Synthesis and spectroscopic studies of some transition metal complexes derived from bis-2-pyrazoline ligand

M N Abid¹, A M Fahad, T M Musa and A H Ismail¹

¹Mustansiriyah University, College of Science, Department of Chemistry, Baghdad-Iraq

Abstract. The present work focuses on the synthesis and spectroscopic studies of some metal complexes based on a novel bis-2-pyrazoline ligand; 5-(4-(1-carbamothioyl-5-(pyridin-3-yl)pyrazolidin-3-yl)phenyl)-3-(pyridin-3-y1)pyrazolidine-1-carbothioamide. This ligand was prepared via the cyclization reaction of 3-(4-(E)-3-oxo-3-(pyridin-3-yl)prop-1-en-1-yl)phenyl)-1-(pyridin-3-yl)prop-2-en-1-one with alkaline solution of thiosemicarbazide. The resulted 2-pyrazoline ligand was identified by the FT-IR, NMR and LC-MS spectroscopes, in addition to (C.H.N.S) elemental analyses. The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared from their metal chlorides and ethanolic solution of the prepared ligand in 10% ammonia (mole ration 2:1 M:L). The octahedral geometry for all complexes was confirmed by atomic absorption, FT-IR, UV-Visible, magnetic moments and molar conductivity measurements. The thermal stability of the prepared complexes was confirmed by the thermal gravimetric analyses and the observed results indicated that the suggested chemical structure are in agreement with other data of elemental micro-analyses and flame atomic absorption spectroscopy.

1. Introduction
Metal complexes of 2-pyrazoline ligands have intensively studied in the recent years [1-3]. Binuclear metal complexes of pyrazole type ligands showed considerable analytical, industrial and biochemical applications [4,5]. These type of complexes have been widely used as antitumor (Kratz F. etal, 2010), antifungal [6], antiviral and insecticides agents [7]. The heterocyclic derivatives of pyrazole and their metal complexes are an important class of coordination compounds because of their high biological and pharmacological activities [8,9]. Recently many serious diseases such as cancer, AIDS, cardiovascular and Alzheimer have been treated new drugs containing 2-pyrazoline and thiocarbamide moieties [10]. The x-ray crystallography and high-resolution mass spectra for some metal chelates of bis-2-pyrazoline have confirmed the bidentate behavior through donor nitrogen atoms of the ring [11,12]. In this work, a new bis-2-pyrazoline ligand and its complexes with the first series of transition metal ions were prepared and characterized.

2. Material and Method
2.1. Instrumentals and Reagents
All reagents and chemicals were commercially (Sigma-Aldrich Co.) available and used as received from the suppliers. The conductivity of the complexes was measured using a Philips digital conductivity meter with dipping- type conductivity cell at 27 °C in 10⁻³ M solution in DMF. Shimadzu FT-IR spectrometer was used to collect FT-IR spectra. The UV-Visible spectra of the ligand and its complexes were measured in the region (200–800) nm using Varian Cary 100 Conc. NMR spectra were
collected using 300 MHz Bruker spectrometer. The magnetic moments were measured by Faraday’s method on Sherwood magnetic balance at 300 °K temperature. The metal contents in the solid complexes were estimated by flame atomic absorption spectroscopy (FAAS) via standard methods [13].

2.2. Synthesis of 3-(4-((E)-3-oxo-3-(pyridin-3-yl)prop-1-en-1-yl)phenyl)-1-(pyridin-3-yl)prop-2-en-1-one :
A solution of terphthaldehyde (1.34 g, 0.01 mol) dissolved in 20 ml ethanol, was added gradually to 3-acetyl pyridine (1.2 ml, 0.01 mol). To this mixture, an aqueous solution of NaOH (5 ml, 5%) was added. The reaction mixture was stirred at room temperature for three hours. Deep red precipitate was formed. The precipitate was recrystallized from chloroform. After keeping the clear solution overnight, deep-yellow crystals were deposited. Chemical Formula: C_{22}H_{16}O_{2}N_{2}, Elemental Analysis, Calc.(found): C=77.63 (76.75) ,H=4.74 (4.01),N=7.91(6.89), Scheme(1).

Scheme 1. Synthesis of bis-chalcone.

2.3. Synthesis of 5-(4-(1-carbamothioyl-5-(pyridin-3-yl)pyrazolidin-3-yl)phenyl-3-(pyridin-3-yl)pyrazolidine-1-carbothioamide, ligand L:
A mixture of chalcone (0.34 g, 0.01 mol), thiosemicarbazide (1.35 g, 2.2 mol) and ethanol (100 ml) was refluxed for 30 minutes in a water bath. The pH of the solutions was adjusted to 8.0 by addition of an aqueous solution of NaOH (5 ml, 10%), and the mixture was refluxed in a water bath for 30 minutes. After 12 hours of refluxing, the precipitate was filtered off, dried in oven and then re-crystallized from hot methanol to give yellow crystals of L, Scheme(2).

Scheme 2. Synthesis of bis-2-pyrazoline ligand.

2.4. Synthesis of metal complexes
A solution of (0.340g, 2 mmol) of CuCl_{2}.2H_{2}O in 10 ml methanol was added to a solution of 2-pyrazoline ligand (0.486g, 1 mmol). The reaction mixture was stirred in a water bath (75-80 °C) for 30 minutes until a pale green precipitate observed. This precipitate was filtered off, and recrystallized from hot ethanol, Table(1). Similarly, the complexes of Mn(II), Co(II), Ni(II), and Zn(II) were prepared following the same synthetic procedure, except adjusting the pH of the solution to 8 by adding 5-6 drops of 10% NH_{3}.

3. Results and Discussion
3.1. Physical Properties and Elemental Analyses:
Bis-2-pyrazoline ligand (L) was prepared by the cyclization reaction of chalcone with thiosemicarbazide derivatives in basic medium. The molecular formula of the metal complexes was determined using (C,H,N,S) elemental analyses and flame atomic absorption spectroscopy (FAAS). The results are in well-agreement with their theoretical calculations, Table (1). The molar conductivity of the solutions of C1,C2 and C4 was (5-25) ohm⁻¹.cm²/mole, indicating their non-electrolytic nature, while (143-170) ohm⁻¹.cm²/mole was recorded for C3 and C5 indicating their electrolytic nature [14].

**Table 1.** Some physical properties and elemental analysis of the prepared ligand and its metal complexes.

| Symbol | Compound/Color | Ω ohm⁻¹.cm².mole⁻¹ | M.P °C | %Found | % (Calculated) |
|--------|----------------|-------------------|-------|--------|----------------|
| A      | C2:H6N2O2 Dark Yellow | 5 | 210-212 | 76.75 (77.63) | 4.01 (4.74) | 6.89 (7.91) | - | - |
| L      | C24H22N8S2 Yellow | 9 | 290-292 | 58.77 (59.29) | 3.99 (4.56) | 22.57 (23.03) | 12.77 (13.1) | - |
| C1     | [MnL(H2O)2Cl] Black red | 22 | 303 Dec | - | - | - | - | 13.28 (14.06) |
| C2     | [CoL(H2O)2Cl] Brown | 18 | 290 Dec | - | - | - | - | 13.66 (14.66) |
| C3     | [NiL(H2O)2Cl] Pale green | 170 | 317 Dec | - | - | - | - | 17.33 (18.39) |
| C4     | [CuL(H2O)2Cl] Dark green | 25 | 283 Dec | - | - | - | - | 15.47 (16.11) |
| C5     | [ZnL Cl] White off | 143 | 298 Dec | 35.42 (36.71) | 3.00 (3.28) | 15.22 (14.15) | 7.25 (8.88) | 16.66 (17.15) |

**3.2. NMR Spectra**

The distinct chemical shifts of ¹H NMR spectrum of bis-2-pyrazoline ligand in DMSO-d₆ were 9.103, (8.62-8.50), (8.04-7.40) and (6.85-6.680) ppm which attributed to the proton nuclei of thioamide S=CNH₂, pyridine Py-H and 1,4-disubstituted A-H aromatic ring respectively [16,17]. After closing the ring, pyrazoline protons (H⁸,H⁹) of the final product showed peaks around 1.15-1.35 ppm, 3.20-3.85 and 5.50-6.10 ppm as a triplet peak and doublet of doublet due to vicinal coupling of –CHₓ proton in the pyrazoline ring respectively [12,14]. This supports the cyclization of chalcone into bis-2-pyrazoline, L².
3.3. Mass spectra of chalcone, A and the 2-pyrazoline ligand:
The mass spectrum of chalcone, A showed a peak at \( m/e=340 \) with relative intensity (I=25 \%) belongs to the molecular ion \( M^{+} \) consistent with the proposed chemical formula \( C_{22}H_{16}N_{2}O_{2} \). Whereas the base peak at \( m/e=237 \) (I=100 \%) indicates the fragmentation of \( C_{5}H_{4}-C=O \) moiety (\( M-102=237 \)) which can be considered as a strong evidence for the formation of bis-chalcone, A.

The chemical structure of (L) ligand was also confirmed by its mass spectrum in gas phase, Figure (4) displayed weak intensity peak at \( m/e=486 \) consistent with the chemical formula \( C_{24}H_{22}N_{8}S_{2} \). Most of the peaks that appeared before and after the molecular ion around 476, 439, 400 and 385 are may be assigned to the absorptions of \([M-NH_{2}]^{+} \), \([M-H_{2}S_{2}]^{+} \) and \([M-C_{10}H_{6}N_{2}]^{+} \) respectively. This fact entirely supports the cleavages from weak points of the 2-pyrazoline ligand [17,18].
3.4. IR Spectra of the L and its Complexes:
The spectrum of chalcone, A exhibited strong bands at 1658 and (1600-1583) cm$^{-1}$ which are consistent with the vibrations of –C=O and –C=CH- respectively. However the FT-IR spectrum of the bis-pyrazoline L$_2$ showed disappearance of stretching of carbonyl related to the chalcone compound, and this is evidence for the ring closure of thiosemicarbazide with the chalcone derivative [18]. The appearance of new bands around 1587,1471,1382 and 1081 cm$^{-1}$ that are mainly belong to –C=N, -H-N- and –C=S moieties respectively, gives strong evidence for the formation of symmetrical bis-2-pyrazoline ligand. The hydrogen bonded –NH$_2$ of thioamide which is linked directly to N1 of pyrazoline ring, was detected at 3441 and 3181 cm$^{-1}$ as asymmetric and symmetric vibrations respectively. The IR spectra of all metal complexes prepared from L$_2$ ligand showed remarkable changes in the active sites (-C=N- and -C=S), especially in the regions (1501-1598), (1375-1365) and (1110-1070) cm$^{-1}$, confirming the tridentate N$_2$S donor system of L with more stable five-member ring [15,19].

3.5. Electronic spectra and magnetic moments measurements:
The electronic spectra of L$_2$ and its metal complexes showed four absorptions at 203,237,312 and 365 nm, see Table 2. These were assigned to $\pi$-$\pi^*$, n-$\pi^*$ and intra-ligand charge transfer (INCT) transitions of the imine –C=N, -C=C- and –C=O involved in the pyrazole moiety [19,20]. All the complexes displayed spin-allowed transitions in the visible regions due to d-d transitions except Mn(II) and Zn(II) complexes, which show only LMCT in the range (285-315) nm [21,22]. Furthermore, the complexes of Mn(II), Co(II), Cu(II) recorded spin-magnetic moments at 5.58, 4.90 and 1.90 BM, which are in good agreement with their valence contributions. This supports the suggested octahedral geometry for these complexes. However, the Ni(II) complex exhibited diamagnetic properties due to low-spin square planar geometry [23].

Table 2. Electronic spectral data and magnetic properties of the prepared compounds.

| Compound | Molar Conc. | $\lambda$ nm | $\varepsilon_\lambda$ L mol$^{-1}$ cm$^{-1}$ | Assignment | $\mu_{eff}$ |
|----------|-------------|--------------|---------------------------------------------|-------------|-------------|
| L        |             | 203          | 2400                                        | $\pi$-$\pi^*$ |             |
|          | 250         | 10600        | INCT                                        |             |
| [MnL]    | 1x10$^{-3}$ | 365          | 150                                         | $^6$Aig $\rightarrow$$^3$T_{1g}(F) | 5.58         |
|          | 255         | 7800         | MLCT                                        |             |
The thermo gravimetric analysis of C1 and C4 was confirmed their thermal stability in argon atmosphere. These complexes are displayed steps of decomposition with expected weight loss. The TG-DSC thermograms of C1 (Figure 5) showed exothermic processes at around (70-169) °C and (169-250) °C with weight loss 5.95 % and 25.66 % respectively. These are due to the loss of lattice water (2H2O), and to the fragmentation of –2CH3 (attached to the pyrazoline ring) and -2Cl (counter ion) [23]. Likewise, the third and fourth steps of thermal process were detected at around (262-365) and (370-499) °C with 18.30 and 23.66 % of weight loss respectively, that associated with the calculated percent of losing inner sphere Cl ions, and two coordinated water molecules since they are considered strong points in the skeletal of the complex structure [24,25]. However, stable phase of the complex was observed as MnS and Mn2O3 which ordinarily possesses elevated melting point. By the same manner where the decomposition steps of Cu(II) complex (C1), C4 formed with L ligand, the dehydration was showed at (42-143) °C with 8.55% weight loss, that is in well agreement with loss of two molecules of hydrated water as lattice water molecules [26]. The steps observed at around (150-350) and (380-595) °C with 36.70% weight loss, was consisted with loss of pyridyl, thiocarbamoyl moiety and terminal coordinated chloride anions. The final products in the stable phase were CuS and CuO with 56% weight loss [27].

3.6. Thermal analyses

|    | (mol) | 1x10^{-3} | 1x10^{-4} | 1x10^{-4} |
|----|-------|-----------|-----------|-----------|
| [CoL] |       | 685       | 590       | 395       |
|      |       | 180       | 290       | 9040      |
|      |       | 310       | 12000     |           |
| [NiL] |       | 4.90      |           | 0.0       |
|      |       |           |           |           |
| [CuL] |       | 4.90      |           |           |
|      |       |           |           |           |
| [ZnL] |       | 4.90      |           |           |

LMCT and MLCT=Ligand to metal charge transfer or *vice-versa*

**Figure 5.** TG-DSC analysis of C1 complex.
4. Conclusion.
The results obtained from the FT-IR spectroscopy showed that nitrogen and sulfur atoms of pyrazole ring and thioamide moiety are the active sites in coordination with the metal ions. In addition, UV-Visible spectra and magnetic moments measurements along with the micro-elemental analyses indicated the octahedral geometry for all complexes except Ni(II) and Zn(II) complexes which are square-planner and tetrahedral respectively, Scheme(3).

Scheme 3. Proposed structures for Mn(II), Co(II) and Cu(II) complexes.

5. Acknowledgement:
Authors are so grateful for the members of chemistry department, College of Science, Mustansiriya University for facilities of FT-IR, UV-Visible spectra and magnetic moments measurements. As well as authors express appreciation for Al-Bait University, Amman for carrying out the measurements of NMR and elemental analyses.

6. Reference
[1] Abdolmalekia, A. and Ghasemi, J.B., 2016. Dual-action hybrid compounds– a new dawn in the discovery of multi-target drugs: lead generation approaches. Curr. Top. Med. Chem. 16 (1), 1–19.
[2] Abid, M., Bhat, A.R., Athar, F. and Azam, A., 2009. Synthesis, spectral studies and antiamoebic activity of new 1-N-substituted thiocarbamoyl- 3-phenyl-2-pyrazolines. Eur. J. Med. Chem. 44, 417–425.
[3] Sayed and N. Saglain, H. Bioorg. 2014, Synthesis and evaluation of pyrazolines bearing benzothiazole as anti-inflammatory agents. Med. Chemistry 23, 5804-5812.

[4] Ali, I., Wani, W.A., Khan, A., Haque, A., Ahmad, A., Saleem, K. and Manzoor, N., 2012. Synthesis and synergistic antifungal activities of a pyrazoline based ligand and its copper(II) and nickel(II) complexes with conventional antifungals. Microb. Pathog. 53 (2), 66-73.

[5] Bogumiška, K., Krzyżtof S., Katarzyna M., KamilaK., Malgorzata C., Bernhard K. and El-Zbieta B. 2013, Copper(II) complexes with derivatives of pyrazole as potential antioxidant enzyme mimics Med. Chem. Research 22,2395-2402.

[6] Attila, K., Katalin M.,Vukadin M.,Zoran D. and Gyorgy, P.2007 J. Organo...
[24] Lever A B . P. 1987 Inorganic Electronic Spectroscopy (Elsevier: Amsterdam – Oxford – New York – Tokyo), 211.

[25] Ting, H.Y. Silva, A.R. Shi & F.N. (2013). Six new 3d–4f heterometallic coordination polymers constructed from pyrazole-bridged CuIILnIII dinuclear units. Dalton Transaction 42, 13997–1405.

[26] Urszula K. & Marek R. (2007). Anion Separation with Metal-Organic Frameworks. Eur. J. Inorg. Chemistry 10, 3728–3735.

[27] Zuhal O., H. Burak K., Bulent G., Unsal C. and Bilgin A. 2008 Synthesis and Biological Evaluation of a Series of Substituted Pyrazolo[3,4-d]-1,2,3-triazoles and Pyrazolo[3,4-d]oxazoles. Arch. Pharm. Chemistry 341, 701-707.