

## Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) Complexes with Multidentate Schiff Bases

Kawakeb A. Aziz

Department of Chemistry / College of Science  
University of Mosul

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$[M(L)_2 \cdot 2H_2O]X_2$

Cu(II)=M )  $[M(L)_2Cl_2]$   $[NO_3^-$  Cl=X Ni(II) Co(II)=M]  
)  
=L  $[Cd(L)_2](NO_3)_2$  ( Hg(II) Zn(II)  
-ñ)- -3- -2 ( -2 - 3,2  
-2- -ñ)- -3- -2,1- --2 (atc) ( -2-  
. (atb) (

Zn(II) Cu(II) Ni(II) Co(II)

.Cd<sup>+2</sup>

Hg(II) Cd(II)

### Abstract

Complexes of the type  $[M(L)_2 \cdot 2H_2O]X_2$  (where M=Co(II) or Ni(II), X=Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>),  $[M(L)_2Cl_2]$  (where M=Cu(II), Zn(II) or Hg(II)) and  $[Cd(L)_2](NO_3)_2$  where L= multidentate Schiff bases ligands (resulted from the condensation of 2,3-butandione or benzil with 2-aminothiazole) 2-oxo-3-imino-(N-thiazole-2-yl) butane (atc) and 1-oxo-1,2-diphenyl-2-imino-(N-thiazole-2-yl) ethane (atb), have been prepared and characterized by elemental analysis, spectral (Infrared, and U.V./Visible), magnetic data and conductivity measurements.

The ligands have been acted as bidentate with Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and tridentate with Cd (II) ions. The prepared complexes had hexacoordinated with octahedral geometries.

## Introduction

Although the subject of Schiff bases has been extensively studied<sup>(1)</sup>, their transition and non-transition metal complexes have been still found to be of great interest in coordination chemistry<sup>(2,3)</sup>, since they exhibited interesting variety of stereochemical behaviors and biochemically relevant studies of metal complexes and found a wide range of applications<sup>(4,7)</sup>.

Schiff bases of hetrocyclic moiety like trizine, pyridine, thiazole have great interest of many authors<sup>(8,9)</sup>, because they possess interesting biological activity due to the strong aromaticity of their ring system, which leads to great in vivo stability<sup>(10)</sup>.

The present study describes the synthesis and characterization of six metal complexes (Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)) with Schiff's bases derived from 2-aminothiazole with 2,3-butanedione and benzil in methanol.

## Materials and Methods

### Analysis and physical measurements:

The complexes and the ligands were analyzed for carbon, hydrogen and nitrogen using an 1106 (Carlo Erba) micro analyzer. Conductance measurements of the complexes were carried out at room temperature ( $\approx 300\text{k}$ ) in DMSO solution ( $10^{-3}\text{M}$ ) with a conductivity meter model 4070 (JENWAY). Magnetic measurements were made at room temperature by the Faraday method using Bruker B.M.6. Infrared absorption spectra have been recorded using a Unicam SP-2000 spectrophotometer as KBr discs in the range ( $200\text{-}4000\text{ cm}^{-1}$ ). The electronic spectral measurements were recorded using Shimadzu U.V./visible spectrophotometer ( $200\text{-}1100\text{nm}$ ), model 160 Shimadzu (Japan), using DMSO as a solvent.

All the chemicals were of Analar grade (B.D.H, Aldrich or Fluka) used as supplied

### Preparation of Schiff base ligands

#### 1) 2-oxo-3-imino-(N-thiazole-2-yl) butane (atc):

It has been prepared by mixing (2.0 gm, 0.02 mole) 2-aminothiazole with (1.72 gm, 0.02 mole) 2,3-butanedione in methanol and the mixture was refluxed for 1 hr. on a water bath. The hot solution was poured into ice cold water, brown crystalline precipitate of the Schiff base was separated out. It has been filtered off, washed with methanol and dried in vacuum.

## 2) 1-oxo-1,2-diphenyl-2-imino-(N-thiazole-2-yl) ethane (atb)

It has been prepared as above with the following quantities (2.0 gm, and 0.02 mole) of 2-amino thiazole and (4.12 gm, 0.02 mole) of benzil.

### Preparation of the complexes:

The metal salt was dissolved in a minimum amount of methanol. The ligand was also dissolved in a minimum amount of methanol (Table 1). The two solutions were mixed with continuous stirring until the product appears. The resulting mixture was filtered, washed with petroleum spirit b.p.= (60-80°) and dried under vacuum for several hours.

### Results and Discussion

The molar conductance values (Table1) of the complexes  $[M(L)_2Cl_2]$  (where M=Cu(II),Zn(II),Hg(II)) in DMSO were below  $10 \Omega^{-1} cm^{-2} mol^{-1}$ , indicating non-electrolytic behavior. Where as the conductivity of the complexes  $[M(L)_2.2H_2O]Cl_2$  (where M=Co(II),Ni(II)) and  $[Cd(L)_2](NO_3)_2$  were in the range  $(70.5-90.3 \Omega^{-1} cm^{-2} mol^{-1})$  indicating a (1:2) electrolyte revealing the ionic character of these complexes.<sup>(11)</sup>

The magnetic moment values (Table2) showed the presence of three, two and one unpaired electrons for the Co (II), Ni (II) and Cu (II) complexes, respectively.<sup>(12-15)</sup>

The IR spectra of the Schiff bases (Table3) showed characteristic bands in the region  $(1675, 1665 cm^{-1})$ ,  $(1655, 1650 cm^{-1})$  and  $(1530 cm^{-1})$  which were assigned to carbonyl group, imine group and  $\nu_{C=N_{ring}}$  (in atc and atb ligands), respectively.<sup>(16-19)</sup>

The values of  $\nu_{C=O}$ ,  $\nu_{C=N_{ring}}$  bands (Table3) showed that  $\nu_{C=O}$  is shifted towards lower frequency by  $(55-50 cm^{-1})$  for atc complexes and by  $40-50 cm^{-1}$  for atb complexes), also  $\nu_{C=N_{ring}}$  is shifted towards lower frequency by  $(50-55 cm^{-1})$  for atc complexes and by  $50-55 cm^{-1}$  for atb complexes) respectively. While  $\nu_{C=N}$  frequency did not change. These observations indicated that Co(II), Ni(II) and Cu(II) complexes of both ligands occurred through carbonyl oxygen and thiazole ring nitrogen.

Thus these metals were preferred the more base nitrogen although 7-membered ring is formed.<sup>(20)</sup>

For Zn (II), Hg (II) complexes the  $\nu_{C=N}$  and  $\nu_{C=N_{ring}}$  were shifted to lower frequencies by  $(45-60 cm^{-1})$  for atc complexes and by  $50 cm^{-1}$  for atb complexes)  $(55-60 cm^{-1})$  for atc complexes and by  $45-50 cm^{-1}$  for atb complexes) respectively, indicated that the coordination took place through two nitrogen, while  $\nu_{C=O}$  band was not shared in the coordination.<sup>(21)</sup>

For the Cd (II) complexes  $\nu_{C=O}$ ,  $\nu_{C=N}$ , and  $\nu_{C=N_{ring}}$  were shifted to lower frequencies by (50, 65, 50  $\text{cm}^{-1}$  for atc complexes and 40,60,50  $\text{cm}^{-1}$  for atb complexes) respectively, indicating that the coordination occurred through (O, N,  $N_{ring}$ ).<sup>(16-19)</sup>

New bands were observed in the IR spectra of all the complexes at (450-475 $\text{cm}^{-1}$ ), (410-430 $\text{cm}^{-1}$ ), (265-285 $\text{cm}^{-1}$ ) and (290-315 $\text{cm}^{-1}$ ) corresponding to  $\nu_{M-O}$ ,  $\nu_{M-N}$ ,  $\nu_{M-N_{ring}}$  and  $\nu_{M-Cl}$  stretching vibration respectively.<sup>(22-26)</sup>

The absorption bands of  $M-N_{ring}$  group for atc complexes were in the range (265-285  $\text{cm}^{-1}$ )<sup>(16,27)</sup>, whereas the expected regions for  $\nu_{M-N_{ring}}$  of the atb complexes with their metals appeared at a point lower than (220  $\text{cm}^{-1}$ )<sup>(28,29)</sup>. These bands could not be noticed practically because they are near the end of the used instrument range.

The stretching vibration rocking and wagging of the water in the complexes  $[M(L)_2 \cdot 2H_2O]X_2$  have been observed at (760-790  $\text{cm}^{-1}$ ) and (640-650  $\text{cm}^{-1}$ ), respectively, where as  $\nu_{M-OH_2}$  band have been appeared in the region (400-410 $\text{cm}^{-1}$ ), indicated that the water molecule coordinated with central metal ion<sup>(30,31)</sup>(Table 4).

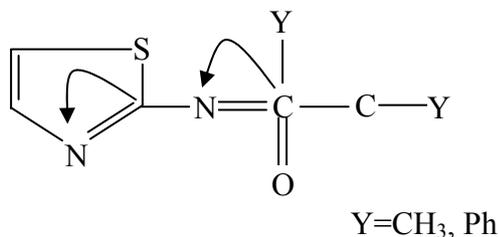
The electronic spectra of Co (II) complexes (Table2), showed two bands at (15800, 16242  $\text{cm}^{-1}$ ) and (19640, 19474  $\text{cm}^{-1}$ ) assigned to  ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)(\nu_2)$  and  ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(p)(\nu_3)$  transitions respectively.  $(\nu_1){}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$  transition has been calculated mathematically it was in the region (7370, 7572  $\text{cm}^{-1}$ )<sup>(32-36)</sup>, Ni(II) complexes exhibited three absorption bands at (9037, 9788  $\text{cm}^{-1}$ ), 14890,14848 $\text{cm}^{-1}$  and 25777,23148  $\text{cm}^{-1}$  attributed to  ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)(\nu_1)$ ,  ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)(\nu_2)$  and  ${}^3A_{2g} \longrightarrow {}^3T_{1g}(p)(\nu_3)$  transitions<sup>(16,32,34,37)</sup>, respectively.

One broad band was observed in case of Cu (II) complexes at (15347 and 15198  $\text{cm}^{-1}$ ) region. This broad band belongs to  ${}^2E_g \longrightarrow {}^2T_{2g}$  transition, indicating octahedral configuration for these complexes.<sup>(24, 25)</sup>

## Conclusions:

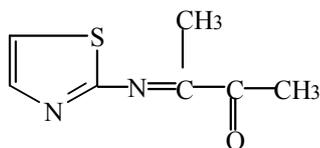
Different modes of interactions of metal ions with the donor sites of the ligands would occur, which may be depends on the ionic size of the metals. Zinc and mercury complexes coordinated through the two nitrogen forming 4-membered rings (Figure 5). Cadmium coordinated through the three active sites of the ligands forming 5 and 4-membered rings (Figure 6). While in Co (II), Ni (II), and Cu (II) complexes, the metal ions coordinated through carbonyl oxygen and thiazole nitrogen as supported by IR spectroscopic data (Table 3), but this result in 7-membered ring (Figure 3, 4) which are rarely occurred. This may be

depends on the basicity of the donor atoms in which the imine nitrogen seems to be the lowest one<sup>(20)</sup>. The thiazole nitrogen is more basic than imine nitrogen since it belongs to the thiazole group<sup>(21)</sup>, because the coordination through the thiazole nitrogen pulls the electronic density from C=N bond of the ring as well as the azomethine nitrogen<sup>(38)</sup> as explained below:

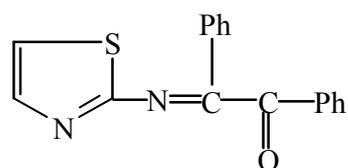


For Co (II) and Ni (II) complexes the molar absorptivity values, position of absorption band and magnetic moment values indicated high spin octahedral geometry.

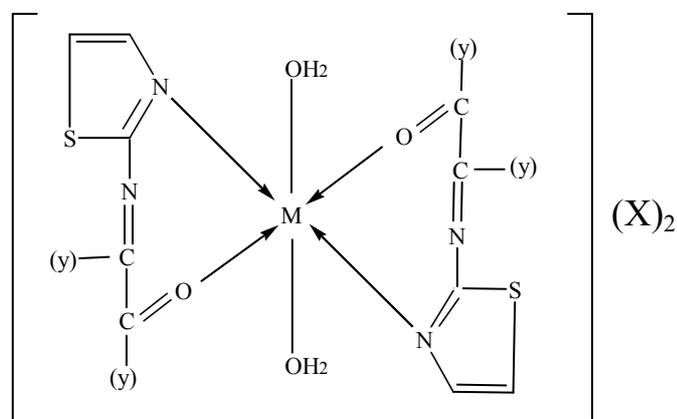
All metals complexes that have been studied indicated six coordinated and had an octahedral environment around the metal ions.



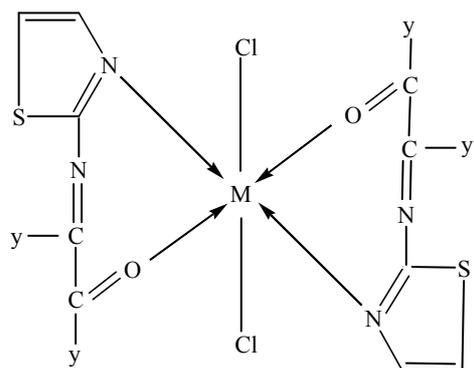
(Figure 1) atc



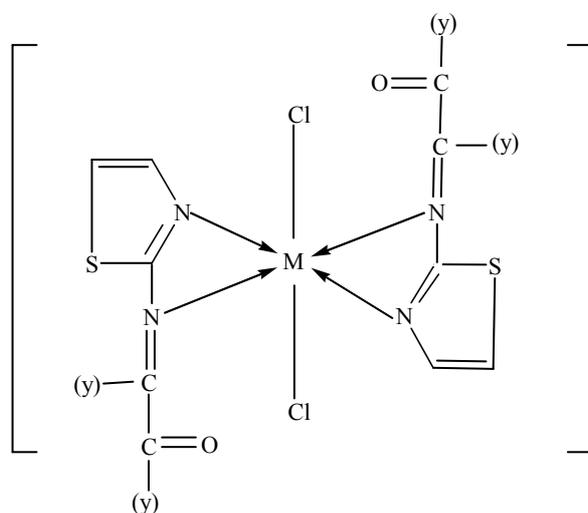
(Figure 2) atb



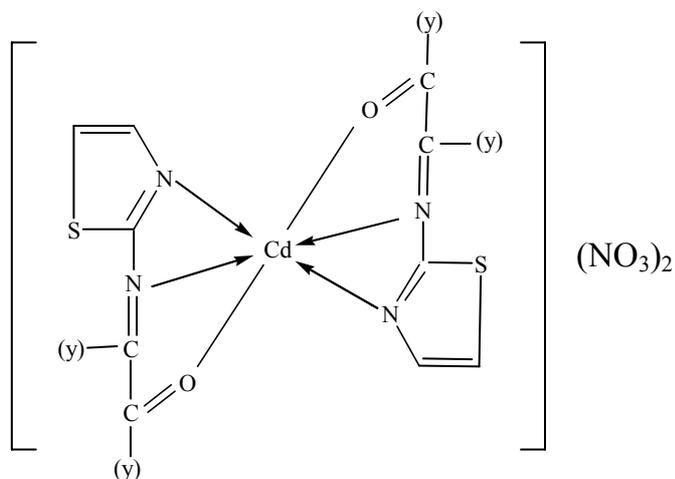
(Figure 3) M= Co (II), Ni (II); y=CH<sub>3</sub>,Ph; X=Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup>



(Figure 4) M= Cu (II); y=CH<sub>3</sub>, Ph



(Figure 5) M= Zn (II), Hg (II); y=CH<sub>3</sub>, Ph



(Figure 6) y = CH<sub>3</sub>, Ph

**Table (1): Physical and analytical data for the ligands and their complexes**

No.	Compound	Colour	M.P. °C	Found (calc.)%			$\Lambda_m$ $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$	Molar ratio 1:2	
				C	H	N		Metal (0.001 mol)	Ligand (atc,atb) (0.002 mol)
	atc	Dee grey	57	50.00 (50.05)	4.76 (4.73)	16.7 (16.9)	---		
	atb	Brown	76	69.86 (69.88)	4.11 (4.12)	9.59 (9.56)	---		
1	[Co(atc) <sub>2</sub> ·2H <sub>2</sub> O]Cl <sub>2</sub>	Deep yellow	119	36.06 (36.16)	3.43 (3.44)	12.019 (12.1)	70	0.237 g	0.336 g
2	[Ni(atc) <sub>2</sub> ·2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	Yellow	213d	30.29 (30.18)	3.61 (3.72)	15.14 (15.12)	90	0.290 g	0.336 g
3	[Cu(atc) <sub>2</sub> Cl <sub>2</sub> ]	Pale yellow	139d	35.71 (35.69)	3.40 (3.46)	11.90 (11.86)	9	0.170 g	0.336 g
4	[Zn(atc) <sub>2</sub> Cl <sub>2</sub> ]	Pale yellow	216d	35.56 (35.49)	3.39 (3.41)	11.85 (11.89)	4	0.136 g	0.336 g
5	[Cd(atc) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Pale brown	90	29.35 (29.29)	2.80 (2.85)	14.68 (14.65)	80	0.308 g	0.336 g
6	[Hg(atc) <sub>2</sub> Cl <sub>2</sub> ]	Yellow	189	27.65 (27.64)	2.63 (2.69)	9.22 (9.19)	6	0.271 g	0.336 g
7	[Co(atb) <sub>2</sub> ·2H <sub>2</sub> O]Cl <sub>2</sub>	Deep yellow	122.5	57.15 (56.60)	3.36 (3.31)	7.84 (7.92)	81	0.237 g	0.584 g
8	[Ni(atb) <sub>2</sub> ·2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	Brown	89.5	50.83 (50.79)	3.49 (3.58)	10.46 (10.49)	70	0.290 g	0.584 g
9	[Cu(atb) <sub>2</sub> Cl <sub>2</sub> ]	Brown	114.3	56.78 (56.64)	3.34 (3.45)	7.79 (7.69)	8	0.170 g	0.584 g
10	[Zn(atb) <sub>2</sub> Cl <sub>2</sub> ]	Pale brown	98	56.64 (56.59)	3.33 (3.37)	7.77 (7.79)	9	0.136 g	0.584 g
11	[Cd(atb) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Yellow brown	84.2	49.73 (49.70)	2.93 (3.00)	10.24 (10.20)	85	0.308 g	0.584 g
12	[Hg(atb) <sub>2</sub> Cl <sub>2</sub> ]	Deep yellow	119	47.69 (46.71)	2.81 (2.89)	6.55 (6.53)	7	0.271 g	0.584 g

d=decomposition temp.

**Table (2): Electronic spectra (in DMSO) and magnetic moment.**

No.	Compound	d-d transitions (cm <sup>-1</sup> )			$\mu_{eff}$ (B.M)
		$\nu_1$	$\nu_2$	$\nu_3$	
1	[Co(atac) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	7370	15800	19640	4.85
2	[Ni(atac) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	9037	14890	25774	3.55
3	[Cu(atac) <sub>2</sub> Cl <sub>2</sub> ]	15347	----	----	1.85
7	[Co(atb) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	7572	16242	19474	4.80
8	[Ni(atb) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	9788	14848	23148	3.13
9	[Cu(atb) <sub>2</sub> Cl <sub>2</sub> ]	15198	----	----	1.77

**Table (3): IR frequencies (in cm<sup>-1</sup>) of the complexes.**

No.	Compound	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C-Nring}$	$\nu_{M-N}$	$\nu_{M-O}$	$\nu_{M-Cl}$
1	[Co(atac) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	1625 <sub>b</sub>	1655 <sub>s</sub>	1480 <sub>b</sub>	(265) <sub>mring</sub>	475 <sub>m</sub>	---
2	[Ni(atac) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	1620 <sub>m</sub>	1650 <sub>m</sub>	1475 <sub>m</sub>	(275) <sub>mring</sub>	475 <sub>m</sub>	---
3	[Cu(atac) <sub>2</sub> Cl <sub>2</sub> ]	1625 <sub>s</sub>	1650 <sub>m</sub>	1475 <sub>m</sub>	(260) <sub>mring</sub>	450 <sub>m</sub>	295 <sub>m</sub>
4	[Zn(atac) <sub>2</sub> Cl <sub>2</sub> ]	1670 <sub>s</sub>	1590 <sub>m</sub>	1470 <sub>b</sub>	425 <sub>m</sub> 285 <sub>mring</sub>	---	300 <sub>m</sub>
5	[Cd(atac) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1625 <sub>b</sub>	1590 <sub>s</sub>	1480 <sub>s</sub>	420 <sub>w</sub> 270 <sub>mring</sub>	470 <sub>m</sub>	---
6	[Hg(atac) <sub>2</sub> Cl <sub>2</sub> ]	1665 <sub>m</sub>	1610 <sub>s</sub>	1475 <sub>s</sub>	420 <sub>m</sub> 285 <sub>mring</sub>	---	310 <sub>w</sub>
7	[Co(atb) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	1620 <sub>s</sub>	1650 <sub>s</sub>	1480 <sub>b</sub>	---	475 <sub>m</sub>	---
8	[Ni(atb) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	1625 <sub>s</sub>	1655 <sub>s</sub>	1475 <sub>b</sub>	---	470 <sub>m</sub>	---
9	[Cu(atb) <sub>2</sub> Cl <sub>2</sub> ]	1615 <sub>s</sub>	1650 <sub>s</sub>	1475 <sub>b</sub>	---	470 <sub>m</sub>	290 <sub>m</sub>
10	[Zn(atb) <sub>2</sub> Cl <sub>2</sub> ]	1675 <sub>s</sub>	1600 <sub>s</sub>	1485 <sub>b</sub>	410 <sub>m</sub>	---	290 <sub>m</sub>
11	[Cd(atb) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1625 <sub>m</sub>	1590 <sub>s</sub>	1480 <sub>s</sub>	430 <sub>m</sub>	470 <sub>m</sub>	---
12	[Hg(atb) <sub>2</sub> Cl <sub>2</sub> ]	1665 <sub>s</sub>	1600 <sub>m</sub>	1480 <sub>m</sub>	420 <sub>m</sub>	---	315 <sub>m</sub>

b = broad, m = medium, s = strong

**Table (4): Stretching vibration rocking and wagging of the aqua complexes**

No.	Compound	Rocking (H <sub>2</sub> O) P <sub>r</sub> (H <sub>2</sub> O)	Wagging (H <sub>2</sub> O) P <sub>w</sub> (H <sub>2</sub> O)	M-OH <sub>2</sub>
1	[Co(atac) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	790 <sub>m</sub>	650 <sub>s</sub>	400 <sub>w</sub>
2	[Ni(atac) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	780 <sub>m</sub>	645 <sub>b</sub>	410 <sub>w</sub>
7	[Co(atb) <sub>2</sub> .2H <sub>2</sub> O]Cl <sub>2</sub>	780 <sub>m</sub>	640 <sub>b</sub>	410 <sub>w</sub>
8	[Ni(atb) <sub>2</sub> .2H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	760 <sub>m</sub>	645 <sub>b</sub>	405 <sub>w</sub>

b = broad, m = medium, w = week

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