

Synthesis and Characterization of New Schiff Bases and Using Them Us Tri Dentate Ligands in Metal Complexes

Ahemd Ahmed

Department of Chemistry
College of Science
Al-Nahrain University
Baghdad, Iraq

Reyahd Ahmed

Ismaeel Majed

Department of Chemistry
College of Education- Ibn Al-Haitham
Baghdad University
Baghdad, Iraq

Abstract

New ligands were synthesized and characterized by (FTIR, ^1H NMR and ^{13}C NMR), then use the ligands to prepare a series of coordination complexes of Cd(II), Co(II), Mn(II) and Ni(II) metal. The new ligands act as tridentate that coordination to the metal ions; the spectral data of the complexes an octahedral geometry was suggested for these complexes, also new complexes were characterized in FTIR spectroscopy, UV-visible spectroscopy, ^1H and ^{13}C NMR.

Keywords: Metal complexes, octahedral complexes, tri dentate, synthesis, coordination

1. Introduction

There is great interest in synthesis and characterization of ligands which contain O,N-sequence and their metal complexes. Heterocyclic chemistry has now become a separate field of chemistry with long history, present society and future prospects. Nitrogen, oxygen and sulfur are considered the most hetero atoms known. Heterocyclic compounds are considered one of an important type of organic compounds due to their implication in drugs and industrial studies (Ibtisam, Sawsan, Rua and Ali, 2012; Carey, 1980). A little work has been done concerning the preparation and investigation of the metal complexes having 1,3,4- thiadiazole nucleus. Metal complexes has been used as photographic layer stabilizer (Khalil, 2006), and in marine anti- fouling and anti-corrosion paints (Rajendran, Ravichandran and Rajeswari, 1995). The ligand has also been used as an analytical reagent in the detection and determination of metal ions (David and Paul, 2006). Mono and disubstituted 1,3,4-thiadiazole ligands and their complexes have pharmacological properties (Margaret, Stewart, John and Abraham, 1960). Five membered aromatic systems containing three hetero atoms at symmetrical positions have been studied due to their interesting physiological properties (Sabir and Jyoti, 2008), 1,3,4-Thiadiazole can act as a ligand and its complexes have a wide variety applications especially as antifungal and antibacterial agents (Samee and Vajragupta, 2011; Kumar, Yadav, Dudhe and Sharma, 2010). 1,3,4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field (Farzin and Rahil, 2008; Lu and Chen, 2000).

2. Materials and Methods

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The Infrared (FTIR) spectra were recorded by using FTIR 8400 Shimadzu spectrophotometer by using CsI disc in the frequency range of 4000-200 cm^{-1} . The ultraviolet-visible (UV-VIS) spectra were recorded by using Shimadzu UV-VIS. 160 A-Ultra-violet spectrophotometer in the range of 200-1100 nm. Conductivity measurements were carried out by using WTW conductivity meter. Atomic absorption measurements were obtained by using Shimadzu 680cc-flame.

The spectra of ^1H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz in Jordan, using deuterated DMSO- d_6 as the solvent and tetramethylsilane, TMS as the internal standard.

2.1 Synthesis of 1, 3, 4-Thiadiazole-2, 5-dithiol (1)

Mixtures of (80%) hydrazine hydrate (5 ml., 0.02 mol.) and carbon disulfide (15 ml., 0.02 mol.) with dry pyridine (50 ml.) was refluxed for (5 hours). Then the excess solvent was then distilled off, and the resulting solid was separated out by adding (25 ml.) of water and (5 ml.) of hydrochloric acid. The mixture was then filtered and the solid was recrystallized from ethanol, yield (82.01%).

FTIR: 1624 (C=N), 1330(C-S), 2550 (S-H).

^1H NMR: δ 3.21 (H, s,SH).

^{13}C NMR: 114.32 (C, thiadiazolering).

2.2 Synthesis of O, O'-Diethyl-S, S'-1,3,4-Thiadiazol-2,5-Diyl dicarbonot-Hioate (2)

Ethyl chloroformate (22.64 g., 0.1848 mol.) was added drop wise to a stirred cold solution of 1,3,4-thiadiazole-2,5-dithiol (2 g., 0.0924 mol.). The reaction mixture was refluxed for (6 hours), after cooling the solvent was evaporated and the crude product was obtained as a powder, yield (86%).

FTIR: 1624 (C=N), 1330(C-S), 2550 (S-H).

^1H NMR: δ 1.26 (3H, t, CH_3), δ 3.39 (2H, q, CH_2).

^{13}C NMR: 116.86 (C, thiadiazole ring), 159.56 (C, carbonyl group), 62.91 (C, methylene group), 12.02 (C, methyl group).

2.3 Synthesis of S, S'-1, 3, 4-thiadiazol-2,5-diyl bis (hydrazine car bothio-ate) (3)

Compound (3) was synthesized by addition of hydrazine hydrate (10 ml.) to ethanolic solution of compound (2) (5 g., 0.0178 mol.), the mixture was refluxed for (4 hours), and then cooled and filtered off, recrystallized from ethanol, yield (89%).

FTIR: 1624 (C=N), 1330(C-S), 2550 (S-H).

^1H NMR: δ 7.57 (H, s, N-H), δ 4.22 (2H, s, NH_2).

^{13}C NMR: 117.95 (C, thiadiazole ring), 167.08 (C, carbonyl group).

2.4 Synthesis of S, S'-1, 3, 4-thiadiazol-2,5-diyl bis[2-(2-hydroxybenzylidene) hydrazinecarbothioate] (4)

A mixture of compound (3) (1 g., 0.0022 mol.) and 2-hydroxybenzaldehyde (1 g., 0.0022 mol.) in (20 ml.) of ethanol and two drops of glacial acetic acid was refluxed for (7 hours). The mixture was cooled to form the precipitate and recrystallized from ethanol, Yield (92%).

FTIR: 1624 (C=N), 1330(C-S), 2550 (S-H)

^1H NMR: δ 8.20 (H, s, NH), δ 8.73 (H, s, CH=N), δ 6.88-7.31 (4H, m, aromatic ring), δ 10.21 (H, s, OH).

^{13}C NMR: 115.69 (C, thiadiazole ring), 166.30 (C, carbonyl group), 147.00 (C, CH=N), 120.36-160.89 (6C, aromatic ring).

2.5 Synthesis of S, S'-1, 3, 4-thiadiazol-2, 5-diyl bis {2-[(1-hydroxynaphthalen-2-yl) methylidene] hydrazinecarbothioate} (5)

Follows the same procedure for preparation of compound(4), but using 2-hydroxy-1-naphthaldehyde (1 g., 0.0022 mol.) Instead of 2-hydroxybenzaldehyde, yield (88%).

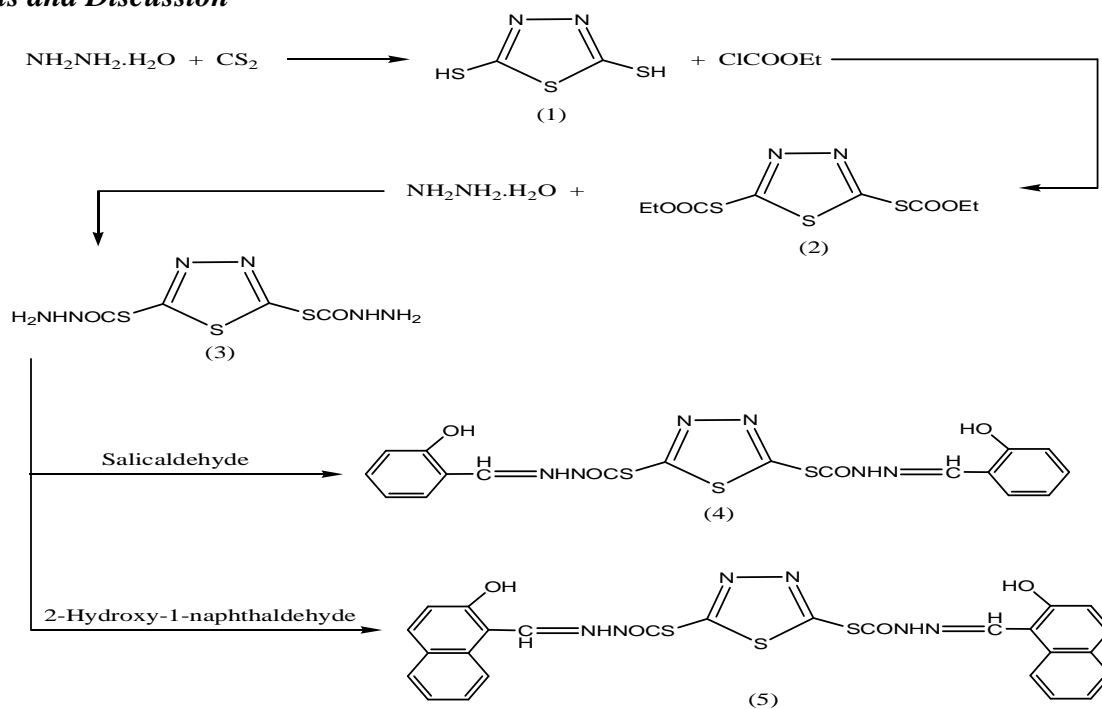
^1H NMR: δ 8.42 (H, s, NH), δ 8.89 (H, s, CH=N), δ 7.12-8.78 (6H, m, aromatic ring), δ 11.75 (H, s, OH).

^{13}C NMR: 115.55 (C, thiadiazole ring), 168.98 (C, carbonyl group), 145.20 (C, CH=N), 108.58-172.08 (10C, naphthalene ring).

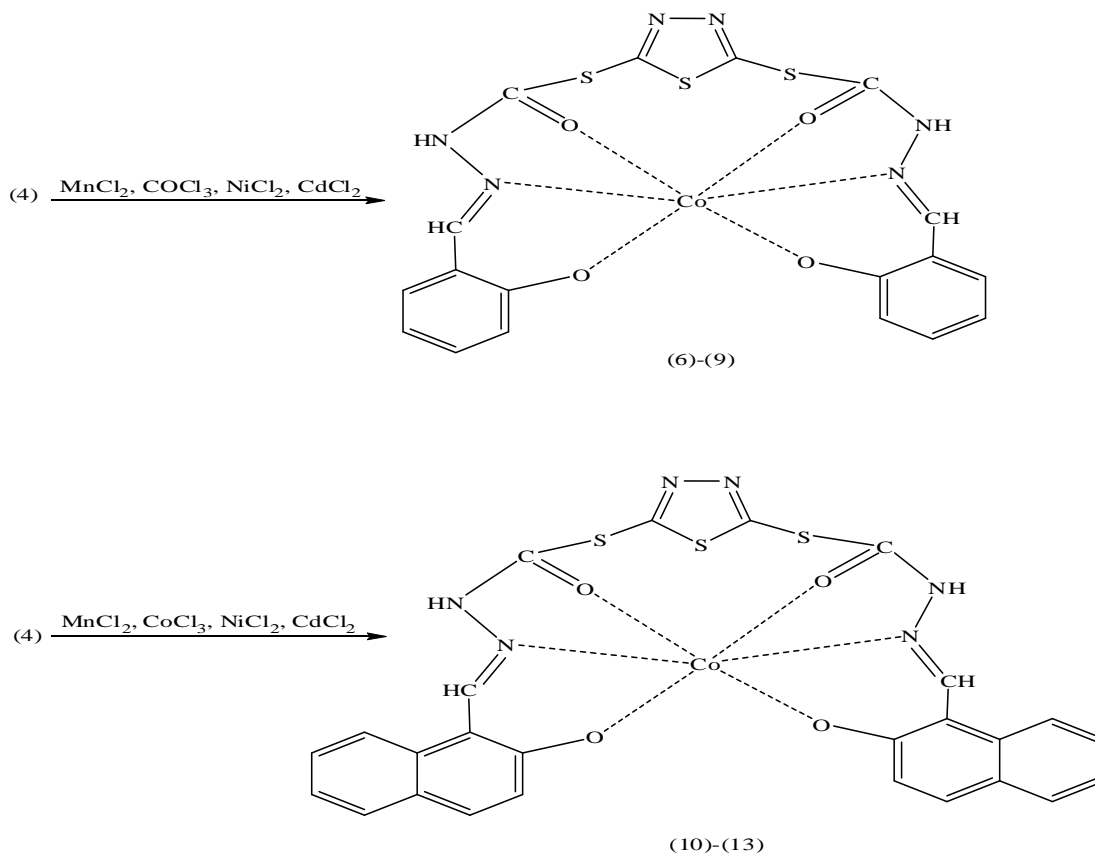
2.6 Synthesis of the Ligand's Complexes

Ethanolic solution of the suitable metal salts [Cadmium(II) chloride, Cobalt(II) Chloride, Manganese(II) chloride and Nickel(II) chloride] was added to an ethanolic solution of compounds (4) and (5) respectively in 2:1 (metal:ligand) molar ratio and refluxed for two hours, crystalline colored precipitates was formed at room temperature. The resulting solids were washed by hot methanol and left to dried.

3. Results and Discussion



Scheme 1: Synthesis Route of the Ligands (4) and (5)



M= Mn, Co, Ni, Cd

Scheme 2: Synthesis Route of the Complexes (6)-(13)

3.1 FTIR Spectroscopy

The characteristic bands of complexes (6)-(13) in FTIR spectroscopy were showed in Table (1).

Complexes	NH cm^{-1}	CH aromatic cm^{-1}	C=O cm^{-1}	CH=N cm^{-1}	C=N endocyclic cm^{-1}
(6)Mn	3205	3062	1620	1604	1573
(7)Co	3213	3069	1627	1618	1559
(8)Ni	3234	3098	1616	1601	1564
(9)Cd	3190	3107	1631	1622	1571
(10)Mn	3294	3083	1638	1600	1566
(11)Co	3072	3057	1622	1605	1579
(12)Ni	3151	3078	1625	1617	1570
(13)Cd	3246	3174	1624	1610	1588

Table (1): Key Infrared Data of Complexes (6)-(13)

3.2 Electronic Spectra and Magnetic Measurement

The UV-Vis spectra of the ligands exhibit a high intense absorption peaks around 263-270 and 314-376 nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively (Mohamad, Amar and Alyaa, 2009). The electronic spectra of all complexes with L^1 and L^2 exhibit high intense peaks at 263-277, due to intraligand. The absorption bands at 362-381 nm for L^1 attributed to charge transfer. The spectrum of the Mn(II) complex for 1 and 2 exhibited band at 579 and 661 which can be attributed to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition, corresponding to octahedral Mn(II) complexes (El-Sonbati, Al-Shihri and. El-Bindary, 2004). The spectrum of the Co(II) complex for 1 and 2 exhibited band which can be attributed to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ transition, corresponding to octahedral Co(II) complexes (Ahlam, Mohamad and Ahmed, 2009; Modi, 2009). The spectrum of the Ni(II) complex for 1 and 2 exhibited bands at 616 and 671 nm assigned to $3A_{2g} \rightarrow 3T_{1g}(F)$, which indicate octahedral geometries (Jin, Hanyoung, Alan and Ju, 2010). The spectrum of the Cd(II) complex for 1 and 2 show peak at 264 and 265 nm assigned to $\pi \rightarrow \pi^*$ (Mohamad, Hasen and Worood, 2009). The metal normally prefers tetrahedral geometry.

Complex	Absorption
(6)Mn	9.95
(7)Co	11.83
(8)Ni	11.75
(9)Cd	18.63
(10)Mn	9.17
(11)Co	9.45
(12)Ni	8.91
(13)Cd	15.89

Table (2): Atomic Absorption of the Complexes (7)-(13)

4. Conclusion

The preparation procedure follow in this work for the synthesis of title compounds offers reduction in thereaction time, operation simplicity, cleaner reaction and easy work-up. All the data of the spectroscopic analysis confirmed the proposed structures for these compounds and complexes.

Acknowledgment

The authors acknowledge the staffs of Al- Nahrain University, College of Science, Chemistry Department and Baghdad University, College of Education- Ibn Al- Haitham, Chemistry Department.

References

- Ibtisam, K. J., Sawsan, S. H., Rua, M. D., and Ali O. A. (2012). Synthesis and study the biological activity of some six, five and fused ring heteroatome systems derived from 2-mercapto benzothiazole. *Tikrit J. Pharmaceutical Sci.*, 8(1), 96–105.
- Carey, F. (1980). *Organic Chemistry*. McGraw-Hill Inc, America.
- Khalil, K. Abid. (2006). Lanthanide metal complexes of 1, 3, 4- thiadiazole ligands. *National J. Chem.*, 24, 596–607.
- Rajendran, N., Ravichandran, K., Rajeswari, S. (1995). Influence of substituents in thiadiazole on the localized corrosion of 316L stainless steel in simulated flue gas desulphurization environment, *Anti-Corrosion Methods and Materials*. *Anti-corrosion method and materials*, 42, 8–10.
- David, B. T., Paul, B. (2006). *The Science and Practice of Pharmacy*. Lippincott Williams & Wilkins, 21st edition, America.
- Margaret, M., C., Stewart, R. H., John, M. V., Abraham, G. (1960). The Antileukemic Action of Two Thiadiazole Derivatives. *Cancer Res*, 20, 1195–1201.
- Sabir, H., Jyoti, S., Mohd, A. (2008). Synthesis and Antimicrobial Activities of 1,2,4-Triazole and 1,3,4-Thiadiazole Derivatives of 5-Amino-2-Hydroxybenzoic Acid. *CODEN ECJHAO E-J. Chem.*, 5(4), 963–968.
- Samee, W., Vajragupta, O. (2011). Antifungal, cytotoxic activities and docking studies of 2,5-dimercapto-1,3,4-thiadiazole derivatives. *African J. Pharmacy and Pharmacology*, 5(4), 477-485,
- Kumar, J. G., Yadav, R. K., Dudhe, R., Sharma, P. K. (2010). Recent Advancements in the Synthesis and Pharmacological Evaluation of Substituted 1, 3, 4-Thiadiazole Derivatives. *International J. of PharmTech Research*, 2(2), 1493–1507.
- Farzin, H., Rahil, V. (2008). Synthesis of α -[5-(5-Amino-1, 3, 4-thiadiazol-2-yl)-2-imidazolylthio]acetic acids. *J. Heterocyclic Chem.*, 45, 1–3.
- Lu, S. M., Chen, R. Y. (2000). Facial and efficient synthesis aminophosphate derivatives of 1, 3, 4-oxadiazole and 1,3,4-thiadiazole. *Organic Preparations and Procedures International*, 32(3), 302–306.
- Mohamad, J., Amar, H., Alyaa, E. (2009). Coordination of carbonyl oxygen in the complexes of polymeric N-crotonyl-2-hydroxyphenylazomethine. *Transition Met. Chem.*, 34(1), 109–113.
- El-Sonbati, A. Z., Al-Shihri, A. S., El-Bindary, A. A. (2004). Stereochemistry of new nitrogen containing heterocyclic aldehyde: Part XI. Novel ligational behaviour of quinoline as chelate ligand toward transition metal ions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 60, 1763–1768.
- Ahlam, J. A., Mohamad, J., Ahmed, J. M. (2009). Synthesis and spectral studies of new N₂S₂ and N₂O₂ Mannich base ligands and their metal complexes. *J. Coord. Chem.*, 62(16), 2736–2744.
- Modi, C. K. (2009). *Molecular Biomecular Spectroscopy*. *Spectrochimica Acta Part A*: 71, 1741.
- Jin, S. K., Hanyoung P., Alan, J. L., Ju, C. K. (2010). A Macrocyclic Nickel (II) Complex Salt Containing Six-Coordinate Nickel(II) Ions in a Different Coordination Environment. *Bull. Korean Chem. Soc.*, 31(1), 189–192.
- Mohamad, J., Hassan, A. H., Worood, A. J. (2009). Formation of polymeric chain assemblies of transition metal complexes with a multidentate Schiff-base. *Transition Met. Chem.*, 34(6), 593–598.