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Thermodynamics of mixed-ligand complex formation of copper (II) ethylenediaminetetraacetate with hexamethylenediamine in an aqueous solution

D. F. Pyreu · E. V. Kozlovskii

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Abstract The mixed-ligand complex formation in the system $Cu^{2+}-Edta^{4-}-(CH_2)_6(NH_2)_2$ (L), where L is hexamethylenediamine has been calorimetrically, pH-potentiometrically and spectrophotometrically studied in aqueous solution at 298.15 K and the ionic strength of $I = 0.5$ (KNO_3). The thermodynamic parameters of formation of the $CuEdtaL^{2-}$, $CuEdtaHL^{-}$ $(CuEdta)_2L^{4-}$ and $(CuEdta)_2En^{4-}$ complexes have been determined. The most probable coordination mode for the complexone and the ancillary ligand in the mixed-ligand complexes was discussed.

Keywords Thermodynamic parameters · Mixed-ligand complex · Copper (II) ethylenediaminetetraacetate · Hexamethylenediamine · Denticity

Introduction

The complex formation of the type $CuEdtaEn^{2-}$, where En is ethylenediamine, has been studied earlier in the papers [1–6] mainly using NMR, EPR, IR and UV-visible spectroscopy. The authors of these works considered that En in mixed complex was bidentately coordinated due to decrease of chelate number (or denticity) of EDTA till six for four. At the same time the values of thermodynamic parameters of this reaction were absent in literature. The thermodynamic parameters of formation of CuEdtaEn that show the monodentate character of En have recently been received [7]. To evident of this suggestion it was necessary to study and compare the thermodynamic parameters of mixed-ligand complex formation with diamine ligand that can be coordinated only by one NH_2 group. The thermodynamic approach often permits us to make a valid suggestion about coordination mode and denticity of ligands. So in the paper [8] the monodentate character of En and L in the complexes of the type HgEdtaL $(HgEdta)_2En$ and $(HgEdta)_2L$ have been revealed. The system $Cu^{2+}-Edta^{4-}-(CH_2)_6(NH_2)_2$ was taken as object for this studying.

The copper (II) complex formation is very interesting due to tetragonal distortion of Cu^{2+} ion. The recent papers [9–11] show some interesting features of Cu (II) under complexation and biologically activity of these complexes.

Experimental

Sodium salt of copper (II) ethylenediaminetetraacetate $Na_2CuEdta \cdot 4H_2O$ used in the work was purified by recrystallization from an aqueous-DMFA solution. A working solution of the complexonate was prepared from en exact weight of the reagent. Carbonate-free NaOH solution was prepared as described in [12]. A working solution of the hexamethylenediamine was prepared by dissolving of the reagent in CO_2-free distilled water. The concentration of diamines in solution was potentiometrically determined. Hexamethylenediamine sulfate $NH_2(CH_2)_6NH_2 \cdot H_2SO_4$ was prepared by careful neutralization of a solution of hexamethylenediamine (high purity grade) with sulfuric acid followed by recrystallization from an aqueous-ethanolic solution. Analytical grade KNO_3 used for adjusting the solution ionic strength was doubly recrystallized from distilled water.

A series of pH-potentiometric titrations of solutions containing $Na_2CuEdta$, $L \cdot H_2SO_4$ and supporting electrolyte

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D. F. Pyreu (✉) · E. V. Kozlovskii
Ivanovo State University, Ermak 39, Ivanovo 153025, Russia
e-mail: pyreu@ivanovo.ac.ru

Table 1 The Lg*K* of reactions (6) and (7) determined by different methods at 298.15 K and $I = 0.5$ (KNO_3)

Complex	Method		
	Spectrophotometric	Calorimetric	Potentiometric
$CuEdtaL^{2-}$	2.56 ± 0.1	2.56 ± 0.02	2.57 ± 0.3
$CuEdtaHL^{-}$	3.07 ± 0.46	2.35 ± 0.05	2.75 ± 0.2

KNO_3 (at CuEdta:L ratios of 1:1 and 1:2) were potentiometrically titrated with a NaOH solution. The emf of the transfer chain including glass and Ag/AgCl electrodes was measured by the compensation method. The experimental pH-metric data were processed using the PHMETR program [13]. Received equilibrium constants of addition of L and HL^+ to the $CuEdta^{2-}$ (the weighted average values are given in Table 1) have a sufficiently big uncertainties first of all due to relatively low sensitivity of pH-potentiometrical method to the presence of complexes CuEdtaL and CuEdtaHL in solution in the equilibrium constant range of 1–2 log units. At the same time the calorimetry is very useful method in this range of lg*K*.

The mathematical simulation of the equilibrium compositions of solutions containing $CuEdta^{2-}-L-H^+$ in a wide pH range at various $CuEdta^{2-}$ to L ratios has been carried out using the RRSU program [14]. The possibility of occurrence of the following reactions has been taken into account:

$$H_2O = H^+ + OH^- \tag{1}$$

$$L + iH^+ = H_iL^{i+}, \quad i = 1,2 \tag{2, 3}$$

$$CuEdta^{2-} + H^+ = CuHEdta^- \tag{4}$$

$$CuEdta^{2-} + OH^- = CuEdtaOH^{3-} \tag{5}$$

$$CuEdta^{2-} + L = CuEdtaL^{2-} \tag{6}$$

$$CuEdta^{2-} + HL^+ = CuEdtaHL^- \tag{7}$$

The $\lg K_1$ value was received by extrapolation technique at an ionic strength of I = 0.5 using Davis's equation. The lg*K* and $\Delta_r H$ values of reactions (2) and (3) have earlier been determined by us [8]. For the reactions (6) and (7) the lg*K* values that potentiometrically determined were taken. The possibility of occurrence of the substitution processes has not been considered. The values of stability constants of copper (II) complexes with hexamethylenediamine in database [15] are absent. The stability of copper (II) complexes with hexamethylenediamine witch evidently have not chelate structure is sufficiently low than stability of copper (II) complexes with En. It decreases the possibility of EDTA substitution under excess of L.

The computer simulation showed that small excess of NaOH in solution containing 0.005 M $Na_2CuEdta$ and 0.05 M L increased the relative amount of $CuEdtaL^{2-}$ from 80 to 91% and the relative amount of protonated particle $CuEdtaHL^-$ didn't exceed 5%. It permitted us to simultaneously calculate the Lg*K* and $\Delta_r H$ of reaction (6) neglecting the contribution of the formation of $CuEdtaHL^-$. At the same time the small excess of HNO_3 in solution containing 0.005 M $Na_2CuEdta$ and 0.05 M $L{\cdot}HNO_3$ increased the relative amount of $CuEdtaHL^-$ from 40 to 68% and the relative amount of $CuEdtaL^{2-}$ decreased from 30 to 24%. The simultaneous treatment of Lg*K* and $\Delta_r H$ of reaction (7) was performed taking into account the contribution of the formation of $CuEdtaL^{2-}$.

The heats of reactions were measured on an isothermal-jacket ampoule flow-mixing calorimeter equipped with a thermistor temperature gage and automated recording of temperature-time curves. The calorimeter was verified against the heat of solution of KCl in water at 298.15 K. According the first method the heats of mixing $\Delta_{mix}H$ of a solution of Cu (II) complexonate with solutions of hexamethylenediamine containing the supporting electrolyte (KNO_3) and the heat of dilution $\Delta_{dil}H$ of a solution of Cu (II) complexonate in a solution of the supporting electrolyte were measured. A weighed sample of a Cu (II) complexonate solution was placed into a glass ampoule. A diamine with supporting electrolyte solution was contained in the reaction vessel of the calorimeter. A series of calorimetric data of mixing of a solution of L with solutions containing the big excess of Cu (II) complexonate (the second method) showed that the values of $\Delta_{mix}H$ calculated to amount of diamine ligand are significantly more than the heats of reactions (6) and (7). It can be explain by binuclear complex formation only:

$$2CuEdta^{2-} + (CH_2)_6(NH_2)_2 = (CuEdta)_2(CH_2)_6(NH_2)_2{}^{4-} \tag{8}$$

The analogical series of calorimetric data with a solution of En has been carried out. The experimental data are given in Tables 2 and 3. The simultaneous treatment of lg*K* and $\Delta_r H$ of reaction (8) for L and En taking into account the contributions of processes (1)–(3) and (5)–(7) permits us to evaluate its full thermodynamic characteristics. The heats of the reactions computed using the HEAT program [14] and other thermodynamic parameters are listed in Table 4. The heats of water ionization ($\Delta_r H_1 = -56.90$ kJ/mol [16]), ligand protonation ($\Delta_r H_3 = -51.60$ and $\Delta_r H_4 = -95.20$ [17] for En and $\Delta_r H_3 = -63.31$ и $\Delta_r H_4 = -114.06$ kJ/mol [8] for hexamethylenediamine) and the formation of hydroxocomplexonate $CuEdtaOH^{2-}$ ($\Delta_r H_5 = -25.5$ kJ/mol [19]) were accepted according to published data. Data from [17] have a good agreement with the recommended in [18].

After calorimetric measurements the electronic spectra of solutions have been recorded using a spectrophotometer

Table 2 Heats of mixing of a solution of $Na_2CuEdta$ (0.4985 mol/kg of solution) with solutions of hexamethylenediamine at 298.15 K and $I = 0.5$ (KNO_3)

No	Weighed sample of $Na_2CuEdta$ solution, g	Concentration of $Na_2CuEdta$ after mixing, mol/L	$\Delta_{mix}H$, kJ mol^{-1}	$\Delta_{mix}H - \Delta_{dil}H$, kJ mol^{-1}
$C_L = 0.01121$ mol/L, $C_{KOH} = 0.002074$ mol/L				
1	0.46455	0.004624	−24.33	−24.79
2	0.48180	0.004796	−24.27	−24.73
3	0.39215	0.003904	−23.89	−24.36
4	0.41280	0.004109	−24.05	−24.52
5	0.33010	0.003291	−24.16	−24.63
$C_L = 0.02243$ mol/L, $C_{KOH} = 0.004149$ mol/L				
6	0.48800	0.004858	−28.22	−28.68
7	0.47505	0.004729	−28.98	−29.45
8	0.46370	0.004616	−28.16	−28.62
9	0.43810	0.004361	−26.24	−26.71
10	0.27780	0.002770	−28.50	−28.97
$C_L = 0.03364$ mol/L, $C_{KOH} = 0.006231$ mol/L				
11	0.46510	0.004630	−29.72	−30.19
12	0.52495	0.005226	−29.97	−30.43
13	0.48140	0.004792	−29.85	−30.31
14	0.52520	0.005228	−29.47	−29.93
15	0.47320	0.004718	−29.35	−29.81

Table 3 Heats of mixing of solutions of hexamethylenediamine (0.5025 mol/kg of solution) and ethylenediamine (1.164 mol/kg of solution) with solutions of $Na_2CuEdta$ at 298.15 K and $I = 0.5$ (KNO_3)

Weighed sample of $(CH_2)_n(NH_2)_2$ solution, g	Concentration after mixing, mol/L		$\Delta_{mix}H$, kJ mol^{-1}	$\Delta_{mix}H - \Delta_{dil}H$, kJ mol^{-1}
	$CuEdta^{2-}$	$(CH_2)_n(NH_2)_2$		
$n = 2$ (En)				
0.37315	0.03010	0.008673	−45.14	−44.62
0.36705	0.03010	0.008545	−45.17	−44.65
0.22750	0.03032	0.005296	−46.04	−45.52
0.24490	0.03011	0.005701	−46.12	−45.59
0.23960	0.03010	0.005569	−45.84	−45.31
0.10340	0.03010	0.002403	−46.60	−46.07
0.12365	0.03010	0.002874	−46.19	−45.66
0.18065	0.1003	0.004206	−52.51	−51.98
0.19470	0.1002	0.004533	−52.59	−52.07
$n = 6$ (L)				
0.21955	0.01004	0.002203	−39.86	−35.52
0.29485	0.01004	0.002959	−36.78	−32.44
0.34825	0.01004	0.003494	−35.30	−30.96
0.40810	0.01004	0.004095	−33.21	−28.88
0.46235	0.01004	0.004647	−31.83	−27.49
0.23265	0.03002	0.002334	−54.57	−50.24
0.26685	0.03002	0.002678	−53.51	−49.17
0.43380	0.03002	0.004353	−52.34	−48.00
0.49010	0.03002	0.004918	−51.46	−47.12
0.42370	0.03002	0.004258	−51.73	−47.39
0.41075	0.100	0.004128	−63.45	−59.11
0.49430	0.100	0.004968	−63.17	−58.83

Table 4 The thermodynamic parameters of mixed-ligand complex formation in the systems $CuEdta^{2-}-(CH_2)_n(NH_2)_2-H^+$ ($n = 2, 6$) at 298.15 K and $I = 0.5$ (KNO_3)

Process	lg$K$	$-\Delta_rG^0$, kJ mol^{-1}	Δ_rH, kJ mol^{-1}	Δ_rS, J mol^{-1} K^{-1}
$CuEdta^{2-} + NH_3 = CuEdtaNH_3^{2-}$	2.06 ± 0.02	11.76 ± 0.11	−34.9 ± 0.4	−77.6 ± 1.4
$CuEdta^{2-} + Gly^- = CuEdtaGly^{3-}$	1.8 ± 0.1	10.27 ± 0.57	−29.3 ± 1.3	−63.8 ± 4.8
$CuEdta^{2-} + En = CuEdtaEn^{2-}$	4.32 ± 0.10	24.66 ± 0.57	−34.77 ± 0.28	−33.9 ± 2.1
$CuEdta^{2-} + L = CuEdtaL^{2-}$	2.56 ± 0.02	14.58 ± 0.11	−33.61 ± 0.24	−63.8 ± 0.9
$CuEdta^{2-} + HL^+ = CuEdtaHL^-$	2.35 ± 0.05	13.41 ± 0.29	−31.23 ± 1.70	−59.8 ± 5.8
$2CuEdta^{2-} + En = (CuEdta)_2En^{4-}$	6.02 ± 0.05	34.36 ± 0.29	−56.75 ± 0.26	−75.1 ± 1.3
$2CuEdta^{2-} + L = (CuEdta)_2L^{4-}$	4.13 ± 0.05	23.57 ± 0.29	−66.85 ± 1.67	−145.2 ± 5.7
$CuEdtaEn^{2-} + CuEdta^{2-} = (CuEdta)_2En^{4-}$	1.70 ± 0.11	9.70 ± 0.64	−21.98 ± 0.38	−41.2 ± 2.5
$CuEdtaL^{2-} + CuEdta^{2-} = (CuEdta)_2L^{4-}$	1.57 ± 0.06	8.96 ± 0.34	−33.24 ± 1.69	−81.4 ± 5.8

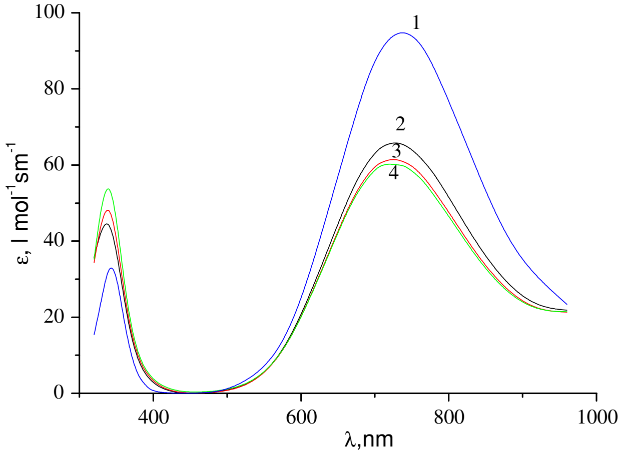


Fig. 1 The electronic spectra of solutions: *1* 0.005 mol/L $Na_2CuEdta$, *2* 0.005 mol/L $Na_2CuEdta$, 0.0111 mol/L $(CH_2)_6(NH_2)_2$, 0.0111 mol/L HNO_3, *3* 0.005 mol/L $Na_2CuEdta$, 0.0236 mol/L $(CH_2)_6(NH_2)_2$, 0.0236 mol/L HNO_3, *4* 0.005 mol/L $Na_2CuEdta$, 0.0334 mol/L $(CH_2)_6(NH_2)_2$, 0.0334 mol/L HNO_3

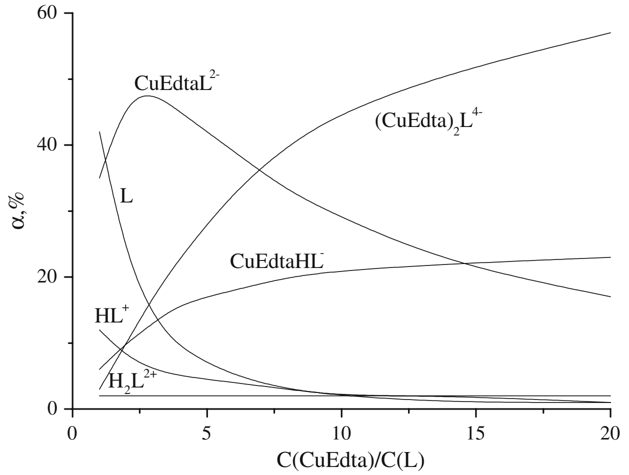


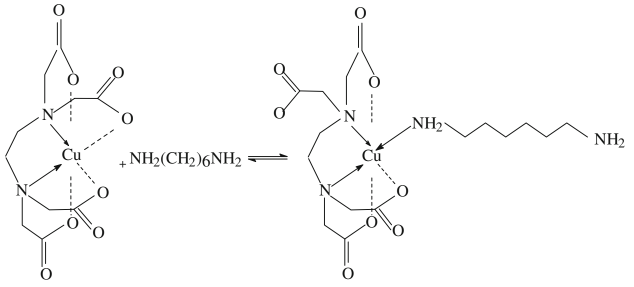
Fig. 2 Diagram of the fractional distribution of the L containing species in the $Cu^{2+}-Edta^{4-}-L$ system ($C_L = 0.005$ mol/L)

CFC-3 and 1 cm cells. The received electronic spectra in the system $Cu^{2+}-Edta^{4-}-HL^+$ are shown in Fig. 1. The spectrophotometric data were processed using the FTMT program [14]. The calculated LgK values of reactions (6) and (7) are given in Table 1.

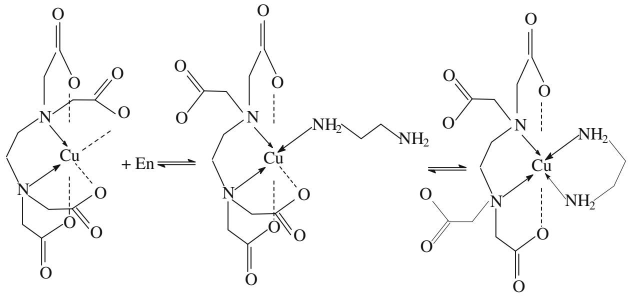
Results and discussion

The thermodynamic characteristics of addition of L and HL^+ to Cu (II) complexonate are given in Table 4. The uncertainties of indirect treated values are given taking into account the rule of error sum. The diagram of the fractional distribution in the $Cu^{2+}-Edta^{4-}-L$ system is shown in the Fig. 2. Data for NH_3 and Gly^- (Table 4) have been calorimetrically received at 298.15 K and I = 1.5 (KNO_3) [19].

As can be shown from the Table 4 the addition of L and HL^+ to $CuEdta^{2-}$ is accompanied by negative changes in the enthalpy and entropy, which is characteristic of mixed-ligand complex formation involving the coordinately saturated copper (II), nickel (II), zinc (II), and cadmium (II) complexonates and occurring with a decrease in the EDTA denticity due to the opening of one or two glycinate chelate rings. The factors that cause such thermodynamic characteristics are comprehensively described in [19, 20]. Also for the En the heat effects of reactions (6) (7) are close to the heats of addition of the ammonia and glycinate ion to the copper (II) complexonate (Table 4). Since the formation of the nine-membered chelate ring in the case of hexamethylenediamine is energetically unfavorable due to the loss of configurational entropy of the ligand [21] (especially under opposition with the donor atoms of EDTA), it can be assumed that hexamethylenediamine is coordinated through one donor nitrogen atom. The close values of the heats of addition of NH_3, Gly^-, L, HL^+ and En to the $CuEdta^{2-}$ indicate not only the monodentate character of hexamethylenediamine but also probable monodentate character of ethylenediamine (Scheme 1).



Scheme 1 The addition of hexamethylenediamine to the copper (II) ethylenediaminetetraacetate



Scheme 2 The addition of ethylenediamine to the copper (II) ethylenediaminetetraacetate

Appearance of noncoordinated NH_2 group in the complexes CuEdtaL and CuEdtaEn can results in binuclear complex formation with bridging function of diamine ligand. Such effect has been studied previously [8] in the case of Hg(II) complexonate. Thermochemical data using the second method show it. Also the close values of the thermodynamic parameters of reaction:

$$\mathrm{CuEdta(CH_2)_n(NH_2)_2}^{2-} + \mathrm{CuEdta}^{2-} = \mathrm{(CuEdta)_2(CH_2)_n(NH_2)_2}^{4-},\quad n = 2, 6 \tag{9}$$

(Table 4) confirm the monodentate character of diamines in the complexes being studied. It should be noted that the entropy change in reaction (9) involving the hexamethylenediamine is sufficiently less than the same involving En due to the loss of configurational entropy of the ligand with long aliphatic chain.

The thermodynamic data received does not exclude the possible existence of the complex $\mathrm{CuEdtaEn}^{2-}$ with bidentate character of the En due to opening of two glycinate chelate [4, 6] (Scheme 2). The equilibrium between the forms of the mixed complex $\mathrm{CuEdtaEn}^{2-}$, in which the ethylenediamine is bi- and monodentate apparently is shifted to the complex with monodentate character of the En. The reaction (9) is less exothermic in comparison with the En. This can be due to the participation of the noncoordinated NH_2 group of En in a weak interaction with the acetate groups of the complexone through hydrogen bonding. All these facts permit us to consider that under saturation of coordination sphere and opposition between donor atoms of two ligands the coordination of the En can takes place without chelate structure arising. So the ethylenediamine can be monodentate in the mononuclear mixed complex or bidentate with the bridging function in the binuclear complex.

The Fig. 1 shows that the changes in the electronic spectra of copper (II) complexonate in solution under adding of the hexamethylenediamine provide one more evidence of mixed complex formation. Spectrophotometrically received values of the equilibrium constants of reactions (6) and (7) sufficiently good agree with the values obtained using other methods (Table 1). But more reliable value of LgK_7 has been obtained using calorimetry as the most informational experimental method in this case.

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References

1. Kirson B, Israeli YJ. Le complexe triple: cuivre – ethylenediamine – ethylenediamine-tetraacetate. Bull Soc Chem France. 1963;11:2527–31.
2. Bhat TR, Radhamma D, Shanker J. Studies on EDTA complexes-VI. Mixed complexes of copper (II), nickel (II) and cobalt (II) versenates with pyridine, hydrazine, hydroxylamine, ethylenediamine and propylenediamine. J Inorg Nucl Chem. 1965;27:2641–51.
3. Korsse J, Pronk LA, van Embden C, Leurs G, Louwrier PWF. Ternary complexes of the Cu(II) and Ni(II) chelates of EDTA and DCTA with cyanide and ethylenediamine. Talanta. 1983;30:1–7.
4. Citron I. Infrared study of the copper-EDTA complex and its reaction with various amino compounds. Anal Chim Acta. 1962;26:446–57.
5. Shapnik MS, Gilmanov AN, Petrova TP, Gubaidullin FF. Studies on copper(II) complexes with ethylenediaminetetraacetic acid and ethylenediamine by proton magnetic relaxation method. Rus J Inorg Chem. 1975;20:2148–51.
6. Vishnevskaya GP, Shapnik MS, Safina R Sh. Studies on copper(II) complexes with ethylenediaminetetraacetic acid and ethylenediamine by EPR method. Rus J Inorg Chem. 1981;26:2781–5.
7. Pyreu DF, Khrenova EV, Kozlovskii EV. Thermodynamics of complex formation of Cu(II) ethylenediaminetetraacetate with ethylenediamine in aqueous solution. Rus J Coord Chem. 2008;34:750–5.
8. Pyreu DF, Titova ES, Kozlovskii EV. Thermodynamics of mixed-ligand complex formation of mercury(II) ethylenediaminetetraacetate with ethylenediamine and hexamethylenediamine in an aqueous solution. Rus J Inorg Chem. 2008;53:334–6.
9. Kalia SB, Kaushal G, Lumba K, Priyanka. Thermoanalytical investigations of 4-methylpiperazine-1-carbodithioic acid ligand

and its iron(III), cobalt(II), copper(II) and zinc(II) complexes. J Therm Anal Calorim. 2008;91:609–13.

10. Olar R, Badea M, Grecu MN, Marinescu D, Lazar V, Balotescu C. Copper(II) complexes with N,N-dimethylbiguanide: thermal, spectroscopic and biological characterization. J Therm Anal Calorim. 2008;92:239–43.
11. Verma RK, Verma L, Ranjan M, Verma BP, Mojumdar SC. Thermal analysis of 2-oxocyclopentanedithiocarboxylato complexes of iron(III), copper(II) and zinc(II) containing pyridine or morpholine as the second ligand. J Therm Anal Calorim. 2008; 94:27–31.
12. Korostelev PP. Solution preparation for chemical analysis. Moscow: Akad. Nauk SSSR; 1962.
13. Borodin VA, Kozlovskii EV, Vasiliev VP. The treatment of results of potentiometric studies of complex formation in solutions by computer program. Rus J Inorg Chem. Rus J Inorg Chem. 1986; 31:10–6.
14. Borodin VA, Vasiliev VP, Kozlovskii EV. Mathematical problems in chemical thermodynamics. Novosibirsk: Nauka; 1985.
15. IUPAC Stability Constants Database SCUERY ©1997, IUPAC and Academic Software SCQUERY version 3.09 Computer release complied by Pettit LD, Powell HKJ, UK.
16. Vasiliev VP. Thermodynamic properties of electrolyte solutions. Moscow: Vysschaya Shkola; 1982.
17. Borodin VA. Cand Sci (Chem.). Dissertation, Ivanovo: Ivanovo Institute of Chemical Technology; 1983.
18. Paoletti P. Formation of metal complexes with ethylenediamine: a critical survey of equilibrium constants, enthalpy and entropy values. Pure Appl Chem. 1984;56:491–522.
19. Kozlovskii EV. Doctoral (Chem.). Dissertation, Ivanovo: Ivanovo State University; 1995.
20. Kozlovskii EV, Fridman A Ya. Structural and thermodynamic features of addition of mono- and bidentate ligands to the nickel, copper and zinc ethylenediaminetetraacetates in an aqueous solution. Rus J Inorg Chem. 1991;36:1500–2.
21. Lewis J, Wilkins RG. Modern coordination chemistry. New York: Interscience Publishers Inc; 1960.