



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Synthesis and Characterization of 3,6-(2-pyridyl)-1,2,4,5-tetrazine Complexes with Gold(III)

Arab K. EL-Qisairi and Hanan A. Qaseer
Department of Chemistry, Mu'tah University, Mu'tah, Jordan

Abstract: The reactions of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (abbreviated as dptz) with $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of sodium salts (NaX , $\text{X} = \text{Br}^-$, NO_3^- , SCN^-) have been investigated. The new complexes $[\text{AuCl}_2(\text{dptz})]\text{Cl} \cdot 1/2\text{H}_2\text{O}$, $[\text{AuBr}_2(\text{dptz})]\text{Br} \cdot 1/2\text{C}_2\text{H}_5\text{OH}$, $[\text{AuCl}(\text{NO}_3)(\text{dptz})]\text{Cl} \cdot 1/2\text{C}_2\text{H}_5\text{OH}$ and $[\text{AuCl}(\text{SCN})(\text{dptz})]\text{Cl}$ have been characterized by elemental analyses, conductivity measurements, infrared, ^1H - and ^{13}C -NMR.

Key words: Au(III) complexes, 3,6-(2-pyridyl)-1,2,4,5-tetrazine, dptz

INTRODUCTION

The 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz) ligand is a best potential polydentate pyridyl ligand (Kaim, 2002). It has been widely used to form mono and dinuclear transition metal complexes (El-Qisairi, 2007; Yeh *et al.*, 2006; Maekawa *et al.*, 2005; Sarkar *et al.*, 2003; Kaim, 2002; Chellamma and Lieberman, 2001; Glöckle and Kaim, 1999; Klein *et al.*, 1998). In mononuclear complexes, the dptz has two uncoordinated imine nitrogen atoms available for hydrogen bonding (Kaim and Kohlmann, 1987). On the other hand, the dinuclear transition metal complexes has found considerable interest for use as electron propagating components in electron transfer agents, model systems for biological studies and light-capturing antennas via charge transfer transitions (Marshall *et al.*, 2000; Ronco *et al.*, 1998; De Munno *et al.*, 1998). However, dptz may exist in two different conformations as shown in Fig. 1. X-ray diffraction analysis show that the free dptz exist in *trans* conformation (Klein *et al.*, 1998).

Gold (III) complexes with N-donor ligands are of great importance for their possible biochemical and pharmacological activities (Kolev *et al.*, 2007; Marcon *et al.*, 2003). The discovery of cisplatin in cancer chemotherapy has led other complexes to be investigated

as potential anticancer agents (Kaim and Schwederski, 2001; Cowan, 1997). In particular, various Au(III) complexes which are of sufficient stability in the physiological environment have been prepared and evaluated for *in vitro* anticancer properties (Marcon *et al.*, 2003). Recently, reactions of several Au(III) complexes with serum albumin have been reported and discussed (Marcon *et al.*, 2003).

All of these considerations encouraged us to investigate the reactions of dptz with Au(III). In the present study, the preparation and characterization of some new mononuclear complexes of gold(III) with dptz ligand is reported.

MATERIALS AND METHODS

Materials: All materials were of reagent grade and were used without further purification. The $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Aldrich Chemical Co. The dptz ligand was prepared following literature procedure (Geldard and Lions, 1965; Butte and Case, 1961).

Instrumentation: Elemental analyses for the complexes were run by M-H-W Laboratories, Phoenix, Arizona, USA. Conductivity measurements were carried out on a

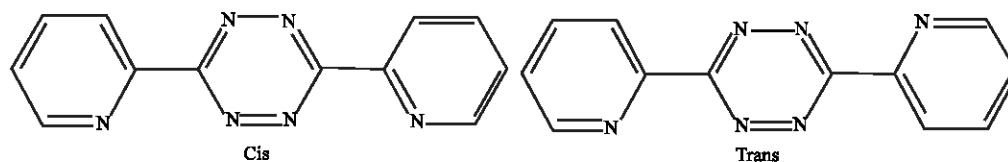


Fig. 1: Conformational structures of the free ligand dptz

Jeneway 4010 digital conductivity meter at 25°C using 1.0×10^{-3} M solutions in N,N-dimethylformamide (DMF). IR spectra (KBr pellets) were recorded on a Mattson 5000 FT-IR spectrophotometer. Proton and ^{13}C NMR spectra were determined with a Bruker AC-200 NMR spectrometer in DMSO- d_6 using TMS as internal standard. Melting points were obtained using an electrothermal melting point apparatus.

Synthesis of complexes: All of the products were dried under vacuum at 40°C.

[AuCl₂(dptz)]Cl.1/2H₂O: To a solution of AuCl₃.3H₂O (0.08 g, 0.22 mmol) in ethanol (5 mL), a solution of dptz (0.04 g, 0.17 mmol) in ethanol (15 mL) was added. The solution was heated at reflux for 1 h. Then the reaction mixture was allowed stirring at room temperature for overnight. The precipitated formed were collected and washed well with ethanol and diethyl ether.

[AuBr₂(dptz)]Br.1/2C₂H₅OH, [AuCl(NO₃)(dptz)]Cl.1/2C₂H₅OH and [AuCl(SCN)(dptz)]Cl: A solution of dptz (0.04 g, 0.17 mmol) in ethanol (15 mL) was added dropwise to a solution of AuCl₃.3H₂O (0.08 g, 0.22 mmol) in ethanol (5 mL). Then the solution was treated with an aqueous solution (5 mL) of an appropriate sodium salt (0.44 mmol; NaX, where X = Br⁻, NO₃⁻ and SCN⁻). After the solution was heated at reflux for 1 h, the reaction mixture was stirred at room temperature for overnight. During the course of reaction, the product was formed. The product was collected and washed well with water, ethanol and diethyl ether.

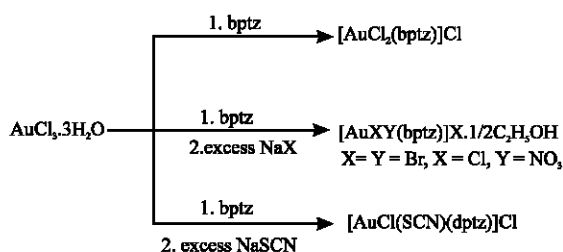
RESULTS AND DISCUSSION

Synthesis: The synthetic strategy applied for the synthesis of Au(III) complexes containing the 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz) ligand is summarized in Scheme 1. The elemental analyses of the new complexes are shown in Table 1. The compounds are colored solid, stable in air and were isolated in fair to good yields (Table 1). They are insoluble in water and common organic solvents while they are soluble in DMF and DMSO.

Conductivity measurements: The ionic or neutral nature of the complexes was checked by measuring their molar conductivity in DMF, in which all compounds proved to be soluble. The molar conductance values for 10^{-3} M solutions for the complexes (Table 1) are in good agreement with those reported (Angelici, 1977) and confirmed that these complexes behave as 1:1 electrolyte.

IR spectroscopy: The important infrared absorption bands for the dptz ligand and its complexes are presented in Table 2. The bands were assigned by comparison with the reported spectral data for dptz and its complexes (El-Qisairi, 2007; Kaim and Kohlmann, 1987; Jaradat *et al.*, 1986) and other related α -diimine ligands and their complexes (Zaghal *et al.*, 2001, 1999; Nakamoto, 1997; Ghedini *et al.*, 1985). The vibrational spectral data have been used to distinguish the monometallic from the bimetallic complexes (Zaghal *et al.*, 2001, 1999; Nakamoto, 1997; Ghedini *et al.*, 1985).

Infrared spectra of the mono complexes prepared in this study showed the typical features of the



Scheme 1

Table 1: Analytical and physical data for the dptz complexes

Complex	Anal. Calcd. (found) %			M.p. °C (Dec.)	Color	Yield (%)	Λ_m^a (S)
	C	H	N				
[AuCl ₂ (dptz)]Cl.1/2H ₂ O	26.27 (26.38)	1.65 (1.62)	15.32 (15.38)	263	Bright-Red	87	88
[AuBr ₂ (dptz)]Br.1/2C ₂ H ₅ OH	22.43 (22.33)	1.59 (1.54)	12.07 (12.10)	254	Orange-Red	53	87
[AuCl(NO ₃)(dptz)]Cl.1/2C ₂ H ₅ OH	26.50 (26.49)	1.88 (1.90)	16.64 (16.65)	258	Red	44	77
[AuCl(SCN)(dptz)]Cl	27.77 (27.68)	1.43 (1.44)	17.44 (17.50)	190	Brown	65	70

^a: Molar conductance for 10^{-3} M solutions in DMF at 25°C

Table 2: Important IR frequencies for dptz and its complexes (KBr pellets; cm^{-1})^a

Compound	Ring breathing vibration	$\beta(\text{C-H})$	Py ring vibration	$\gamma(\text{C-H})$
dptz ^b	1638m, 1600m, 1582m, 1443s, 1391vs	1130s, 1092m	993m, 920m	799s, 745s
[AuCl ₂ (dptz)]Cl.1/2H ₂ O ^c	1678sh, 1640s, 1618s, 1560w, 1530m, 1508m, 1460m, 1430m, 1371m	1142w, 1100w,	1005m, 985w,	791m, 700m
[AuBr ₂ (dptz)]Br.1/2C ₂ H ₅ OH ^d	1680sh, 1638s, 1618s, 1585w, 1554m, 1508m, 1465m, 1430m, 1378w	1148w, 1105w	996m	775m
[AuCl(NO ₃)(dptz)]Cl.1/2C ₂ H ₅ OH ^e	1683w, 1638s, 1618s, 1585w, 1541m, 1508m, 1465m, 1408m, 1378w	1132m, 1100w	999m	776m
[AuCl(SCN)(dptz)]Cl ^f	1678sh, 1639s, 1618s, 1585w, 1541m, 1521m, 1458m, 1408m, 1378w	1138m, 1100sh	995w	784m

^a: All complexes show $\nu(\text{C-H})$ for aromatic ring in the region 3075-3060 cm^{-1} and band characteristic of coordinated pyridine $\beta(\text{py})$ in the range 615-625 cm^{-1} ,
^b: El-Qisairi, 2007, ^c: $\nu(\text{O-H})$: 3550s, $\gamma(\text{HOH})$: 1600sh, ^d: $\nu(\text{O-H})$ hydrogen bonded ethanol group: 3480sb, ^e: Coordinated NO₃: $\nu(-\text{NO}_2)$: 1420m, 1352s;
 $\delta(\text{NO})$: 1000w, ^f Coordinated SCN: $\nu(\text{SCN})$: 2105s, s: strong, m: medium, w: weak, sb: strong and broad, sh: shoulder

coordinated dptz (Table 2). The presence of the band in the range 615-625 cm^{-1} indicates the coordination of pyridine to the Au(III) (Nakamoto, 1997). Upon complexation, the ring breathing bands are showing appreciable changes (Table 2). They are increased in number as compared to the free dptz ligand. The pyridine ring vibrations are undergoing increasing in number and/or reduction in intensity. All these changes suggest that upon coordination of Au(III), the ligand dptz is no more symmetric and thus supporting the structure shown in Fig. 2. This result is consistent with what was reported by El-Qisairi (2007). Moreover, based on the fact that most common geometry for Au(III) is four with square planar geometry (Cotton *et al.*, 1999; Greenwood and Earnshaw, 1998) which confirm the proposed structure shown in Fig. 2.

It is to be noted that the bimetallic complexes of related ligands such as 2,2'-bipyrimidine and 3,6-bis(2-pyridyl)pyridazine have been reported to show a decrease in the number of bands in ring breathing with respect to the monometallic complexes (Zaghal *et al.*, 1999; Nakamoto, 1997; Ghedini *et al.*, 1985).

The appearance of strong absorption at 3550 cm^{-1} (Table 2), together with the other band at 1600 cm^{-1} , supports the presence of lattice water in the complex [AuCl₂(dptz)]Cl.1/2H₂O (Nakamoto, 1997). The IR spectra of [AuBr₂(dptz)]Br.1/2C₂H₅OH and [AuCl(NO₃)(dptz)]Cl.1/2C₂H₅OH exhibit a strong-broad band at 3480 cm^{-1} which is characteristic of intermolecular hydrogen bonding of ethanol (Silverstein *et al.*, 2005; Pavia, 2001). In addition, the IR spectrum of [AuCl(NO₃)(dptz)]Cl.1/2C₂H₅OH shows three bands at 1420 m, 1352 s and 1000 w (Table 2) supports the presence of the unidentate NO₃⁻ rather than the chelating bidentate group (Nakamoto, 1997). The complex [AuCl(SCN)(dptz)]Cl gives a strong band at 2105 cm^{-1} which confirm the presence of coordinated SCN to Au(III) (Nakamoto, 1997; Zaghal and Ali, 1995).

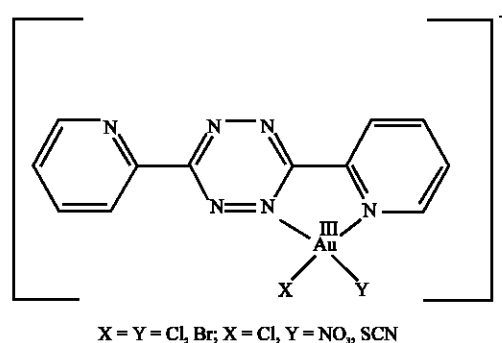


Fig. 2: Possible structure of the complexes

¹H- and ¹³C-NMR: The ¹H- and ¹³C-NMR data are given in Table 3 and 4, respectively. Assignments of signals were made according to previously reported results for dptz and its complexes (El-Qisairi, 2007; Maekawa *et al.*, 2005; Chandra *et al.*, 2002; Kaim and Kohlmann, 1987).

The ¹H-NMR spectrum of free dptz ligand displays four different proton resonances for the two equivalent pyridyl groups (El-Qisairi, 2007; Kaim and Kohlmann, 1987). Our complexes give eight different peaks for the two pyridyl groups. This result indicates that these groups are chemically not equivalent upon complexation of dptz to Au(III) and strongly confirms the monometallic rather than bimetallic nature of these complexes. Previous studies (El-Qisairi, 2007; Kaim and Kohlmann, 1987) have reported that the dptz mononuclear complexes showed 8 different proton resonances while the bimetallic ones gave 4 peaks as the free ligand (Kaim and Kohlmann, 1987).

The ¹³C-NMR spectra for the Au(III) complexes show 12 peaks as expected for the unsymmetrical coordinated ligand while the free symmetrical dptz shows only six peaks. In addition, the ¹³C-NMR spectrum of [AuCl(SCN)(dptz)]Cl also shows signal at 115.6 ppm, which assigned to carbon atom of the thiocyanato group (Qaseer *et al.*, 2003; Zaghal *et al.*, 1999). The ¹H- and ¹³C-NMR results of the complexes further support the proposed structure shown in Fig. 2.

Table 3: ¹H NMR chemical shifts for dptz and its complexes^a

Compound	NMR band shifts: δ, ppm (J, Hz)
dptz ^b	8.97 (d, 2H, J = 6.1 Hz); 8.63 (d, 2H, J = 6.0 Hz); 8.17 (t, 2H, J = 8.0 Hz); 7.75 (t, 2H, J = 6.0 Hz)
[AuCl ₂ (dptz)]Cl.1/2H ₂ O	8.90 (br. d, 1H); 8.78 (br. d, 1H); 8.60 (br. d, 1H); 8.50 (br. d, 1H); 8.02 (br. t, 1H); 7.92 (br. t, 1H); 7.70 (br. t, 1H); 7.56 (br. t, 1H)
[AuBr ₂ (dptz)]Br.1/2C ₂ H ₅ OH	8.84 (br. d, 1H); 8.70 (br. d, 1H); 8.60 (br. d, 1H); 8.14 (t, 1H, J = 6.0 Hz); 8.08-8.02 (d, 1H, J = 6.5 Hz); 7.92 (t, 1H, J = 6.4 Hz); 7.64 (br. d, 1H); 7.54 (br. t, 1H)
[AuCl(NO ₃)(dptz)]Cl.1/2C ₂ H ₅ OH	8.80 (br. d, 1H); 8.71 (br. d, 1H); 8.64 (br. d, 1H); 8.44 (br. d, 1H); 8.16 (br. d, 1H); 8.08-7.88 (br. d, 1H); 7.64 (br. d, 1H); 7.54 (br. d, 1H)
[AuCl(SCN)(dptz)]Cl	8.80 (br. d, 1H); 8.70 (br. d, 1H); 8.61 (br. d, 1H); 8.40 (br. d, 1H); 8.22 (br. d, 1H); 8.10-7.90 (br. d, 1H); 7.72 (br. d, 1H); 7.60 (br. d, 1H)

^a: ¹H-NMR were obtained in DMSO-d₆ with TMS as internal standard, at 200 MHz. ^b: El-Qisairi, 2007. d, doublet; dd, doublet of doublet; br, broad; s, singlet; t, triplet; m, multiplet

Table 4: ¹³C NMR chemical shifts for dptz and its complexes^a

Compound	NMR band shifts (δ, ppm)
dptz ^b	164.0, 151.1, 150.0, 137.0, 126.6, 124.5
[AuCl ₂ (dptz)]Cl.1/2H ₂ O	162.6, 150.0, 148.8, 147.8, 147.0, 145.0, 137.9, 137.0, 128.1, 124.9, 123.6, 122.6
[AuBr ₂ (dptz)]Br.1/2C ₂ H ₅ OH	161.8, 149.6, 148.9, 148.3, 147.9, 146.8, 138.6, 137.9, 127.5, 126.0, 124.1, 123.2
[AuCl(NO ₃)(dptz)]Cl.1/2C ₂ H ₅ OH	161.4, 149.4, 148.6, 148.1, 147.7, 147.2, 137.9, 137.1, 127.2, 125.8, 125.1, 123.4
[AuCl(SCN)(dptz)]Cl	161.1, 149.1, 148.2, 147.8, 147.2, 146.8, 138.1, 137.8, 127.8, 126.0, 125.4, 123.0, 115.6

^{a13}:¹³C-NMR were obtained in DMSO-d₆ with TMS as internal standard, at 50 MHz. ^b: El-Qisairi, 2007

CONCLUSION

In conclusion, we have successfully synthesized and characterized a new mononuclear gold(III) complexes with dptz of the formula [AuCl₂(dptz)] Cl.1/H₂O, [AuBr₂(dptz)]Br.1/2C₂H₅OH, [AuCl(NO₃)(dptz)] Cl.1/2C₂H₅OH and [AuCl(SCN)(dptz)] Cl. All data discussed above suggest the proposed structure shown in Fig. 2.

ACKNOWLEDGMENT

The partial financial support from the Deanship of Research and Graduate Studies at Mu'tah University (Jordan) is greatly appreciated.

REFERENCES

Angelici, R.L., 1977. Synthesis and Technique in Inorganic Chemistry. Saunders; Philadelphia, pp: 213.
 Butte, W.A. and F.H. Case, 1961. The synthesis of some pyridylpyridazines and pyrimidines. *J. Org. Chem.*, 26: 4690-4692.
 Chandra, M., A.N. Sahay, D.S. Pandey, M.C. Puerta and P. Valerga, 2002. Synthetic, spectral and structural aspects of some mono- and binuclear (homo/hetero) Ru(II) hydrido carbonyl complexes. *J. Organomet. Chem.*, 648: 39-48.
 Chellamma, S. and M. Lieberman, 2001. Synthesis and properties of [Ru₂(acac)₄(bptz)]ⁿ⁺ (n = 0,1) and crystal structure of [Ru₂(acac)₄(bptz)]. *Inorg. Chem.*, 40: 3177-3180.
 Cotton, F.A., G. Wilkinson, C.A. Murillo and M. Bochman, 1999. *Advanced Inorganic Chemistry*. 6th Edn., John Wiley and Sons, New York.

Cowan, J.A., 1997. *Inorganic Biochemistry*. 2nd Edn., Wiley-VCH, New York, pp: 345.
 De Munno, G., T. Poerio, M. Julve, F. Lloret, J. Faus and A. Caneschi, 1998. Synthesis, crystal structures and magnetic properties of one-, two- and three-dimensional 2,2'-bipyrimidine-containing copper (II) complexes. *J. Chem. Soc., Dalton Trans.*, 1679-1685.
 El-Qisairi, A.K., 2007. Synthesis, characterization and semiempirical calculations of mercury(II) complexes of 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine. *J. Coord. Chem.*, 60: 1069-1076
 Geldard, J.F. and F. Lions, 1965. The organic chemistry of a new weak field tridentate chelating agent. 3,5-di(2'-pyridyl)-1,2,4-triazole. *J. Org. Chem.*, 30: 318-319.
 Ghedini, M., F. Neve, F. Morazzoni and C. Oliva, 1985. 3,6-Bis(2'-pyridyl)pyridazine dinuclear complexes: Palladium(II), platinum(II) and first row transition metal(II) mixed complexes. *Polyhedron*, 4: 497-503.
 Glöckle, M. and W. Kaim, 1999. The Fe^{III}/Fe^{II} vs Fe₂^{2.5} formation in mixed-valent species [(NC)₄Fe(BL)Fe(CN)₄]3-, BL=2,2'-bipyrimidine and 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine. Distance and size do not always matter. *Inorg. Chem.*, 38: 3270-3274.
 Greenwood, N.N. and A. Earnshaw, 1998. *Chemistry of the Elements*. 2nd Edn., Butterworth-Heinemann, Oxford.
 Jaradat, Q., K. Barqawi and T.S. Akasheh, 1986. Complexes of 2,2'-bipyrimidine and 3,6-di(2'-pyridyl)tetrazine. *Inorg. Chem. Acta*, 116: 63-73.
 Kaim, W. and S. Kohlmann, 1987. Four bridging bis chelate ligands with very low lying π* orbitals. MO perturbation calculations, electrochemistry and spectroscopy of mononuclear and binuclear group 6 and references cited therein. *Metal tetracarbonyl complexes*. *Inorg. Chem.*, 26: 68-77.

- Kaim, W. and B. Schwederski, 2001. *Biinorganic Chemistry: Inorganic Elements in the Chemistry of Life*. John Wiley and Sons, New York.
- Kaim, W., 2002. The coordination chemistry of 1,2,4,5-tetrazines. *Coord. Chem. Rev.*, 230: 127-139.
- Klein, A., E.J.L. McInnes, T. Scheiring and S. Zalis, 1998. Electronic structure of radical anionic binuclear organoplatinum complexes. A multiple frequency EPR investigation. *J. Chem. Soc., Faraday Trans.*, 94: 2979-2984.
- Kolev, T., B.B. Ivanova and S.Y. Zareva, 2007. An Au(III) complex of glycyl-S-serine: A linear polarized IR and ¹H- and ¹³C-NMR investigation. *J. Coord. Chem.*, 60: 109-115.
- Maekawa, M., H. Konaka, T. Minematsu, T. Kuroda-Sowa, Y. Suenaga and M. Munakata, 2005. Synthesis and structural characterization of dinuclear iridium hydro complex with 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine, [Ir₂(H)₄(PPh₃)₄(bptz)](PF₆)₂·4CH₂Cl₂. *Inorg. Chim. Acta*, 358: 1317-1321.
- Marcon, G., L. Messori, P. Orioli, M.A. Cinellu and G. Minghetti, 2003. Reaction of gold(III) complexes with serum albumin. *Eur. J. Biochem.*, 270: 4655-4661.
- Marshall, S.R., C.D. Incarvito, J.I. Manson, A.L. Rheingold and J.S. Miller, 2000. Synthesis, structure and magnetic properties of Co₂{[N(CN)₂]₄bpym}.H₂O and M {[N(CN)₂]₂bpym}.H₂O (M = Mn, Fe, Co; bpym = 2,2'-bipyrimidine). *Inorg. Chem.*, 39: 1969-1973.
- Nakamoto, K., 1997. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry*. 5th Edn., John Wiley and Sons, New York.
- Pavia, D.L., G.M. Lampman and G.S. Kriz, 2001. *Introduction to Spectroscopy*. 3rd Edn., Harcourt College Publishers, Philadelphia.
- Qaseer, H.A., N. Al-Rawashdeh and A.K. El-Qisairi, 2003. Synthesis and spectroscopic characterization of mercury(II) complexes with 2-(2'-pyridyl)quinoline. *Acta Chim. Slov.*, 50: 687-696.
- Ronco, S.E., D.W. Thompson, S.L. Gahan and J.D. Petersen, 1998. Synthesis of, characterization of and photoinduced processes in polymetallic triad complexes containing Fe(II), Ru(II) and Rh(III) metal centers. *Inorg. Chem.*, 37: 2020-2027.
- Sarkar, B., W. Kaim, A. Klein, B. Schwedrki, J. Fiedler, C. Duboc and G.K. Lahiri, 2003. What a difference ancillary thienyl: Unexpected additional stabilization of the diruthenium(III,II) but not the diosmium(III,II) mixed-valent state in tetrazine ligand-bridged complexes. *Inorg. Chem.*, 42: 6172-6174.
- Silverstein, R.M., F.X. Webster and D.J. Kiemle, 2005. *Spectrometric Identification of Organic Compounds*. 7th Edn., John Wiley and Sons, New York.
- Yeh, W.Y., G.H. Lee and S.M. Peng, 2006. Synthesis, characterization and crystal structures of [Cu(PCHO)₂(2,2'-bipy)][BF₄], [Cu₂(PCHO)₄(4,4'-bipy)][BF₄]₂ and [Cu₂(PCHO)₄(bptz)][BF₄]₂ (PCHO = o-(diphenylphosphino)benzaldehyde and bptz = 3,6-bis(2'-pyridyl)-1,2,4,5-tetrazine. *Inorg. Chim. Acta*, 339: 659-664.
- Zaghal, M.H. and B.F. Ali, 1995. Substitution reactions of cis-dichlorobis(2,2'-biquinoline)rhodium(III)chloride. *Polyhedron*, 14: 1011-1019.
- Zaghal, M.H., A.K. El-Qisairi and H.A. Qaseer, 1999. Preparation of new 2,2'-bipyrimidine complexes of palladium(II) via substitution reaction. Part II. High resolution ¹H- and ¹³C-NMR and mass spectral studies. *Abhath Al-Yarmouk, Pure Sci. Engin. Sci.*, 8: 29-47.
- Zaghal, M.H., M.A. Abu-Obeid, M.A. Atfah, A.K. El-Qisairi, H.A. Qaseer and B.F. Ali, 2001. Substituted dipyriddyldiazine rhodium(III) complexes. *Transition Met. Chem.*, 26: 517-522.