Iraqi Journal of Scientific and Industrial Research
Volume 4, Issue 3, July-September 2025, pp. 86-90

Spectral and Physical Studying of Dithiocarbamate Mixed Ligand Complexes

Abd A. Athuiny

Center of Agriculture, Scientific Research Committee, Ministry of Higher Education, P.O. Box 765, Baghdad, IRAQ

Abstract

A number of mixed ligand dithiocarbamate complexes with the general formula $[ML_2(py)_2]$ have been prepared and characterized by elemental analysis, FTIR and UV spectroscopy, magnetic moment, thermogravimetric and conductance analysis, and M = Mn (II), Co (II), Ni (II), and Cu(II), py = pyridine, and L = N-methyl-N-phenyl dithiocarbamate. It was demonstrated by the infrared spectra that the pyridine molecule in the complexes experienced neutral monodentate coordination through the nitrogen atom, whereas the dithiocarbamate moiety experienced symmetrical bidentate coordination through the sulfur atoms. It was demonstrated by the results of the magnetic moment, elemental analysis, and electronic spectra that the complexes adopted an octahedral geometry.

Keywords: Potato, *in vitro*, Phytohormone, Crystal protein

Received: 8 April 2025; **Revised:** 14 May 2025; **Accepted:** 21 May 2025; **Published:** 1 July 2025

1. Introduction

Dithiocarbamate complexes adduct formation is influenced by the electron density drifting towards the sulfur atoms of dithiocarbamate bases as a result of the $–NR_2$ group's mesomeric action[1,2]. Metal complexes inclinations to form adducts vary and are strongly correlated with the ionic size of the central metal ion, the geometry of the coordinated ligand, and the Lewis base's capacity to take in π-electrons [3]. The sulfur atoms donate electrons to the metal's nonbonding molecular orbital because the $–NR_2$ group gives them more electrons than other dithiolates, such xanthate [4]. Therefore, it is not always preferred to take the traditional path of further reaction that results in the development of an addict. The stability and additional physicochemical characteristics of a metal complex are influenced by the characteristics of the R-group in the $-NR_2$ moiety. Electrons may flow more or less towards the ligating CS_2 group, depending on the inductive impact (positive or negative) of the groups on the nitrogen atom [5,6]. It is interesting to note that their adducts of pyridine,2,2-bipyridine, triphenylphosphine, and 1,10-phenanthroline have been shown to have antifungal qualities [5,7,8].

In comparison to their parent metal complexes and uncomplexed ligand, some exhibit actions against a broad spectrum and are more active. The literature has documented several dithiocarbamate adducts with different geometries, including square planar, octahedral, and trigonal prismatic [9-12]. Due to its potent chelating capacity toward inorganic species, dithiocarbamates have also been used in the environment in the significant field of solvent extraction for the separation of metal ions. Because of its simplicity, speed, and broad applicability, solvent extraction—which involves chelation—has been described as one of the most popular methods for preconcentrating and separating metal ions from aqueous samples for analytical reasons [13,14]. The introduction of specific chelating agents for trace metal identification in recent years has increased the technique's use[15-17]. With the right extracting agents, group separation or selective separation of trace elements can be accomplished in solvent extraction with great efficiency.

In a previous study, the antibacterial characteristics was evaluated of some N-methyl-N-phenyl dithiocarbamate transition metal complexes, which showed promise as antibacterial agents[18]. For Mn(II), Co(II), Ni(II), and Cu(II), we provide the synthesis, characterization, and antifungal properties of the pyridine adducts of N-methyl-N-phenyl dithiocarbamate complexes. For the first time, we also report that N-methyl-N-phenyl dithiocarbamate may extract Ni(II) and Cu(II) ions from the aqueous phase into the organic phase. Employing Job's approach of continuous variation, the nature of the isolated substance was also examined.

2. Experimental Part

In physical Measurement, every chemical reagent utilized was of analytical grade and was used just as supplied, requiring no additional purification. Sigma-Aldrich provided the sodium hydroxide, carbon disulfide, and N-methyl aniline. Merck Co. supplied the following: pyridine, nickel (II) chloride hexahydrate, cobalt (II) chloride dihydrate, copper

(II) nitrate trihydrate, anhydrous copper (II) sulphate, manganese (II) nitrate hexahydrate, nickel (II) nitrate hexahydrate, ammonia, distilled water, hydrochloric acid, ammonia, and chloroform.

In chemical synthesis, pyridine reacted with the hydrated metal salts in the first stage of the reaction, which was followed by a displacement reaction with the dithiocarbamate ligand. The production of sodium N-methyl-N-phenyl dithiocarbamate [NaL] is covered in. Following the stated protocol, sodium N-methyl-N-phenyl dithiocarbamate was made[18]. Using a thermometer and a two-necked flask, a solution of sodium hydroxide (8 g, 0.2 mol) in 10 mL of distilled water was made. This solution was mixed with 21.80 mL of N-methyl aniline (density 0.985) and agitated for around two hours at a low temperature of 2–4 °C. Following separation, the yellowish-white solid product was filtered, cleaned with a small amount of ether, and then recrystallized in acetone. The Complexes of $MCl_2·(py)_2$ were synthesized as followed in 1:2 molar ratios, a 25 mL solution of the corresponding hydrated metal (II) chlorides in methanol was mixed with 15 mL of pyridine methanol solution. After refluxing the combination for one hour, the solution was allowed to separate from the solvent.

After gathering the precipitates, they were repeatedly cleaned with a methanol-water mixture to get rid of any unreacted starting components, and then they were dried in a vacuum. $[ML_2(py)_2]$ are synthesized. The addition of a 20 mL methanolic solution of sodium N-methyl-N-phenyl dithiocarbamate (NaL) (2 mmol) to a 20 mL solution of $MCl_2·(py)_2$ [where M = Mn (II), Co (II), Ni (II), and Cu (II)] in methanol (1 mmol) was done while stirring continuously for approximately 60 minutes at room temperature. After filtering and washing with methanol and water, the precipitate was vacuum-dried. Using a Bruker alpha-P FT-IR spectrometer, infrared spectra in the 500–4000 cm^{-1} range were collected. An elemental analyzer was used for the microanalyses.

Using a Johnson Matthey magnetic susceptibility balance, magnetic susceptibilities were measured, and Pascal's constant was used to compute diamagnetic corrections. Mark V conductivity meter with a cell constant of 1.0, conductivity measurements were made. Solid reflectance from UV-Vis spectra recorded using a Perkin Elmer Lambda 40 UV-Vis spectrometer. In this experiment, the Hitachi-18050 atomic absorption spectrometer was utilized.

The extraction process was done by taking equal amounts of the ligand's chloroform and methanol solutions (4×10^{-4} M) were added to aqueous solutions containing 1.5×10^{-3} M metal salt in a suitable buffer with a pH of 1–10 to equilibrate them. The shaker was mechanically operated at 25 °C. Since it was insoluble in chloroform, the ligand was dissolved in methanol. In order to prevent diffusion from limiting the complexation reaction, the aqueous and organic phases were thoroughly shaken, increasing contact and bringing the concentrations of the various species into uniformity. Following agitation, the solutions were left to stand for fifteen minutes. After the solution was moved to a separating funnel, the organic and aqueous layers were allowed to separate before being put into a volumetric flask. Five milliliters of chloroform were used to repeat the extraction. AAS was used to measure the concentration of copper (II) and nickel (II) ions in the aqueous phase, and the mass balance was taken into consideration to determine the concentration of the organic phase based on the difference.

The method of continuous variation procedure for nickel and copper salt solutions, pipettes were used to transfer 0, 1, 2, 3, 4, 5, and 6 mL 4×10^{-4} M into separate 50 mL volumetric flasks (7 numbers). The mole fraction of solution was maintained by adding aliquots of the ligand in increments of 6, 5, 4, 3, 2, 1, and 0 mL 4×10^{-4} M. The pH 10 of the solution was buffered. The wavelength at which the greatest absorbance was recorded was 622 nm for copper solution and 640 nm for nickel solution, respectively. We took all of the measurements at 25 °C (Fig. 2).

3. Results and Discussion

The precursor compounds for the synthesis of the pyridyl adducts of the dithiocarbamate were the pyridine complexes, which were produced by the interaction of pyridine with the corresponding metal salts in methanol solution. The traditional approach of preparing pyridine adducts, which typically entails adding Lewis's base to the premade dithiocarbamate complex, did not work. Room temperature did not affect any of the compounds' stability.

The FTIR spectra of all compounds exhibit (=C–H) stretching vibrations around 3040 cm^{-1}, but the CH_3 group's (–C–H) stretching vibrations emerged about 2864 cm^{-1}. The thiouridine bond is identified by a prominent band that appears in the spectra of all the compounds between 1430 and 1444 cm^{-1}. In pyridine adducts, the comparatively reduced electron flow of the nitrogen lone pair of electrons towards the central metal ion results in a decrease in the stretching frequency of thiouridine [4]. The electron density rises as a result of the more pyridine molecules. The v(CS2) vibration manifested as a single band between 910 and 920 cm^{-1}, suggesting that the two sulfur atoms were symmetrically bonded to the metal ion. In every compound, the pyridine-related bands were seen in the 1601–1608 cm^{-1} range. Additionally, the dithiocarbamate ligands obscured other peaks.

According to the protocol described in the literature, the electronic spectra of each compound were captured as solid reflectance[18]. Electronic changes in the ligands ($n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$), metal d-d transitions, and charge transfer transitions (metal to ligands and ligand to metal charge transitions) are the causes of absorption bands [19,20]. The $n\rightarrow\pi^*$ transition from the C=N group of the pyridine molecule and dithiocarbamate moiety was responsible for the bands centered between 340 and 366 nm in the metal adducts. Absorption bands at around 366 nm, 352 nm, 670 nm, and 762 nm were visible in the cobalt adducts' electronic spectrum. The $n\rightarrow\pi^*$ transitions of the C=N group in the pyridine and the dithiocarbamate moiety are responsible for the bands at about 352 and 366 nm [18]. The $4T_{1g}\rightarrow 4A_{2g}$ and $4T_{1g}\rightarrow 4T_{1g(p)}$ transitions are responsible for the d-d bands at 670 nm and 762 nm, respectively, for an octahedral d^7 geometry with a 4F ground term. With a magnetic moment value of 1.82 BM, the cobalt adducts low spin octahedral geometry was confirmed. Magnetic moment ranges from 1.70 to 1.85 BM in low spin octahedral cobalt complexes and from 4.7 to 5.2 BM in high spin octahedral cobalt complexes [19-21]. According to an octahedral d^8 system in the 3F ground term, the nickel adducts displayed visible bands for the $3A_{2g}\rightarrow 3T_{1g(F)}$ and $3A_{2g}\rightarrow 3T_{1g(P)}$ transitions, as well as bands at 341 nm, 650 nm, and 686 nm caused by the $n\rightarrow\pi^*$ transition in the UV region [19]. It is not seen in the visible spectrum because the $3A_{2g}\rightarrow 3T_{2g}$ transition frequently tails into the infrared [22,23]. The magnetic moment value of 2.78 BM supports an octahedral geometry; an octahedral d^8 system should have a magnetic moment between 2.90 and 3.30 BM. Perhaps antiferromagnetic is the cause of the lower value. A square planar nickel (II) complex will have a zero moment, whereas a tetrahedral d8 system will have a magnetic moment of 3.20–4.10 BM [22].

A large spectrum is anticipated for octahedral d^9 copper complexes because of the $2E_g\rightarrow 2T_{1g}$ with a 2D ground term. However, a splitting of $2E_g$ and $2T_{2g}$ into $2B_{1g}$, $2A_{2g}$, and $2B_{2g}$, $2E_g$, respectively, is typically found for the Jahn-Teller effect, which is generated by asymmetrical filling of the E_g set of orbitals[24]. The transitions may therefore resolve into two or three absorption band components, or they may lie inside a single envelope. At 355 nm, the ligand bands for the copper adduct were detected and attributed to the $n\rightarrow\pi^*$ transition. Due to the Jahn-Teller effect, the d-d transition was detected at 539 and 545 nm. Regardless of shape, the magnetic moment for a mononuclear copper complex ranges between 1.9 and 2.2 BM. The mononuclear character of the copper adduct was aided by its magnetic moment of 2.02 BM.

Three weak bands, one ligand band, and two forbidden transition bands characteristic of 6-coordinate octahedral geometry were observed in the Mn(II) adduct at 340, 556, and 650 nm. These bands were attributed to $n\rightarrow\pi^*$ and the forbidden transitions of $6A_{1g}\rightarrow 4T_{1g}$ and $6A_{1g}\rightarrow 4T_{2g\ (G)}$. Mn(II) complexes' effective magnetic moments should be near the spin-only value of 5.90 BM. The ground term is 6A1g, hence the orbital contribution is zero. Accordingly, this complex is high spin and complementary to octahedral geometry, as evidenced by the measured moment of 5.71 B.M [25].

The measurement of molar conductivity of complexes electrolytic nature was assessed at a concentration of 10^{-3} M in DMSO. For NiL_2Py_2, CuL_2Py_2, CoL_2Py_2, and MnL_2Py_2, the molar conductivity values were 19.16 $\Omega^{-1}cm^2\ mol^{-1}$, 13.06 $\Omega^{-1}cm^2\ mol^{-1}$, 24.4 $\Omega^{-1}cm^2\ mol^{-1}$, and 10.84 $\Omega^{-1}cm^2\ mol^{-1}$. The complexes were nonelectrolyte in nature, according to the data [26,27].

Studies of solvent extraction of ligand added to the aqueous phase, it combines with nickel and copper to create colorful metal complexes that move from the aqueous phase into the organic phase. In just three minutes, the color developed to its fullest (Scheme 1). The ligand caused the nickel solution to turn greenish and the copper solution to turn reddish-brown. At various pH levels, the simultaneous measurement of Ni^{2+} and Cu^{2+} in the aqueous phase was used to study the ligand's metal ion extraction (table 1).

Table (1) Extraction efficiency of nickel ion at different pH levels

pH	Amount of metal found in the aqueous phase (μg/mL)	Amount of metal found in the organic phase (μg/mL)	Percentage extraction (%)
1.2	2.95	85.86	96.7
2.5	3.42	85.39	96.2
3.2	3.04	85.77	96.6
4.2	1.96	86.85	97.8
5.3	1.52	87.29	98.3
6.5	1.14	87.67	98.7
7.3	1.02	87.79	98.9
8.2	1.21	87.60	98.6
9.3	1.18	87.63	98.7
10.2	0.86	87.95	99.0

The extractability and selectivity of metal ions were evaluated as a function of pH. The pH of the aqueous solution before extraction was varied from 1.2 to 10.2 by using solutions of HNO_3 (0.1 M) and NaOH (0.1 M). The percentage extraction and distribution ratio are described in Tables 2 and 3, and the graphical presentation is given in Figure 1. The obtained results are expressed in terms of the extraction ratio (%) and the partition coefficient *D* (tables 2 and 3)

$$\left.\begin{aligned} R\% &= \frac{[M_i]-[M_f]}{[M_i]}\times 100\% \\ D &= \frac{[M_i]-[M_f]}{[M_i]} \end{aligned}\right\} \qquad (1)$$

$$S_f = \frac{D_{\mathrm{Ni}}}{D_{\mathrm{Cu}}} \qquad (2)$$

where $[Mi]$ and $[Mf]$are the initial and final concentrations in the aqueous phase. The degree of separation was determined in terms of separation factor, Sf, defined as the ratio of distribution ratio for copper ion.

Table (2) Extraction efficiency of copper ion at different pH levels

pH	Amount of metal found in the aqueous phase (µg/mL)	Amount of metal found in the organic phase (µg/mL)	Percentage extraction (%)
1.2	4.08	91.40	95.70
2.5	4.29	91.19	95.50
3.2	4.63	90.85	95.10
4.2	3.99	91.49	95.80
5.3	3.27	92.21	96.60
6.5	3.05	92.43	96.80
7.3	2.68	92.80	97.20
8.2	2.71	92.77	97.20
9.3	2.42	93.06	97.50
10.2	1.32	94.16	98.60

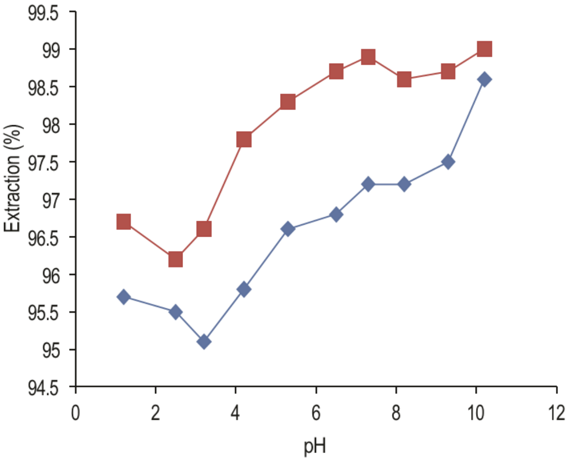


Fig. (1) Effect of pH on the extraction of copper ion or nickel ion extraction by *N*-methyl-*N*-phenyl dithiocarbamate

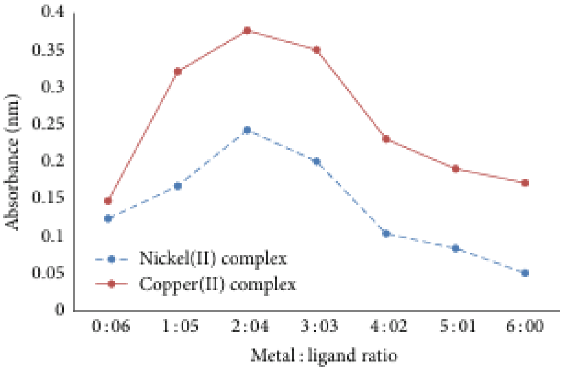
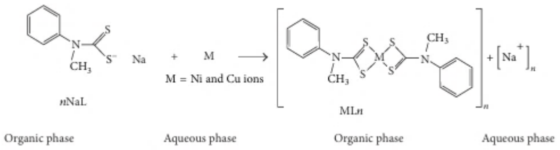


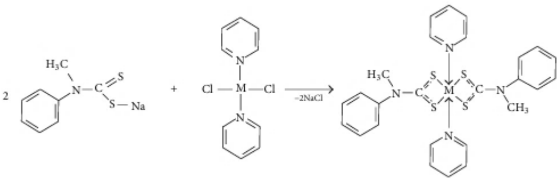
Fig. (2) Job's curves of equimolar solutions at 622nm copper ion and 640nmnickel ion extraction

Table (3) Experimental data for nickel (II) and copper (II) extraction by Job's continuous variation method

Metal: ligand mL	Absorbance for nickel (II) complex	Absorbance for nickel (II) complex
0: 6	0.124	0.148
1: 5	0.168	0.322
2: 4	0.243	0.377
3: 3	0.201	0.351
4: 2	0.104	0.231
5: 1	0.084	0.191
6: 0	0.051	0.172



SCHEME 1: Schematic representation of the extraction process.



Scheme (1) Studies of Solvent Extraction with ligand nickel and copper

References

[1] B. K. Shashi, K. Geetanjli, and Priyanka, "Synthesis and characterization of pyridine adducts of some transition metal 4methylpiperazine-1-carbodithioic acid complexes," *Himachal Pradesh University Journal*, pp. 1–8, 2011.

[2] B. A. Prakasam, K. Ramalingam, G. Bocelli, and A. Cantoni, "Spectral, BVS, and thermal studies on bisdithiocarbamates of divalent Zn, Cd, and their adducts: single crystal x-ray structure redetermination of (Diiodo) (Tetraethylthiuramdisulfide)mercury (II), $[Hg(tetds)I_2]$," *Phosphorus, Sulfur and Silicon and the Related Elements*, vol. 184, no. 8, pp. 2020–2033, 2009.

[3] D. Coucouvanis and J. P. Fackler Jr., "Square-planar sulfur complexes. VI. Reactions of bases with xanthates, dithiocarbamates, and dithiolates of nickel (II)," *Inorganic Chemistry*, vol. 6, no. 11, pp. 2047–2053, 1967.

[4] R. G. Xiong, J. L. Zuo, and X. Z. You, "A novel dimeric zinc complex: bis{μ-[(dimercaptomethylene)propanedinitrilato*S*, *S*']} tetrakis(4-methylpyridine) dizinc (II)-chloroform," *Inorganic Chemistry*, vol. 36, no. 11, pp. 2472–2474, 1997.

[5] S. M. Mamba, *Synthesis, characterization and application of dithiocarbamate transition metal complexes [Ph.D. thesis]*, University of Johannesburg, Johannesburg, South Africa, 2011.

[6] G. G. Mohamed, N. A. Ibrahim, and H. A. E. Attia, "Synthesis and anti-fungicidal activity of some transition metal complexes with benzimidazole dithiocarbamate ligand," *Spectrochimica Acta—Part*

A: Molecular and Biomolecular Spectroscopy, vol. 72, no. 3, pp. 610–615, 2009.

[7] A. Manohar, et al. "Synthesis, spectral and single crystal X-ray structural studies on bis(2,2'-bipyridine)sulphidoM(II) (M = Cu or Zn) and diaqua 2,2'-bipyridine zinc(II)sulphate dehydrate," *Journal of the Serbian Chemical Society*, vol. 75, no. 8, pp. 1085–1092, 2010.

[8] N. Geetha and S. Thirumaran, "Characterization studies and cyclic voltammetry on nickel (II) amino acid dithiocarbamates with triphenylphosphine in the coordination sphere," *Journal of the Serbian Chemical Society*, vol. 73, no. 2, pp. 169–177, 2008.

[9] D. C. Onwudiwe and P. A. Ajibade, "Synthesis, characterization and thermal studies of Zn (II), Cd (II) and Hg (II) complexes of N-Methyl-N-Phenyldithiocarbamate: the single crystal structure of [(C_6H_5) (CH_3) $NCS_2]_4Hg_2$," *International Journal of Molecular Sciences*, vol. 12, no. 3, pp. 1964–1978, 2011.

[10] A. A. Osowole, G. A. Kolawole, and O. E. Fagade, "Synthesis, physicochemical, and biological properties of nickel (II), copper (II), and zinc (II) complexes of an unsymmetrical tetradentate Schiff base and their adducts," *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*, vol. 35, no. 10, pp. 829–836, 2005.

[11] G. A. Kolawole and A. A. Osowole, "Synthesis and characterization of some metal (II) complexes of isomeric unsymmetrical Schiff bases and their adducts with triphenylphosphine, *"Journal of Coordination Chemistry*, vol. 62, no. 9, pp. 1437–1448, 2009.

[12] T. Guo, et al. "Bis (diethyldithiocarbamato) (4,7-dimethyl-1,10-phenanthroline) cadmium (II) acetonitrile solvates," *Acta Crystallographica—Section E: Structure Reports Online*, vol. 58, no. 8, 2002, pp. m439– m440.

[13] C. M. Wai and S. J. Wang, "Ion exchange and solvent extraction: a series of advances," *Journal of Chromatography A*, vol. 785, pp. 369–383, 1997.

[14] W. A. Zoubi, F. Kandil, and M. K. Chebani, "Solvent extraction of chromium and copper using Schiff base derived from terephthaldialdehyde and 5-amino-2-methoxy-phenol," *Arabian Journal of Chemistry*, 2011.

[15] B. Dede, F. Karipcin, and M. Cengiz, "Novel homo- and heteronuclear copper(II) complexes of tetradentate Schiff bases: synthesis, characterization, solvent-extraction and catalase-like activity studies," *Journal of Hazardous Materials*, vol. 163, no. 23, pp. 1148–1156, 2009.

[16] S. Kanchi, P. Singh, and K. Bisetty, "Dithiocarbamates as hazardous remediation agent: a critical review on progress in environmental chemistry for inorganic species studies of 20th century," *Arabian Journal of Chemistry*, vol. 7, no. 1, pp. 11–25, 2014.

[17] M. M. Aniruddha, H. Sung-H, A. A. Mansing, and S. K. Sanjay, "Liquid–liquid anion exchange extraction studies of samarium (III) from salicylate media using high molecular weight amine," *Arabian Journal of Chemistry*, vol. 8, no. 4, pp. 456–464, 2015.

[18] A. C. Ekennia, D. C. Onwudiwe, and A. A. Osowole, "Spectral, thermal stability and antibacterial studies of copper, nickel and cobalt complexes of *N*-methyl-*N*-phenyl dithiocarbamate," *Journal of Sulfur Chemistry*, vol. 36, no. 1, pp. 96–104, 2015.

[19] M. G. Abd El-Wahed, M. S. Refat, and S. M. El-Megharbel, "Metal complexes of antiuralethic drug: synthesis, spectroscopic characterization and thermal study on allopurinol complexes," *Journal of Molecular Structure*, vol. 888, no. 1–3, pp. 416– 429, 2008.

[20] T. L. Yang and W. W. Qin, "Transition metal manganese (II), nickel (II), copper (II) and zinc (II) complexes of a new Schiff base ligand: synthesis, characterization and antitumor activity studies," *Polish Journal of Chemistry*, vol. 80, no. 10, pp. 1657– 1662, 2006.

[21] B. N. Figgis, *Introduction to Ligand Fields*, Interscience, New York, NY, USA, 1966.

[22] M. Soenmez, A. Levent, and M. Sekerci, "Synthesis, characterization, and thermal investigation of some metal complexes containing polydentate ONOdonor heterocyclic Schiff base ligand," *Russian Journal of Coordination Chemistry*, vol. 30, no. 9, pp. 655–659, 2004.

[23] M. Soenmez and M. A. Sekerci, "New heterocyclic Schiff base and its metal complexes," *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, vol. 34, no. 3, pp. 489–502, 2004.

[24] D. Nicholls, *Comprehensive Inorganic Chemistry*, vol. 3, Wiley, 1973.

[25] A. Earnshaw, *The Introduction to Magnetochemistry*, Academic Press, London, UK, 1980.

[26] W. J. Geary, "The use of conductivity measurements in organic solvents for the characterisation of coordination compounds," *Coordination Chemistry Reviews*, vol. 7, no. 1, pp. 81–122, 1971.

[27] A. A. Osowole, R. Kempe, R. Schobert, and K. Effenberger, "Synthesis, spectroscopic, thermal, and *in vitro* anticancer properties of some M(II) complexes of 3-(-1-(4,6-dimethyl-2pyrimidinylimino) methyl-2-naphthol," *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*, vol. 41, no. 7, pp. 825–833, 2011.