauk, 97 (1989) 101.
[7] G.D. Levitskaya, L.Z. Dubas and I.I. Kachmarskaya, Zh. Anal. Khim, 44 (1989) 311.
[8] Yositaka Takahashi, Fujio Shimizu, Jpn. Kokai Tokkyo Koho Jp 63, 118, 662 [88, 118, 662] (1988), Chem. Abstr., 110 (1989) 72158v.
[9] E. Chruscinska and J. Maslowska, J. Therm. Anal., 32 (1987) 1323.
[10] M. Doering, E. Uhlig, V.I. Nefedov and I.V. Salyn, Z. Anorg. Allg., Cem 556, (1988) 213.
[11] K.C. Satpathy, H.P. Mishra and R. Mishra, J. Inorg. Nucl. Chem., 43 (1981) 2765.
[12] K.L. madhok, Polyhedron, 6 (1987) 1807.
[13] S. A. El-Gyar, H. M. Salman, Z.A. Khafagi, Bull. Fac. Sci. Assiut Univ., 22(1-B) (1993) 17.
[14] M. S. Saleh and Z.A. Khafagy, AFINIDAD LIV, 468 (1997) 147.
[15] W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
[16] A.C. Fabetti, G. Peyronel, A. Gjusti and A.F. Zanoli, polyhedron, 2 (1983) 475.
[17] C. P. Pandey, Inorg. Chim. Acta, 118 (1986) 105.



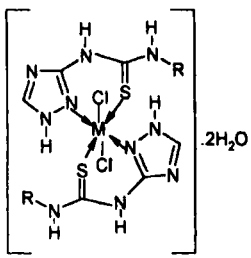
1:1 (Metal-ligand) complexes
M = Co(II) or Ni(II)
R = CH_2CH_3, L1 ; = ph, L2.
(1, 3, 7 and 9)



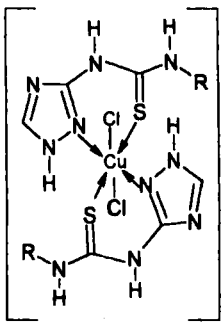
(5,11)



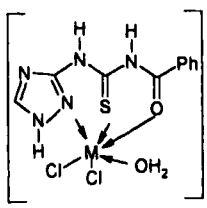
(6,13)



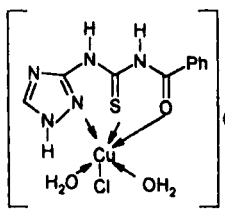
1:2(Metal-ligand) complexes
M = Co(II) or Ni(II)
R = CH_2CH_3, L1; R = ph, L2.
(2, 4, 8 and 10)



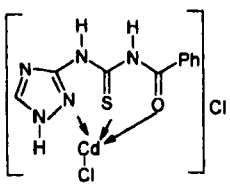
R = ph , L2
(12)



1:1(M-L3) complexes
M = Co , n = 2, **(14)**
M = Ni , n = 4 ,**(15)**



(16)



(17)

[18] F.D. Rochon, J. Bariyanga and C. Chervrotiere DELA, Inorg. Chim. Acta, 132 (1987) 91.
[19] F.D. Rochon, J. Bariyanga and P.C. Kong, Can. J. Chem., 63 (1985) 2425.
[20] H.M. Kandall, J. L. N. Fuson, R. G. Fowler and J. R. Dangl, Infrared Determination of Organic Structure, Van Mostrand, New York, 1949, p. 213.
[21] G.B. Aitken, J.L. Duncan and G.P. McMillan, J. Chem. Soc., (1971) 2695.
[22] K.C. Satpathy and H..P. Mishra, Ind. J. Chem., 20A (1981) 612.
[23] A.C. Fabretti and A. Giusti, Polyhedron, 5 (1986) 1927.

[24] J. Martinez, A. Martinez, M.L. Cuenca and A. Doadrio López, Synth. React. Inorg. Met. -Org. Chem., 18(9) (1988) 881.
[25] K. Nakamoto, Infrared and Raman Spectra of Inorganic and coordination Compounds, 3rd. Ed. Wiley Interscience, New York, 1978, 226.
[26] A.B.P. Lever, Inorganic Electronic Spectroscopy, 4th. Ed. Elsevier, Amsterdam, 1984.
[27] C.K. Jørgensen, Prog. Inorg. Chem., 12 (1970) 101.
[28] A.R. Amundsen, J. Whelan and B. Bosnich, J. Am. Chem. Soc., 99 (1977) 6730.
[29] L. Sacconi, Transition Metal Chemistry, Edited by R.L. Carlin, Marcel Dekker, New York, 4, 1968, p. 199.
[30] K.C. Patel and D.E. Goldberg, J. Inorg. Nucl. Chem., 34 (1972) 637.