

POTENTIAL ANTIFOULING AGENTS: COPPER, COBALT, AND NICKEL COMPLEXES OF 3-(2-ACETYL PYRIDYLIDENE) HYDRAZINO-5, 6-DIPHENYL-1,2,4-TRIAZINE

HEMAIDA H.A.E.*, DISSOUKY ALI A.EL** AND SADEK S.M.M.**

*National Institute of Oceanography and Fisheries, Alexandria, Egypt

** Faculty of Science, Alexandria University, Alexandria, Egypt

Key words: Antifouling, hydrazone, 1, 2, 4-triazine, metal complexes, toxicity, barnacle larvae.

ABSTRACT

Several copper, cobalt and nickel complexes of 3-(2-acetyl pyridylidene) hydrazino-5,6-diphenyl-1,2,4-triazine (L) were prepared and their structure assigned through IR, electronic spectra and magnetic moments at room temperature. The IR data suggested that the ligand (L) acts as a neutral tridentate chelating agent in $[LCoCl_2]$, $[L_2Co] Ac_2.4H_2O$, $[L_2 Co] (ClO_4)_2.2H_2O$, $[L Cu Cl_2].2H_2O$ and $[L_2Cu (H_2O)] (ClO_4)_2$ complexes, but as a neutral bidentate chelating agent in $[L_2 Ni] Ac_2 .H_2O$, $[LCuCl_2]$, $[L_2 Cu] Ac_2 .2H_2O$ and $[L_2 Cu] (ClO_4)_2$. The electronic spectra and room temperature magnetic moments of the complexes indicate a distorted trigonal bipyramidal structure for $[LCoCl_2]$, $[L Cu Cl_2].2H_2O$ and $[L_2Cu(H_2O)](ClO_4)_2$; and the existence of high spin-low spin cobalt(II), while electronic and ESR spectra of $[L_2Co]Ac_2.4H_2O$ and $[L_2 Co] (ClO_4)_2.2H_2O$ indicate a distorted octahedral. In case of $[L_2 Ni] Ac_2 .H_2O$ complex, the room temperature magnetic moment indicates that there is equilibrium between square planar and tetrahedral configurations and the percent of the tetrahedral geometry was estimated and found to be 30.4%. This geometry was changed into distorted octahedron if the electronic spectra was recorded in pyridine or α - picoline. The electronic and ESR spectra of the two complexes $[L_2 Cu] Ac_2 .2H_2O$ and $[L_2 Cu] (ClO_4)_2$ confirmed the presence of distorted tetrahedral copper(II) complexes with $d_{y^2-x^2}$ as a ground state. Finally, upon heating the green complex $[L Cu Cl_2] .2H_2O$, the square planar brown compound $[L Cu Cl_2]$ was obtained. Some compounds were tested for their antifouling activity by measuring their toxicity against barnacle's larvae.

INTRODUCTION

Fouling of ship hulls and marine installations by plant and animal organisms is a well known, world problem which results in significant economic loss due to structural damage or increased fuel consumption. Organotin-based paints are the most commonly used antifouling paints. Due to the lipophilic nature of organotin compounds, they can enter human body either directly or through contaminated seafood (Krowke *et al.* 1986, Adamson 1935 and UNEP1988). These

facts have initiated a programme in 1991 for the synthesis of metal complexes of nitrogen-containing heterocyclic compounds having a triazine ring that might have significant toxicity against barnacle larvae and less hazardous to the marine environment.

The present study deals with the synthesis of several copper, cobalt and nickel complexes of 3-(2-acetyl pyridylidene) hydrazino-5,6-diphenyl-1,2,4- triazine. The incentive in this direction was based on the fact that several 1,2,4-triazines are known to possess antiviral, fungicidal, antifouling and

* Corresponding author
e-mail: hodahemaida@Yahoo.Com.

antibacterial potencies (De La Court *et al.* 1973, Labouta *et al.* 1988 and Eshba *et al.* 1987). In addition, salts of copper (II) complexes have been reported to most acceptable one in the formulation of antifouling paints (US. NAVAL INSTITUTE 1952).

MATERIAL AND METHODS

1. Preparation of 3-(2-acetyl pyridylidene) hydrazino-5,6-diphenyl-1,2,4-triazine (L)

To a stirred solution of 3-hydrazino-5,6-diphenyl-1,2,4-triazine (0.01 mole) in ethanol (20 ml), a solution of 2-acetyl pyridine in ethanol (5 ml) was added gradually, then heated under reflux for 30 minutes. The precipitated product was filtered and purified by crystallization from ethanol. M.p. 186 - 187. ¹H-NMR δ (ppm): 9.00(s, 1 H, N-H), 2.60 (s, 3 H, CH₃), 8.43 - 8.63(d, 1 H, Py-H at C₆), 8.23 - 8.37(d, 1 H, Py-H at C₃), 7.10 - 7.80(m, 12 H, aromatic and pyridine). Mass(m/z): 366(86.3), 351(85.0), 337(10.7), 288(100), 185(7.8), 178(75.0), 160(53.1), 152(7.8), 104(19.0), 89(6.3), 79(31.0).

2. Preparation of metal complexes

Cobalt (II), nickel (II) and copper (II) complexes of the ligand (L) were prepared according to the following procedure: To a solution of the ligand (0.01 mole) in ethanol (100 ml), an ethanolic solution of the divalent metal salts (0.01 mole); namely CoCl₂.6H₂O, Co(Ac)₂.4H₂O, Co(ClO₄)₂.6H₂O, NiCl₂.6H₂O, Ni(Ac)₂.4H₂O, anhydrous CuCl₂, anhydrous Cu(Ac)₂, Cu(ClO₄)₂.6H₂O was added for 1:1 (M:L) complexes. The addition sequence was reversed in case of 1:2 (M:L) complexes. The reaction was heated under reflux for 0.5-5 hours depending on the nature of the metal salts. After cooling to room temperature, the precipitated product in each case was filtered off, washed with ethanol and dried in vacuum over P₄O₁₀. It was observed that under heating the green [L Cu Cl₂].2H₂O, the brown complex [L Cu Cl₂] was obtained.

3. Analysis

Carbon, hydrogen, and nitrogen contents in each sample were estimated at the micro-analytical units on PERKIN ELMER CHNS/O 2400 series (II) at the Faculty of Science, Alexandria University. Copper (II), nickel (II), Cobalt (II) in each complex was estimated by the standard complexometric methods(Vogel 1957).

4. Physical Measurements

The mass spectra of 3-(2-acetyl pyridylidene)hydrazino-5,6-diphenyl-1,2,4-triazine(L) and its related copper, cobalt and nickel complexes were recorded on gas chromatograph mass spectrometer at Cairo University, Cairo, Egypt.

The ¹H-NMR spectrum was recorded on a EM-390 90 MHZ NMR spectrometer in absence and presence of D₂O. tetramethylsilane (TMS) signal ($\delta=0$) was employed as an internal standard.

The IR spectrum was made on a PERKIN-ELMER 1430-Ratio recording infrared spectrophotometer. Calibration of frequency reading was made with polystyrene. The KBr disk technique was followed.

The electronic spectral measurements in the visible and ultraviolet regions were carried out on a Shimadzu U.310/PC spectrophotometer. The spectra of the complexes were measured in nujol mull and in some cases saturated solutions in pyridine or CHCl₃ were employed.

The ESR (X-band) spectra for the polycrystalline samples were recorded at room temperature using a Radiopan SE/X2543 spectrometer (pazn) with a rectangular TE102 cavity and 100KHZ modulation field.

The molar conductivity was measured for 10⁻³ M solution in different solvents at 25C using systronics (303 model) direct reading conductivity meter.

5. Bioassay

The evaluation of antifouling activity of the ligand and some of the prepared metal complexes was carried out as follows:

- Appropriate amounts of solution (10, 100, 1000 μl for 10, 100, 1000 $\mu\text{g/ml}$, respectively) from the tested compounds were transferred into vials 15 ml capacity.
- Certain number of barnacle larvae was transferred to each sample vial and artificial sea water was added to make 5 ml.
- After 24 hours, survivors were counted microscopically. The net percentage deaths were calculated.
- LC_{50} values were determined from the 24 hours counts, by applying the graphical method of calculation on Miller and Tainter (1944), for comparison of the potency.
- The data statistically analyzed according to Bancroft (1963) to calculate the mean, standard deviation and 95% confidence interval of LC_{50} .

RESULTS AND DISCUSSION

1. Chemistry

The synthetic sequence and molar ratio are given in scheme 1. The elemental analysis and some physical properties of the ligand and its metal complexes are listed in Table 1. The ligand, 3-(2-acetyl pyridinylidene) hydrazine-5, 6-diphenyl-1,2,4-triazine, (L) was prepared by condensation of 3-hydrazine-5, 6-diphenyl-1,2,4-triazine (1) with 2-acetyl pyridine (2). The mode of fragmentation of L is shown in scheme 2. Cation (A), $m/z=351$, is formed from the parent ion through elimination of CH_3 radical. Then it undergoes fragmentation through the triazine and the pyridine ring bonds to give ion (B), $m/z=178$ and ion (C), $m/z=152$. The parent also undergoes cleavage through $=\text{C-Py}$ bond giving the pyridine ion (F), $m/z=79$ after combination with one hydrogen radical and cation (G), $m/z=288$ as base peak.

The IR spectrum (Table 2) of the free ligand displays a narrow medium band at

3229 cm^{-1} indicating existence of free NH. While the spectra of all complexes show blue shift with some broadness relative to that of L for NH and appeared in the range of $3405\text{--}3500\text{ cm}^{-1}$. In all cases it may be overlapped with that due to stretching of OH of H_2O molecule. The bands at 1637 , 1611 , 1545 , 992 and 1466 cm^{-1} for L are assigned for (C=N) azine, C=N of the pyridine moiety, C=N of the triazine moiety, N-N azine and N=N of the triazine moiety, respectively (Nakanishi 1962). While the bands at 1637 and 1611 cm^{-1} are red shifted and the band at 1545 cm^{-1} is blue shifted in the spectra of all complexes. These observations can be taken as evidences for the tridentate nature of L in these complexes (Fig.1). Furthermore, the appearance of the NH indicates the neutral nature of the L in all these complexes. Accordingly, L bonded to the metal ions via azine, triazine and pyridine nitrogen atoms. The shift of N-N hydrazone band from 992 cm^{-1} in the free L to $1021\text{--}1025\text{ cm}^{-1}$ (Table 2) in the complexes support the bonding nature of the azine nitrogen atom. The bonding of the triazine nitrogen is proved from the shift N=N to lower frequency in the complexes. Furthermore, three new bands are appeared characteristic of M-N of azine, pyridine and triazine in the ranges of $444\text{--}454$, $408\text{--}409$, and $315\text{--}317\text{ cm}^{-1}$, respectively, indicating the bonding of metal (II) ion with three different nitrogen atoms (Nakamoto 1986). The far IR spectra of all chloro-complexes display bands at $308\text{--}316$ and $269\text{--}280\text{ cm}^{-1}$ characteristic of M-Cl in which their chloride ions are terminally bonded to the metal complexes and the two M-Cl bonds are not identical. On the other hand, the IR spectra of $[\text{L}_2\text{Ni}]\text{Ac}_2\cdot\text{H}_2\text{O}$, $[\text{L}_2\text{Cu}]\text{Cl}_2$, $[\text{L}_2\text{Cu}]\text{Ac}_2\cdot 2\text{H}_2\text{O}$ and $[\text{L}_2\text{Cu}](\text{ClO}_4)_2$ complexes display the band of C=N of the triazine moiety almost at the same frequency while the bands due to (C=N) azine and (C=N) of pyridine moiety are shifted to lower frequency indicating the participation of hydrazone and pyridine nitrogen atoms in bonding to the metal ion. The appearance of new two bands at 440--

461 and 407-408 cm^{-1} due to M-N of azomethine and pyridine, respectively, support the bonding of these two moieties to the metal ion (Covacic 1967 and Teysse et al 1963). Accordingly, L acts as a neutral bidentate coordinated to the copper and nickel ions via azomethine and pyridine nitrogen atoms. The band appeared at 278 cm^{-1} in $[\text{L Cu Cl}_2]$ is assigned to the Cu-Cl and indicates that the chloride ions are terminally bonded to the copper ion. The spectra of the acetate and perchlorate containing complexes indicate their ionic nature (Nakamoto 1986).

The reaction of L with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Co}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in a molar ratio 1:1 or 1:2 under refluxing conditions in ethanol gave only the complexes $[\text{L CoCl}_2]$, $[\text{L}_2\text{Co}] \text{Ac}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{L}_2 \text{Co}] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, respectively (Table 1).

The room temperature magnetic moment values (Table 3) for the prepared complexes are 3.77, 2.05, 2.28 BM for $[\text{L CoCl}_2]$, $[\text{L}_2 \text{Co}] \text{Ac}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{L}_2 \text{Co}] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, respectively. The magnetic moment value for $[\text{L CoCl}_2]$ is found to be in the range reported for high spin cobalt(II) complexes, $S=3/2$, which have quartet spin state.

The electronic spectrum (Table 3) of $[\text{L CoCl}_2]$ showed a series of bands at 15700, 17500, and 19200 cm^{-1} corresponding to ${}^4\text{A}_2 \rightarrow {}^4\text{E}(\text{F})$, ${}^4\text{A}_2 \rightarrow {}^4\text{A}_2(\text{P})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}(\text{P})$, respectively (Boca et al. 1998).

The X-band ESR of $[\text{L CoCl}_2]$ as polycrystalline sample (Table 5) were recorded at various temperatures. The spectrum at room temperature displays only one signal at 2998 G ($g=2.22$) and the same shape was obtained down to 185K. when the temperature is cooled down to 70, 30, 6 K, new lines at 1105 ($g=6.03$), 1886($g=3.55$) 2786(sh)($g=2.40$) and 3230 G (sh) are obtained. When the temperature raised from 6 to 70 K, the intensity of the first two lines broaden and their relative intensities decreased sharply at 70K. on the other hand the intensity of the lines at 2786(sh), 2998 and 3230 G (sh) decreased upon cooling and shoulders at 2786 and 3230 G are diminished. In view of these results the signals at 1105

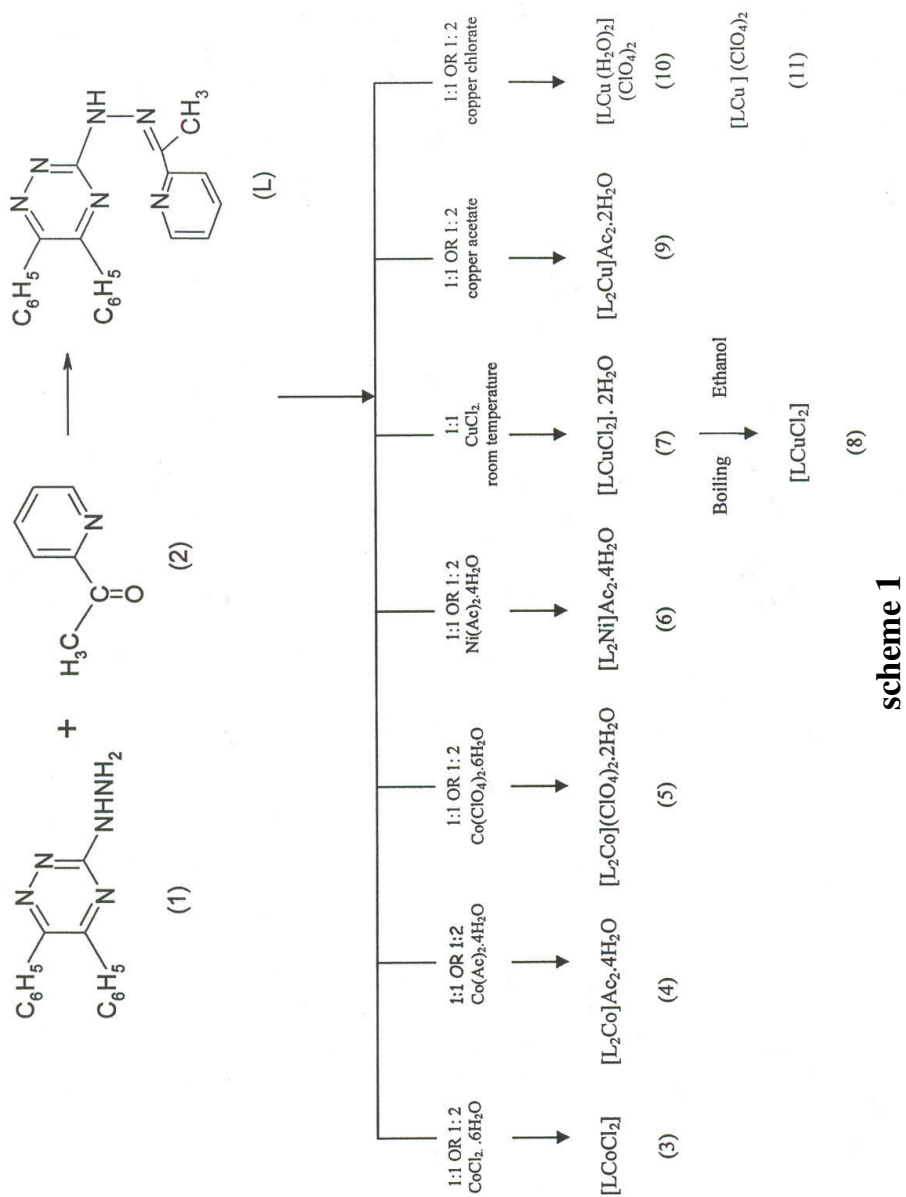
and 1886G are assigned to a high spin species where relaxation time is expected to be small. The signals at 2786, 3230 G and 3230 G (sh) are assigned for the low species. The observed ESR data (Table 5) as a function of temperature suggest the existence of a temperature dependent population of two geometrically different forms in two different spin states (Boca et al. 1998, and Nivorozhkin et al 1994).

The room temperature magnetic moments (Table 3) of $[\text{L}_2 \text{Co}] \text{X}_2 \cdot n \text{H}_2\text{O}$ where $\text{X} = \text{Ac}_2$ or ClO_4 and $n=2 - 4$ are 2.05 and 2.28 BM, respectively, reveal that the complexes are low spin ($S=1/2$) systems and indicate that the values depend on the nature of the anion and number of water molecules (Harris et al. 1969 and Kremer 1982). The ESR of both compounds at 200K display only one broad signal at 3026G ($g=2.21$) which is the low spin region. At 120 K, the spectra exhibit two resonances at 3026, and 3215G for $[\text{L CoCl}_2] \text{Ac}_2 \cdot 4\text{H}_2\text{O}$, and at 150 K, the spectra exhibit two resonance at 3026 and 3199G for $[\text{L}_2 \text{Co}] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. These spectral features are characteristic of axial type with $g_{\parallel} > g_{\perp}$. The value of g_{\parallel} is 2.21 for both complexes and g_{\perp} are 2.08 and 2.09, respectively. At temperature ≤ 70 K a distinct splitting of g_{\perp} is observed leading to an orthorhombic symmetry pattern $g_x = 2.03(3262\text{G})$, $g_y = 2.12(3154\text{G})$, and $g_z = 2.22(3262\text{G})$ for Ac and $g_x = 2.03(3262\text{G})$, $g_y = 2.11(3185\text{G})$, and $g_z = 2.21(3026\text{G})$ for ClO_4 . The spectra at 30 and 6 K for both complexes exhibit another signal at $g=0.95$ and 6.23 corresponding to 962 and 1073G, respectively. This signal is attributed to high spin state supporting the existence of a significant amount of the high spin species at $T \leq 30\text{K}$.

The electronic spectra (Table 3) of $[\text{L CoCl}_2] \text{Ac}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{L}_2 \text{Co}] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ are similar and displaying bands at 9300, 15600, 17300 and 19800 cm^{-1} for acetate-containing complex and at 9300, 15400, 17200 and 20200 cm^{-1} for the perchlorate complex. The bands at 15400 – 15600 and 17200 – 17300 cm^{-1} are attributed to the spin allowed d-d transitions (Kremer 1982). The

weak band at 9300 cm^{-1} in both complexes is assigned to the transition within the octahedral 2E ground state which is split by

the Jahn-Teller effect and the tetragonal ligand field, ${}^4A_2 \rightarrow {}^4B_1g$.



scheme 1

POTENTIAL ANTIFOULING AGENTS: COPPER, COBALT, AND NICKEL COMPLEXES OF 3-(2-ACETYL
PYRIDYLIDENE) HYDRAZINO-5, 6-DIPHENYL-1,2,4-TRIAZINE

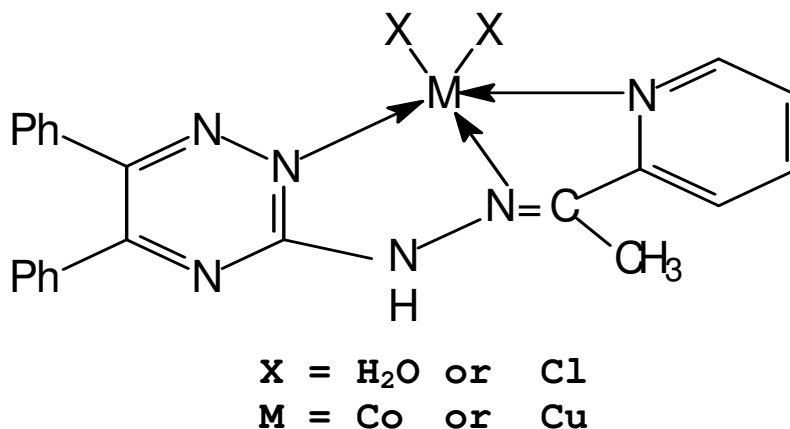


Fig. 1

Table 1: Elemental analysis and some physical properties of L and its metal complexes

Compound	Colour	M.p. (C)	% Found/Calcd			
			C	H	N	M
L C ₂₂ H ₁₈ N ₆	yellow	185 - 86	72.00 72.10	4.90 4.90	22.10 22.90	
[LCoCl ₂] C ₂₂ H ₁₈ N ₆ Cl ₂ Co	brown	> 300	52.90 53.20	3.30 3.60	16.80 16.80	11.80 11.90
[L ₂ Co]Ac ₂ .2H ₂ O C ₄₈ H ₅₀ N ₁₂ O ₈ Co	black	282 - 84	58.30 58.70	5.10 5.10	17.00 17.10	6.00 6.00
[L ₂ Co](ClO ₄) ₂ .4H ₂ O C ₄₄ H ₄₀ N ₁₂ O ₁₀ Cl ₂ Co	black	> 300	51.50 51.50	4-10 4.10	16.60 16.60	5.70 5.70
[L ₂ Ni]Ac ₂ .H ₂ O C ₄₈ H ₅₄ N ₁₂ O ₅ Ni	red	263 - 66	61.60 62.20	4.30 4.70	18.00 18.10	6.50 6.30
[LCuCl ₂]. 2H ₂ O C ₂₂ H ₂₂ N ₆ O ₂ Cl ₂ Cu	green	250 - 52	49.60 49.20	4.30 4.30	15.50 15.70	11.70 11.80
[LCuCl ₂]. C ₂₂ H ₁₈ N ₆ Cl ₂ Cu	brown	204 - 07	52.40 52.70	3.90 3.60	16.70 16.70	12.70 12.70
[L ₂ Cu]Ac ₂ .2H ₂ O C ₄₈ H ₅₄ N ₁₂ O ₆ Cu	violet	218 - 20	60.30 60.70	4.50 4.80	17.80 17.80	6.60 6.70
[LCu (H ₂ O) ₂](ClO ₄) ₂ C ₂₂ H ₂₂ N ₆ O ₁₀ Cl ₂ Cu	dark green	> 300	39.30 39.70	3.60 3.30	12.80 12.60	9.50 9.60
[L ₂ Cu](ClO ₄) ₂ C ₄₄ H ₃₆ N ₈ O ₈ Cl ₂ Cu	green	> 300	51.40 52.1	3.50 3.60	16.70 16.90	6.50 6.40

Table 2: Selected absorption frequencies cm^{-1} , of L and its metal complexes

Compound	(NH) (OH)	(C=N) azine	(C=N) pyridine	(C=N) triazine	(N=N) triazine	(N-N) azine	(M-N) azine pyridine triazine	(M-X)	(M-O)
L	32,293,430	1637	1611	1545	1466	992			
[LCoCl ₂]	3405	1622	1597	1563	1441	1023	454,409,315	316,280	
[L ₂ Co]Ac ₂ .4H ₂ O	3414	1622	1596	1566	1434	1024	449,409,316		
[L ₂ Co](ClO ₄) ₂ .2H ₂ O	3430	1620	1595	1564	1437	1024	452,409,315		
[L ₂ Ni]Ac ₂ .H ₂ O	3434	1625	1590	1549		1024	446,408		
[LCuCl ₂]. 2H ₂ O	3443	1618	1600	1560	1444	1021	454,408,317	308,269	
[LCuCl ₂]	3442	1618	1598	1548	1467	1025	461,407	278	
[L ₂ Cu]Ac ₂ .2H ₂ O	3412	1619	1586	1550		1024	458,407		
[LCu (H ₂ O) ₂](ClO ₄) ₂	3469	1624	1596	1558	1438	1025	444,409,316		163
[L ₂ Cu](ClO ₄) ₂	3450	1622	1596	1546	1466		440,408		

Table 3: Molar conductivity, room temperature magnetic moments and electronic spectral data for cobalt (II) and copper (II) complexes of L

Compound	μ_{eff}	λ_{M}^*	Spectral data cm^{-1}
[LCoCl ₂]	3.77	3.66	15700, 17500, 19200
[L ₂ Co]Ac ₂ .4H ₂ O	2.95	148.6	9300, 15600, 17300, 19800
[L ₂ Co](ClO ₄) ₂ .2H ₂ O	2.28	157.92	9300, 15400, 17200, 20200
[LCuCl ₂]. 2H ₂ O	1.92	6.08	15600, 13300, 10400
[LCuCl ₂].	1.78	3.01	14000, 17000 (br)
[LCu (H ₂ O) ₂](ClO ₄) ₂	1.89	159.09	15800, 13700, 10800
[L ₂ Cu]Ac ₂ .2H ₂ O	2.13	150.81	18400, 14400, 13460, 10800, 12800
[L ₂ Cu](ClO ₄) ₂	2.18	161.63	18480, 14400, 13400, 10900, 12800 (sh)

The reaction of L with Ni Ac₂.4H₂O in a mole ratio 1:2 under refluxing conditions in ethanol gave [L₂ Ni] Ac₂.4H₂O (Table 1).

The complex [L₂ Ni] Ac₂.4H₂O. exhibits anomalous magnetic moment (Table 4) of 1.82 BM at room temperature which is lower than the values reported for regular octahedral, tetrahedral or high spin five coordinate nickel (II) complexes. The electronic spectrum of this complexes displays a broad band centered at 18000 cm⁻¹ which could be assigned to a composite of the tetrahedral, ³T₁→³T₁(P) and the lowest energy spin allowed transition. This in addition to a broad band centered at 20000 cm⁻¹. This band is intense that it can be assigned to LMCT under which the transition due to square planar conformation may be hidden. The CH₂Cl₂ is very similar to that obtained as nujol mull. The percent of the tetrahedral geometry was estimated (Sacconi et al 1964) and found to be 30.4%. While the spectra in pyridine and α-picoline are quite different and display bands at 9200 – 9600, 15100 – 15300, 22900 – 23050 beside a very intense one at 24600 – 25800 cm⁻¹. The band positions and intensities are consistent with tetragonal distorted complexes.

The reaction of L with copper (II) salts in a mole ratio 1:1 or 1:2, gave only the complexes given in Table 1. Reacting copper (II) chloride with the ligand in a mole ratio of 1:1 at room temperature gave a green complex [L Cu Cl₂].2H₂O, while under refluxing condition the brown complex [L Cu Cl₂] was obtained. The complexes [L₂ Cu (H₂O)₂] (ClO₄)₂, [L₂ Cu] (ClO₄)₂ and [L₂ Cu] Ac₂.2H₂O are obtained upon the interaction of L and the corresponding copper (II) salt in 1:1 or 1:2 mole ratio. Only one product was obtained in each case.

The room temperature magnetic moment values of these complexes (Table 3) are in the range of 1.78 – 2.18 BM characteristic of one unpaired electron in the copper(II) ion (El-Dissouky et al 1986 and El-Dissouky *et al.* 1990). The nujol mull electronic spectra (Table 3) of all complexes display intense

bands at 40000, 35000, 33700, 28600, 25600 cm⁻¹. The spectra of [L Cu Cl₂].2H₂O and [L₂ Cu (H₂O)₂] (ClO₄)₂ are similar and display bands at 15600, 13300, and 15800, 13700 cm⁻¹. Besides another band at 10400 and 10800 cm⁻¹ for [L Cu Cl₂].2H₂O and [L₂ Cu (H₂O)₂] (ClO₄)₂, respectively. The spectral data are in consistent with those of five coordinate and cis-distorted octahedral (El-Dissouky 1987, Suzuki *et al.* 1984 and Proctet *et al.* 1960). The broad bands at 15600, 13300 and 15800, 13700 cm⁻¹ for the chloro and aqua complexes, respectively, can be assigned to symmetry allowed ²A₁→²E¹ and ²A₁→²E¹¹ transitions, respectively in D_{3h} symmetry (Reonen and Atanasov 1989).

The X-band ESR spectra of (Table 6) both complexes either as polycrystalline sample or in CH₂Cl₂ at room temperature or at liquid nitrogen temperature show rhombic type with g_x > g_y > g_z. The g-values observed for the powder samples at room temperature were almost the same as those for the frozen CH₂Cl₂ sample. This suggests that the powder g-tensors also equate the g-value of local molecular structure with no exchange between the neighboring copper (II) chromospheres. The ligand field and ESR spectral parameters found for of [L Cu Cl₂].2H₂O and [L₂ Cu (H₂O)₂] (ClO₄)₂ are very consistent with those reported for CuN₃Cl₂ and CuN₃O₂ chromophores, respectively. The distortion of triagonal bipyramidal to square based pyramidal was proven by applying the method given Reinen *et al.* (Reonen and Atanasov 1989 and Reonen *et al.* 1991) the electronic spectral feature of both complexes are similar to those reported for copper (II) ion in a tetrahedral environment and rather similar to those reported for CuN₄ chromospheres.

2. Biological Evaluation

The potential of 3-(2-acetyl pyridylidene) hydrazino-5, 6-diphenyl-1, 2, 4-triazine and its copper and cobalt complexes as antifouling agents was evaluated by measuring their toxicity against *napulius*

larvae of *balanus amphitrite*. The results indicate that $[\text{LCuCl}_2] \cdot 2\text{H}_2\text{O}$ and $[\text{LCu}(\text{H}_2\text{O})_2](\text{ClO}_4)$ complexes where M:L=1:1 have a higher toxicity against barnacle larvae compared with the organic ligand (Table 7), while $[\text{L}_2\text{Cu}](\text{ClO}_4)_2$ and $[\text{L}_2\text{Cu}] \text{AC}_2 \cdot 2\text{H}_2\text{O}$ complexes where M:L=1:2 have lower toxicity than the organic ligand. 1:2 copper complexes have high molecular weight and so its penetration through the thin layer of the larvae might be restricted, which could inprete their low toxicity than the ligand.

The high toxicity of the copper complexes against barnacle larvae may be attributed to their ability to penetrate the cell membrane of the tested larvae and inhibited some essential biochemical pathways.

On the other hand, Cobalt complexes showed lower toxicity towards barnacle larvae in comparison with the organic ligand (Table 7). In general, the high toxicity of the organic ligand may be attributed to its lipophilic nature and its ability to penetrate the barnacle larvae cell membrane.

Table 4: Molar conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$), room temperature magnetic moments (B.M.) and electronic spectral data for $[\text{L}_2\text{Ni}]\text{Ac}_2 \cdot \text{H}_2\text{O}$

Compound	μ_{eff}	A_M^*	State	Spectral data						
				d-d transition	Nt%	ν_2/ν_1	10Dq	B'	β	Dq/B'
[L ₂ Ni]Ac ₂ .H ₂ O	1.82	155.96	CH ₂ Cl ₂	1,800,020,000	30.4	1.59	9600	637	0.62	1.51
			Py	96,001,530,023,050						
			α -pic	92,001,510,022,900						

*molar conductivity as 10^{-3} M DMF solution at $25 \pm 1^\circ\text{C}$

Table 5: ESR data of polycrystalline sample of cobalt(II) complexes of L

Compound	state	T(K)	g-values
[LCoCl ₂]	solid	298,185	2.22
		70	6.03, 3.54, 2.39, 2.22, 2.06
		30	6.03, 3.55, 2.40, 2.22, 2.06
		6	6.03, 3.55, 2.23
[L ₂ Co]Ac ₂ .4H ₂ O	solid	289,200	2.20
		120	2.21(g), 2.08(g _⊥)
		70	2.02(g _x), 2.12(g _y), 2.22(g _z)
		30	2.03(g _x), 2.11(g _y), 2.23(g _z), 6.95
[L ₂ Co](ClO ₄) ₂ .2H ₂ O	solid	289,200	2.21
		150	2.21(g), 2.09(g _⊥)
		65	2.03(g _x), 2.11(g _y), 2.21(g _z)
		20	2.03(g _x), 2.11(g _y), 2.20(g _z), 6.23

POTENTIAL ANTIFOULING AGENTS: COPPER, COBALT, AND NICKEL COMPLEXES OF 3-(2-ACETYL PYRIDYLIDENE) HYDRAZINO-5, 6-DIPHENYL-1,2,4-TRIAZINE

Table 6: ESR data of copper(II) complexes of L

Compound	State*	g_z	g_y	g_x	$A_z \cdot 10^{-4}$	$A_x \cdot 10^{-4}$	g_{iso}	$A_{iso} \cdot 10^{-4}$
		or g_{\parallel}	or g_{\perp}		cm^{-1}	cm^{-1}		cm^{-1}
[LCuCl ₂]. 2H ₂ O	powder(r.t)	2.013	2.093	2.186				
	CH ₂ Cl ₂ (77k)	2.016	2.104	2.19	90	108		
[LCuCl ₂]	powder(r.t)	2.26	2.06					
[L ₂ Cu]Ac ₂ .2H ₂ O	powder(r.t)	2.28	2.06				2.14	83
	powder(77k)	2.27	2.06					
	CH ₂ Cl ₂ (r.t)							
[L ₂ Cu](H ₂ O) ₂ (ClO ₄).2H ₂ O	CH ₂ Cl ₂ (77k)	2.289	2.09	2.06				
	powder(r.t)	2.014	2.129	2.22				
	CH ₂ Cl ₂ (r.t)	2.017	2.09	2.23	78	136		
[L ₂ Cu](ClO ₄) ₂	powder(r.t)	2.27	2.06				2.15	81
	powder(77k)	2.27	2.06					
	CH ₂ Cl ₂ (r.t)							
	CH ₂ Cl ₂ (77k)	2.28	2.09	2.05				

* r.t = room temperature

Table 7: Barnacle larvae bioassay results for L and some of its metal complexes

Compound	Concentration mg/L	% molarity-% control s.w	LC ₅₀ mg/L
L C ₂₂ H ₁₈ N ₆	10	16.7	28
	20	76.7	
	50	93.3	
	70	100	
	100	100	
[LCoCl ₂] C ₂₂ H ₁₈ N ₆ Cl ₂ Co	50	6.7	460
	100	16.7	
	300	17.3	
	700	63.3	
	1000	100	
[L ₂ Co]Ac ₂ .4H ₂ O C ₄₈ H ₅₀ N ₁₂ O ₈ Co	300	16.7	>100
	700	20	
	1000	20	
[L ₂ Co](ClO ₄) ₂ .2H ₂ O C ₄₄ H ₄₀ N ₁₂ O ₁₀ Cl ₂ Co	300	93.3	110
	700	96.7	
	1000	96.7	
[LCuCl ₂]. 2H ₂ O C ₂₂ H ₂₂ N ₆ O ₂ Cl ₂ Cu	8	40	9
	20	90	
	30	100	
	70	100	
[L ₂ Cu]Ac ₂ .2H ₂ O C ₄₈ H ₄₆ N ₁₂ O ₆ Cu	50	6.7	640
	100	16.7	
	300	20	
	700	36.7	
	1000	63.3	
[LCu (H ₂ O) ₂](ClO ₄) ₂ C ₂₂ H ₂₂ N ₆ O ₁₀ Cl ₂ Cu	10	16.7	27
	30	33.3	
	50	73.3	
	70	100	
[L ₂ Cu](ClO ₄) ₂ C ₄₄ H ₃₆ N ₈ O ₈ Cl ₂ Cu	300	90	130
	700	100	
	1000	100	

REFERENCES

- Adamson N.E. 1935. *Paint Industry Magazine*. Technology of ship bottom paints and their importance to commercial and activities.
- Bancroft H. 1963. *Introduction to biostatistics*. 5th edition, Hoeber Medical Division, Harper and Row Publisher.
- Baco R., H. Elias, W. Haase, M. Huber, R. Klement, L. Müller, H. Paulus, I. Sroboda and M. Valko 1998. *Inorg. Chim. Acta* 278: 127.
- Covacic J.E., *Spectrochim. Acta* 23A, 183, 1967.
- De La Court F.H and H. J. De Vries. *Progress in organic coating*, 1, 375, 1973.
- El-Dossouky A., A.M. Hindawy and A. Abdel-salam 1986. *Inorg. Chim. Acta* 118: 109.
- El-Dossouky A. and G.B. Mohammed 1990. *Inorg. Chim. Acta* 168: 241.
- El-Dossouky A. 1987. *Spectrochim. Acta* 43(a): 477.
- Eshba N.H, H.M. Salama, I.M. Labouta and A.M.E. Omar, *Pharmazie*, 42, 664, 1987.
- Harris C.M., T.N. Lockeyer, R.L. Martin, H.R.H. Patil, E.Sinn and I.M. Stewart 1969. *Aust.T.Chem.* 22:2105.
- Kremer S., W.Henke and D. Reinen 1982. *Inorg. Chim.* 21:3013.
- Krowke R., U. Bluth and D. Neubert 1986. *in vitro* studies on the embryotoxic potential of (bis(tributyltin)oxide) in a limb and organ culture system. *Arch. Toxicol*, 58:125 – 129.
- Labouta I.M, N.H. Eshba and H.M. Salama, *Farm., Sci., Ed.*, 16, 29, 1988.
- Miller L.C. and M.L. Tainter 1944. *Proc. Soc. Exp. Med.*, 57: 261 – 265.
- Nakanishi K. 1962. "Infrared Absorption Spectroscopy" Holden-Day, Inc. San Francisco and Nankodo Company Limited, Tokyo.
- Nakamoto A. 1986. "Infrared and Raman Spectra of Inorganic and Coordination Compounds" John Wiley, N.Y.
- Nivorozhkin A.L., H.Toftlund and M. Nielsan 1994. *Aust.T.Chem.* 22:2105.
- Procter I.M., B.J. Hasthaway, D.E. Billing, R.J.Dudley and P.Nicholis 1969. *J.Chem.Soc.(A)*. 1192.
- Reinen D. and M. Atanasov 1989. *J.Chem.Phys.* 136:27.
- Reinen D. and M. Atanasov 1991. *Magn. Resonance Rev.* 15:167.
- Suzuki M., H.Kanatomi, Y.Demura and I.Murase 1984. *Bull. Chem. Soc. J.* 57:1003.
- Sacconi L., M. Ciampalini and N.Nardi 1964. *J. Am. Chem.Soc.* 86:819.
- Teyssi P. and J.J.Charrette, *Spectrochim. Acta* 19, 1407, 1963.
- UNEP 1988. First Meeting of Scientific and Technical committee, Athen 23 – 25 May.
- Vogel A.I., "A Text Book of Quantitative Inorganic Analysis", 3rd edition, Longmans, London, 1957.
- Woods Hole Oceanographic Institute, "Marine Fouling and its Prevention", U.S. Naval Institute, Annapolis, Maryland, pp.37-41, 1952.