Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 63–68

POTENTIOMETRIC AND THERMODYNAMIC STUDIES OF 2-MERCAPTO-5-(2-HYDROXYNAPHTHYLIDEAMINO)-1,3,4-THIADIAZOLE AND ITS METAL COMPLEXES

M. Gaber[1*], *S. S. Al-Shihry*[1] *and A. A. El-Bindary*[2]

[1]Department of Chemistry, College of Science, King Faisal University, P.O. Box 1759, Hofuf 31982, Saudi Arabia
[2]Department of Chemistry, Faculty of Science, King Khalid University Abha, Saudi Arabia

Proton-ligand dissociation constant of 2-mercapto-5-(2-hydroxynaphthylideamino)-1,3,4-thiadiazole (MHT) and the stepwise stability constants of its metal complexes were determined potentiometrically in 40 mass/mass% ethanol–water mixture containing 0.1 M KCl. The stabilities of the complexes follow the order: $Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}$. The dissociation constant (pK^H) of MHT and the stability constants (log$K$) of its metal complexes were determined at different temperatures and the corresponding thermodynamic parameters were calculated and discussed. The proton dissociation process is non-spontaneous, endothermic and entropically unfavoured. The formation of the metal complexes was found to be spontaneous, endothermic and entropically favoured.

Keywords: *dissociation and stability constants, thermodynamics and potentiometry*

Introduction

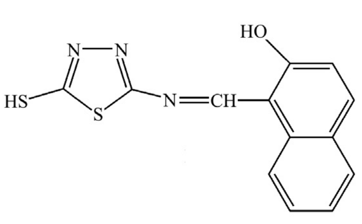
The interest in the study of Schiff bases and their metal chelates have been growing due to their applications in biological systems [1–6], electrochemistry [7] as well as catalysis [8–10]. Thus, their chelating properties towards metal ions drew the attention of many authors [11–15].

In the present article, we report herein the dissociation constant of 2-mercapto-5-(2-hydroxynaphthylideamino)-1,3,4-thiadiazole (MHT) and the stepwise stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} at different temperatures. The corresponding thermodynamic parameters are calculated and discussed.

Experimental

Reagents and materials

MHT was prepared as previously described [11]. The purity was checked by elemental analyses and IR spectrum.



MHT

Metal ion solutions (0.0005 M) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA. The ligand solution (0.001 M) was prepared by dissolving the accurate mass of the solid in ethanol (Analar). A solution of 1 M KC1 was also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40 v/v% ethanol-water mixture was used as titrant and standardized against oxalic acid (Analar).

Apparatus and procedures

Apparatus, general conditions and methods of calculation were the same as reported by El-Bindary *et al.* [16]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.002 M NaOH in 40 v/v% ethanol–water mixture:

- 5 mL 0.00l M HC1+5 mL1 M KC1+20 mL ethanol
- 5 mL 0.001 M HC1+5 mL 1 M KC1+15 mL ethanol+5 mL 0.001 M ligand and
- 5 mL 0.001M HC1+5 mL 1 M KC1+15 mL ethanol +5 mL 0.001 M ligand+5 mL 0.0005 M metal chloride.

For each mixture, the volume was increased to 50 mL with bidistilled water before the titration. These titrations were also carried out at 308 and 318 K. Temperature was kept constant within ±0.05°C. The pH-meter readings in 40 v/v ethanol–water mixture were corrected, according to the procedure of Van Uitert and Hass [17].

---

[*] Author for correspondence: mabuelazm@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Thermodynamic functions for the dissociation of MHT in 40 (*v*/*v*)% ethanol water mixture in the presence of 0.1 M KCl at different temperatures

T/K	Dissociation constant		Free energy change/kJ mol^{-1}		Enthalpy change/kJ mol^{-1}		Entropy change/J mol^{-1} K^{-1}	
	pK_1^H	pK_2^H	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
298	6.20	4.77	35.38	27.22			22.35	9.56
308	6.04	4.64	35.62	27.36	28.72	24.37	22.40	9.71
318	5.90	4.52	35.92	27.52			22.64	9.91

Standard deviation: pK_1 (0.002); pK_2 (0.001), G (0.014–0.035), Correlation coefficients: pK_1 (0.99994); pK_2 (0.99999), G (0.9958–0.9978)

Table 2 Stepwise stability constants for ML and ML_2 complexes of MHT in 40 (*v*/*v*)% ethanol–water mixture in the presence of 0.1 M KCl at different temperatures

M^{n+}	298 K		308 K		318 K	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Mn^{2+}	7.70	5.70	7.83	5.83	7.97	5.95
Co^{2+}	7.89	5.83	8.04	5.98	8.20	6.14
Ni^{2+}	8.00	5.95	8.15	6.09	8.31	6.22
Cu^{2+}	8.20	6.11	8.38	6.26	8.55	6.40

Standard deviation: $\log k_1$ (0.002–0.01); $\log k_2$ (0.001–0.01), Correlation coefficients: $\log k_1$ (0.9988–0.9999); $\log k_2$ (0.9989–0.9999)

Results and discussion

Proton-ligand stability constants

The acid dissociation constant of the Schiff base ligand (MHT) was first determined from the titration curve of HCl with NaOH in the absence and presence of MHT. The average number of protons associated with the MHT at different pH values ($\bar{n}_A$) was calculated according to Irving and Rossotti [18]. Thus, the formation curves ($\bar{n}_A$ *vs*. pH) for the proton-ligand systems were constructed and found to extend between 0 and 2 on the $\bar{n}_A$ scale. This means that MHT has two dissociable protons (the hydrogen ions of the OH and SH groups). The number of replicates are three and the average values obtained are listed in Table 1.

Metal-ligand stability constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}_A$) *vs*. the free ligand exponent (pL), according to Irving and Rossotti [18]. These curves were analyzed and the successive stability constants were determined using different computational methods [19, 20]. The values obtained were in good agreement within 1% error. The average values are represented in Table 2. The following general remarks can be pointed out:

- The maximum value of $\bar{n}_A$ was ≈2 indicating the formation of 1:1 and 1:2 (metal:ligand) complexes.
- The ligand and metal ion solutions used in the present study were very dilute, hence there was no possibility of formation of polymerised complexes.
- The metal titration curves (Fig. 1) were displaced to the right-hand side of the ligand titration curve along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to the ligand titration curves points to the formation of stable metal complexes.

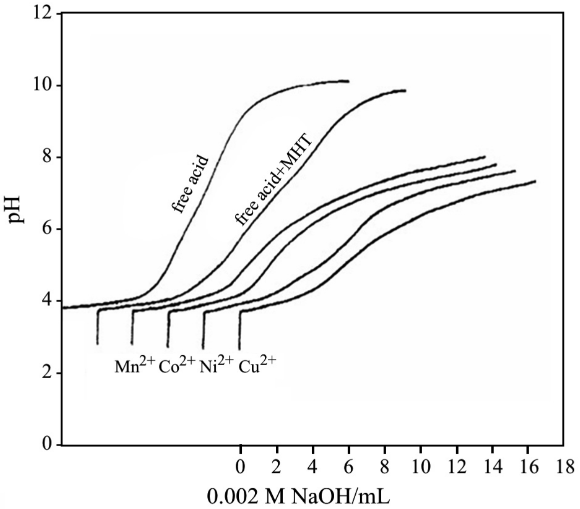


Fig. 1 Potentiometric titraton curves of (MHT) and its metal complexes in 40% ethanol–water mixture at 298 K. The given scale (0, 2...etc. mL) is just for Cu(II) complex and is shifted in parallel for the others

- In most cases, the colour of the solution after complex formation was different from the colour of the ligand at the same pH.
- At constant temperature, the stability of the chelates increases in the order $Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}$ which is in a good agreement with the order observed by Irving and Williams [21].
- The values ($\log k_1-\log k_2$) are usually positive, since the coordination sites of the metal ions are more freely available for binding of the first ligand than the second one. The difference reveals the importance of the electrostatic and steric effects resulting from the addition of the second ligand molecule (the statistical effect contributes only 0.68 log units [20]).

Effect of temperature

The dissociation constant pK^H of MHT, as well as the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} have been evaluated at 298, 308 and 318 K, and the values are given in Tables 1 and 2. The slope of the plot (pK^H or $\log K$ *vs*. $1/T$) was utilized to calculate the enthalpy change (ΔH) for the dissociation or complexation process, respectively (Figs 2 and 3). From the free energy change (ΔG) and (ΔH) values one can determine the entropy change (ΔS) using the well-known relationships (1) and (2):

$$\Delta G=-2.303RT\log K=2.303RTpK \quad (1)$$

$$\Delta S=(\Delta H-\Delta G)/T \quad (2)$$

All thermodynamic parameters of the proton dissociation process of MHT are recorded in Table 1. Inspection of these values reveals that: (*i*) The pK^H values decrease with increasing temperature; (*ii*) A positive value of ΔH indicates that dissociation is an endothermic process and follows the general pattern for ionisation processes of acids; (*iii*) A positive value of ΔG reveals that the dissociation process is not spontaneous and (*iv*) A negative value of ΔS is obtained, as a result of solvation processes i.e. the total number of solvent molecules bound with the dissociated ligand is greater than that originally accompanying the undissociated form [22].

Thermodynamic parameters of the stepwise stability constants of MHT complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: a) release of H_2O molecules and b) metal-ligand bond formation.

It was suggested [23] that the ions in aqueous solution, the order of water molecules around them and complex formation between oppositely charged ions (ligand L^{2-} and M^{n+}) will lead to the breakdown of metal-water arrangement resulting in positive entropy and enthalpy changes. Examination of these values shows that:

(*i*) The stepwise stability constants ($\log K_1$ and $\log K_2$) for MHT complexes increase with increasing temperature; (*ii*) The negative values of ΔG for the

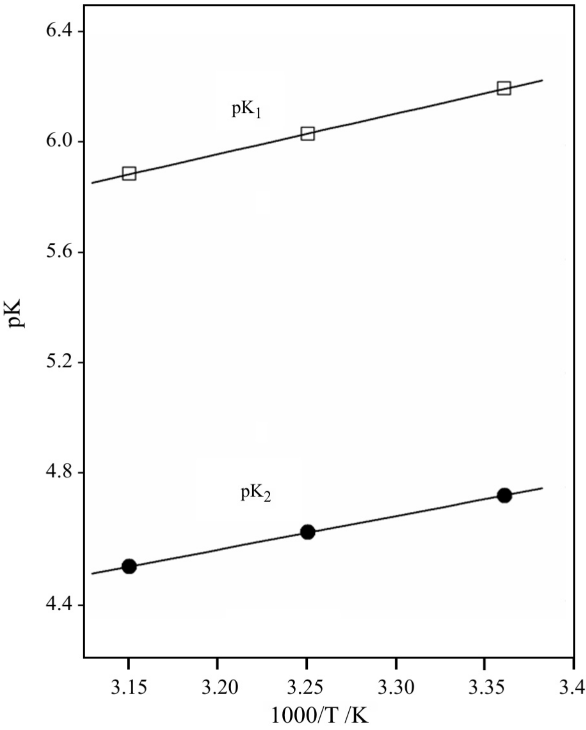


Fig. 2 Variation of *pK* of MHT with the temperature

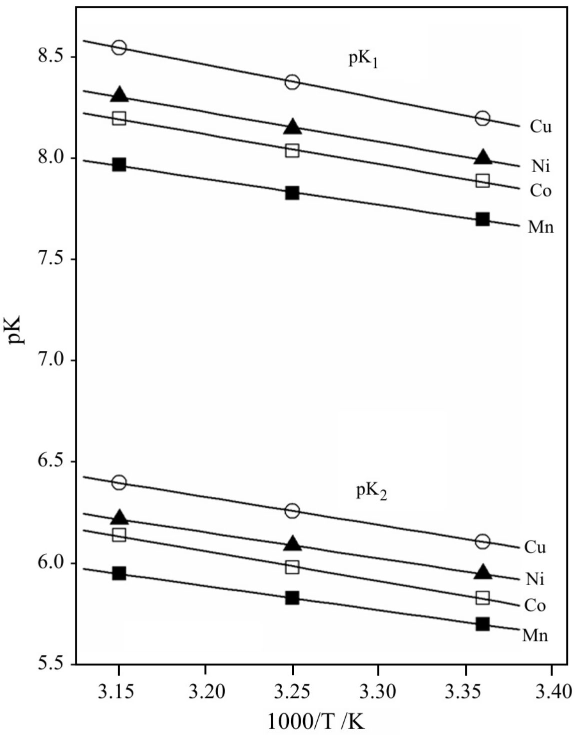


Fig. 3 Variation of *pK* of MHT complex with the temperature

complexation reaction suggests a spontaneous nature of such process. Also, the data indicate that $-\Delta G_1 > -\Delta G_2$. This may be attributed to the steric hindrance produced by the first ligand molecule for the entrance of the second ligand molecule. Due to the complex formation, the electron density on the metal ion generally increases. Thus, its affinity for subsequent ligand decreases, leading to an increase in ΔG of complexation. (*iii*) The positive ΔH values denote that these processes are endothermic and favourable at higher temperature and (*iv*) The ΔS values for the MHT complexes are positive confirming that the complex formation is entropically favourable. This indicates that the increase in entropy by the release of bound solvent molecules on chelation is greater than the decrease resulting from the chelation process itself. This is due to the fact that the solvent molecules which are arranged in an orderly fashion around the ligand and the metal ion have acquired a more random configuration on chelation.This is referred to as a gain in configurational entropy [22].

Relation between pK of the complexes and properties of metal ions

The stability constants of the metal complexes are discussed in terms of the characteristic properties of the metal ions e.g. ionic radius, ionisation enthalpy, hydration enthalpy and electronic configuration. The overall ΔG and ΔH for the formation of MHT metal complexes are correlated well with the reciprocal of the metal ionic radius (Fig 4), the total ionisation enthalpy at 35°C for the process

$M(\text{gas}) \rightarrow M^{2+}(\text{gas}) + 2e$ (Fig. 5) and the enthalpy of hydration ΔH_H (Fig. 6). Figure 5 reveals that the metal complexes are similar in size and geometry of the coordination sphere of the corresponding aquo ions [24]. $-\Delta G$ and $-\Delta H$ increase with increasing the electronegativity of the metal. This is in agreement with the fact that increasing the electronegativity of the metal will decrease the electronegativity between the metal atom and the donor atom of the ligand. Thus, the metal-ligand bond would have more covalent character, which may lead to greater stability of the metal complexes (higher $-\Delta G$ and $-\Delta H$). The overall $-\Delta G$ and $-\Delta H$ (Fig. 7) values for the MHT complexes follow the order $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$, which is in agreement with the

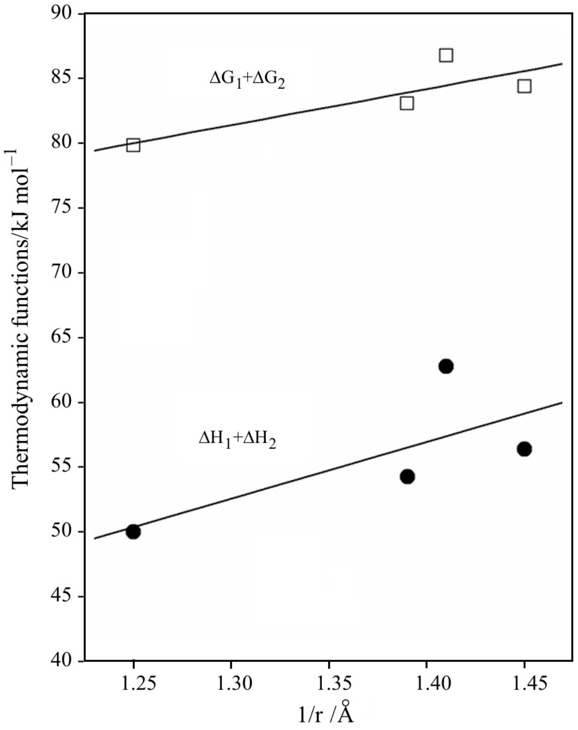


Fig. 4 Variation of the overall thermodynamic functions at 35°C for MHT complexes with the reciprocal of the radius of M^{2+} ions

Table 3 Thermodynamic functions for ML and ML_2 complexes of MHT in 40 (*v*/*v*)% ethanol–water mixture in the presence of 0.1 M KCl

M^{n+}	Temperature/K	Free energy change/kJ mol^{-1}		Enthalpy change/kJ mol^{-1}		Entropy change/J mol^{-1} K^{-1}	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	43.93	32.52	28.72	21.06	243.79	179.80
	308	46.18	33.26			243.18	176.36
	318	48.53	36.22			242.92	180.13
Co^{2+}	298	45.02	33.26	30.64	23.40	253.89	190.13
	308	47.41	35.27			253.41	190.49
	318	49.93	37.38			253.36	191.13
Ni^{2+}	298	45.65	33.95	31.91	24.25	260.27	195.30
	308	48.06	35.91			259.64	195.32
	318	50.60	37.87			259.47	195.35
Cu^{2+}	298	46.79	34.86	35.10	27.38	274.80	208.86
	308	49.42	36.92			274.42	208.77
	318	52.06	38.97			274.09	208.65

Standard deviation: G_1 (0.107–0.149), G_2 (0.076–0.978), Correlation coefficients: G_1 (0.9991–0.9996), G_2 (0.936–0.9997)

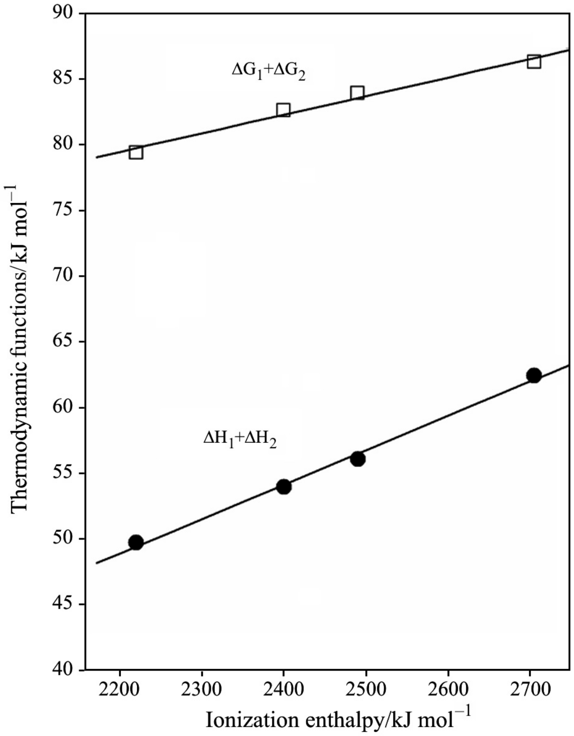


Fig. 5 Variation of the overall thermodynamic functions at 35°C for MHT complexes with the ionization enthalpy of M^{2+} ions

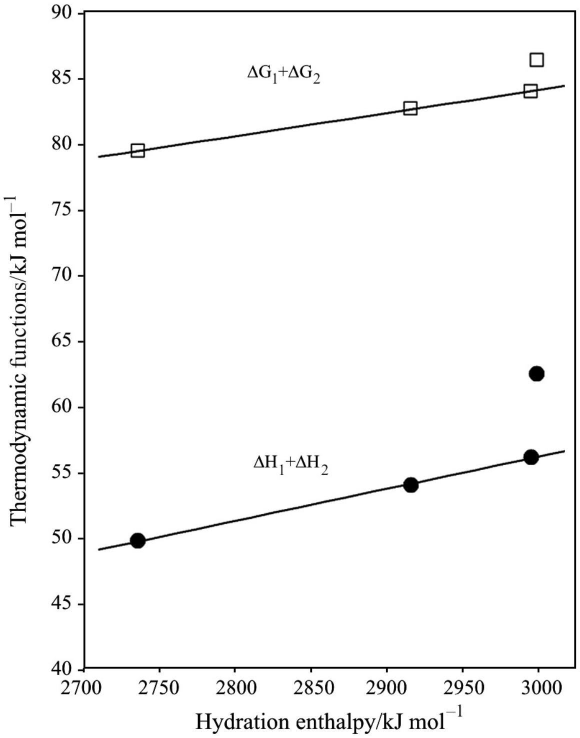


Fig. 6 Variation of the overall thermodynamic functions at 35°C for MHT complexes with the hydration enthalpy of M^{2+} ions

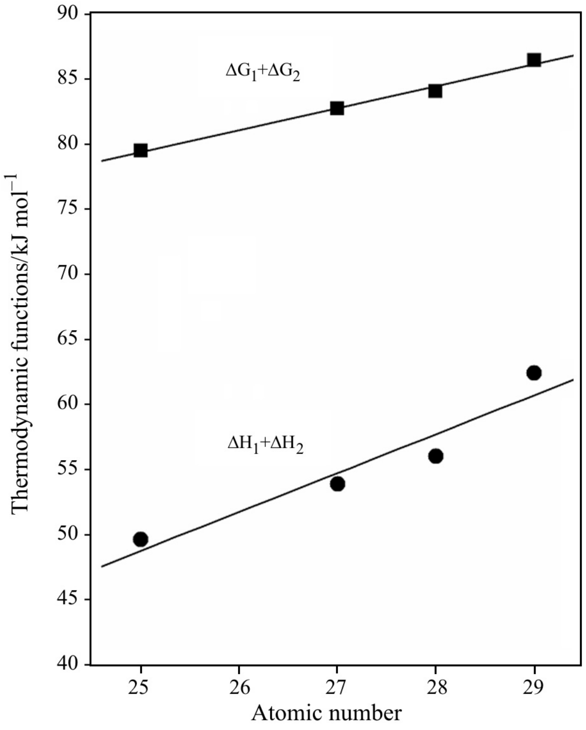


Fig. 7 Variation of the overall thermodynamic functions at 35°C for MHT complexes with the atomic number of M^{2+} ions

Irving–Williams series [25]. The thermodynamic functions of the Cu^{2+} complex are higher than those of the other metal ions, due to the stabilization exerted by its unique electronic configuration (d^9), which results in the Jan–Teller effect. This explains the deviation from the straight line observed for the thermodynamic parameters of the Cu^{2+} complex.

Conclusions

An attempt was made to determine, potentiometrically the dissociation constant of MHT as well as stepwise stability constants of its metal complexes. The results showed that the stabilities of the complexes follow the order Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}. The dissociation process is non-spontaneous, endothermic and entropically unfavoured. Also, complex formation is spontaneous, endothermic and entropically favoured.

References

1 M. S. Yadawe and S A. Patil, Transition Met. Chem., 22 (1997) 220.
2 T. Jeewoth, M. G. Bhowon and H. L. K. Wah, Transition Met. Chem., 24 (1999) 445.
3 K. M. Patel, K. N. Patel, N. H. Patel and M. N. Patel, Synth. React. Inorg. Met. Org. Chem., 31 (2001) 239.

4 H. Temel, U. Cakir, B. Otludii and H. I. Ugras, Synth. React. Inorg. Met. Org. Chem., 31 (2001) 1323.

5 S. M. Annigeri, A. D. Naik, U. B. Gandadharmath, V. K. Revankar and V. B. Mahale, Transition Met. Chem., 27 (2002) 316.

6 F. Hueso-Urena, N. A. Illan-Cabeza, M. N. Moreno-Carretero, J. M. Martinez- Martos and M. J. Ramirez-Exposito, J. Inorg. Bio. Chem., 94 (2003) 326.

7 M. A. Elmorsi and M. Gaber, J. Chimie Phys., 93 (1996) 1556.

8 M. Salavati-Niasari and S. H. Bantiaba, J. Mol. Cat., A, 201 (2003) 43.

9 A. M. Ramadan, W. Sawodny, H. El-Baradie and M. Gaber, Transition Met. Chem., 22 (1997) 211.

10 T. Jeewoth, H. L. Wah, M. G. Bhowon, D. Ghoorohoo and K. Babooram, Synth. React. Inorg. Met. Org. Chem., 30 (2000) 1023.

11 G. B. El-Hefnawy, A. El-Trass and M. Gaber, Synth. React. Inorg. Met. Org. Chem., 23 (1993) 32.

12 O. E. Sherif, Y. M. Issa and S. M. Abbas, J. Therm. Anal. Cal., 59 (2000) 913.

13 A. A. Soliman, J. Therm. Anal. Cal., 63 (2001) 221.

14 G. G. Mohamed and Z. H. Abd El-Wahab, J. Therm. Anal. Cal., 73 (2003) 347.

15 A. M. Donia, H. A. El-Boraey and M. F. El-Samalehy, J. Therm. Anal. Cal., 73 (2003) 987.

16 A. A. El-Bindary, A. Z. E1-Sonbati and H. M. Kera, Can. J. Chem., 77 (1999) 1305.

17 L. G. Van Uitert and G. G. Hass, J. Am. Chem. Soc., 75 (1953) 451.

18 H. Irving and H. S. Rossotti, J. Chem Soc., 11 (1953) 3397; 8 (1954) 2904.

19 F. I. C. Rossotti and H. S. Rossotti, Acta Chem. Scand., 9 (1955) 1166.

20 M. T. Beck and I. Nagybal, ‘Chemistry of Complex Equilibria’, Wiley, (1990).

21 H. M. Irving and R. J. P. Williams, Nature (London) 162 (1948) 746; Analyst (London) 77 (1952) 813.

22 I. Shehatta and A. M. Kiwan, J. Sol. Chem., 30 (2001) 389.

23 H. Frank and L. Evans, J. Phys. Chem., 13 (1945) 507.

24 S. Murakami and Y. Yoshino, J. Inorg. Nucl. Chem., 30 (1981) 2070.

25 H. Irving and J. P. Williams, J. Chem. Soc., 10 (1953) 3192.

Received: March 20, 2005
In revised form: April 20, 2005

DOI:10.1007/s10973-005-6988-x