Scientific paper

Speciation Study on the Interaction of Some Divalent Transition Metal Ions with Succinic acid Dihydrazide in Aqueous Medium

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Abstract

The interaction of succinic acid dihydrazide with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was investigated in aqueous medium at 303K and ionic strength of 0.1 mol dm^{-3}. The speciation and stability constants of the metal complexes formed were determined by pH-metric method. Mononuclear and homo binuclear species in different protonation and deprotonation states were identified, the corresponding formation constants calculated using MINIQUAD-75 computer program, and species distribution diagrams produced using the HYSS computer program. Selection of the best-fit chemical models was based on statistical parameters.

Keywords: Formation constant, speciation, succinic acid dihydrazide, metal complexes

1. Introduction

Dihydrazides, which are synthesized by condensation reaction of hydrazine with corresponding diesters,[1,2] are widely used for coating of epoxy resins in varnishes and nickel corrosion inhibitors.[3,4] Further they are employed as latent hardeners, curing agents, and cross-linkers in many industrial products including semiconductors.[5,6] Hydrazides display antimicrobial, antifungal, antibacterial and anti-tubercular properties[7–10] based on their tendency to form metal chelates with transition metal ions. Majority of the studies reported in the literature on metal complexes of dihydrazides are aimed at preparation and elucidation of their structures by physicochemical methods.[11–16] Studies on the solution equilibria of their metal complexes are scanty.[17,18]

Dihydrazide contains two hydrazide groups and each hydrazide group is known to exist either in ketonic [$NH_2 \cdot NH \cdot C(=O) \cdot R \cdot C(=O) \cdot NH.NH_2$] or enolic [$NH_2 \cdot N=C(OH) \cdot R \cdot C(OH)=N \cdot NH_2$] form. Depending on the pH the terminal amino groups of the neutral ligand may be protonated. These ligands may also lose protons from enolic form either at higher pH or on interaction with metal ions. Hence there is a chance of formation of a variety of coexisting mono nuclear and binuclear species in protonated, unprotonated and deprotonated forms.[19] The formation of binuclear species has special significance. The presence of two metal ions in the same species separated by some distance not too far, leads to several interesting and important applications including unusual magnetic properties.[20] Depending on the degree of flexibility of the molecule between the two coordination sites there is a possibility of formation of supramolecular architectures like double helices and coordination polymers.[21] They can be used to mimic metalloproteins and to study structure- reactivity relationship.[22] The metal centers are found to act synergistically in catalyzing reactions.[23,24] Speciation study which gives the nature and extent of formation of all the species in solution is an essential pre-requisite to understand their behavior in biological and other systems. Therefore, in this paper we report the results of a speciation study on the interaction of succinic acid dihydrazide (SADH) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in aqueous medium.

2. Experimental

2. 1. Material, Solutions & Apparatus

All the chemicals used were of AnalaR or equivalent grade. Succinic acid dihydrazide (SADH) (Fluka) was recrystallized twice from water, dried at 100 °C and a ~0.05 mol dm^{-3} solution was prepared freshly in 0.1 mol dm^{-3} HCl just before the titrations. All other solutions, including metal chlorides, hydrochloric acid, sodium hydroxide, and sodium chloride, were prepared using doubly glass distilled water through which nitrogen gas was purged to expel any dissolved oxygen or carbon dioxide. A Control Dynamics pH-meter model APX 175 E/C in conjunction with a combination electrode (0–14 pH range) was used for pH measurements. The pH correction factor was calculated before each set of experimental titrations by Gran method.[25–27]

2. 2. Titration Procedure and Data Analysis

Calvin-Wilson titration technique modified by Rossotti[28,29] was employed for the study of protonation and complex equilibria of the ligand (SADH). Titrations were carried out at 1:1, 1:2 and 2:1 ratios of initial concentrations of metal to ligand. In some of the titrations, the upper pH limit of rejecting data was determined by the appearance of opalescence leading to precipitation indicated by a downward drift of the pH-meter dial readings.

For a system containing a metal ion and a ligand forming N complexes, the formation constant of a complex can be represented as,

$$\beta_{mlh} = [M_mL_lH_h]_i / [M]_i^m.[L]_i^l.[H]_i^h \qquad (1)$$

where $[M]_i$, $[L]_i$ and $[H]_i$ are the free concentrations of metal, ligand and hydrogen ion respectively at i^th^ experimental point. Different species in solution possess different values of stoichiometric coefficients *m, l* and *h.* The potentiometric titration data obtained was subjected to analysis by Miniquad-75 program.[30] The stoichiometry and stability constants of the species formed in solution were determined by examining various chemically possible composition models for the systems studied. The best-fit models were selected on the basis of U (sum of the squares of residuals in mass balance equations), standard deviations in formation constants and other statistics like χ^2 test which tests the distribution of errors against a normal one. Species distribution diagrams for all the systems under study were generated using HYSS[31] program.

3. Results and Discussion

3. 1. Proton- Ligand Equilibria of Succinic Acid Dihydrazide

A perusal of potentiometric titration data of SADH indicates association of protons in the lower pH region and dissociation at higher pH. The best-fit model obtained using Miniquad-75 program (Table 1) contained three formation constants, β_{011}, β_{012} and β_{01-1}.

Table 1. Protonation constants (*Log* β_{0lh}) of SADH in aqueous medium (Temp. 30 ± 1 °C and ionic strength, I = 0.1 mol dm^{-3})

Log β_{0lh} (SD*)			**Np***	**U*X 10^8**	**χ^2**	**pH-Range**
011	012	01–1				
3.59 (1)	6.16 (1)	–11.89 (2)	113	1.527	42.6	1.8–11.5

* (U- sum of the squares of residuals in mass balance equations, NP= number of experimental points, SD=standard deviation in the least significant digit)

At lower pH (below ~3.0), SADH (L) mostly exists in its diprotonated form, H_2L^{2+}, and with rise of pH, undergoes successive deprotonation to form the mono-protonated (HL^+) and neutral species (L). β_{011} and β_{012} are the formations constants (Fig. 1) of mono and diprotonated forms of SADH from its neutral form. In basic medium hydrazides are prone to lose a proton[32] from the enolic form. As SADH contains two hydrazide groups, there is a chance of losing two enolic protons at higher pH. The formation constant, β_{01-1} in the best-fit model corresponds to the deprotonation of one of the enolic protons leading to the formation of LH_{-1} species. The other (LH_{-2}) which corresponds to the formation constant, β_{01-2} is not observed as its equilibrium may lie well above the pH range of study. However, in the presence of a metal ion the ligand may also lose the second enolic proton forming both deprotonated $M_m L_l H_{-1}$ and $M_m L_l H_{-2}$, type of species.

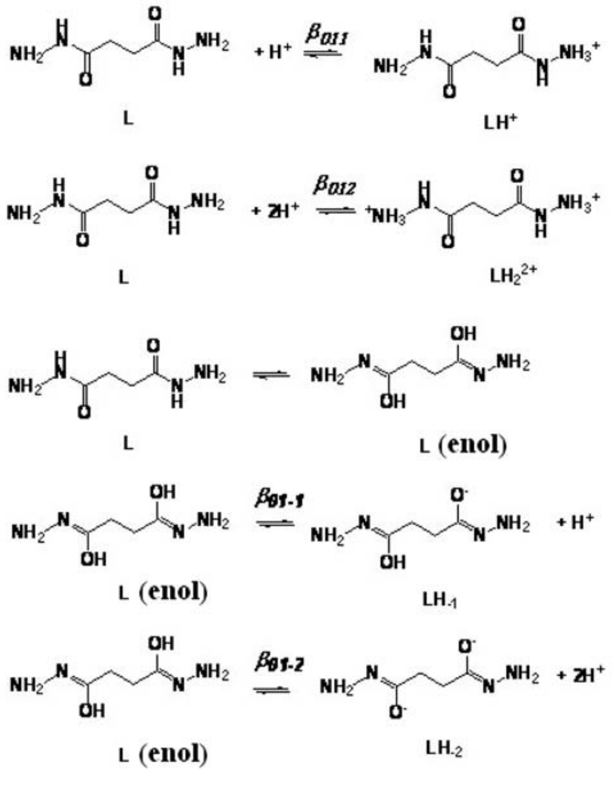

Figure 1. Protonation and deprotonation equilibria of SADH

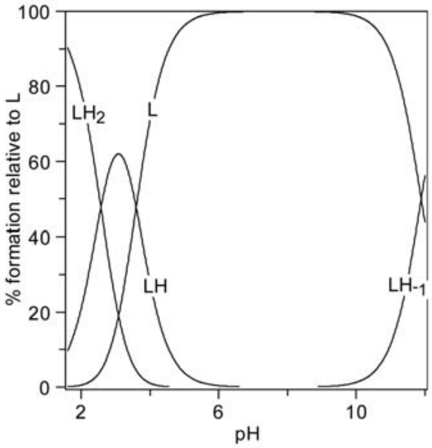

Figure 2. Species distribution diagram for proton-ligand equilibria of SADH

The species distribution diagram (Fig. 2) indicates that SADH exists in protonated form below pH 6, deprotonated form above pH 10 and in neutral form between pH 6–10.

3. 2. Metal- Ligand Equilibria of Succinic Acid Dihydrazide

The acquired data for metal-ligand equilibria was first subjected to analysis by classical procedures[28] to get the formation constants of simple mono-nuclear complexes like ML, ML_2 etc. Simulated titration curves were then generated using computer program SOPHD[33] developed in our laboratory to see whether these species satisfy the experimental data. The simulated titration curves thus obtained were plotted along with the experimental ones to identify the regions of pH where they differ. Titration curves for some representative systems for all the compositions are shown in Fig.3. The wide difference between the simulated and experimental curves reveals the presence of other major species in addition to simple mono-nuclear complexes. Different chemical models containing chemically plausible species depending on the nature of the ligand, metal and the pH region of difference in the curves were tested using Miniquad-75 program. The required initial estimates of the formation constants were calculated basing on the formation constants of simple complexes and protonation/ deprotonation constants of the ligand.

The best-fit models obtained for all the metal ions and compositions are shown in Table 2. For 1:1 and 1:2 compositions the species converged include protonated MLH, ML_2H, ML_2H_2 and deprotonated MLH_{-1}, MLH_{-2}, ML_2H_{-1}, ML_2H_{-2} in addition to simple ML, ML_2 type of complexes. In the case of 2:1 composition, formation of homo binuclear species M_2L, M_2LH_{-1} and M_2LH_{-2} were observed. Charges on the species are omitted for brevity.

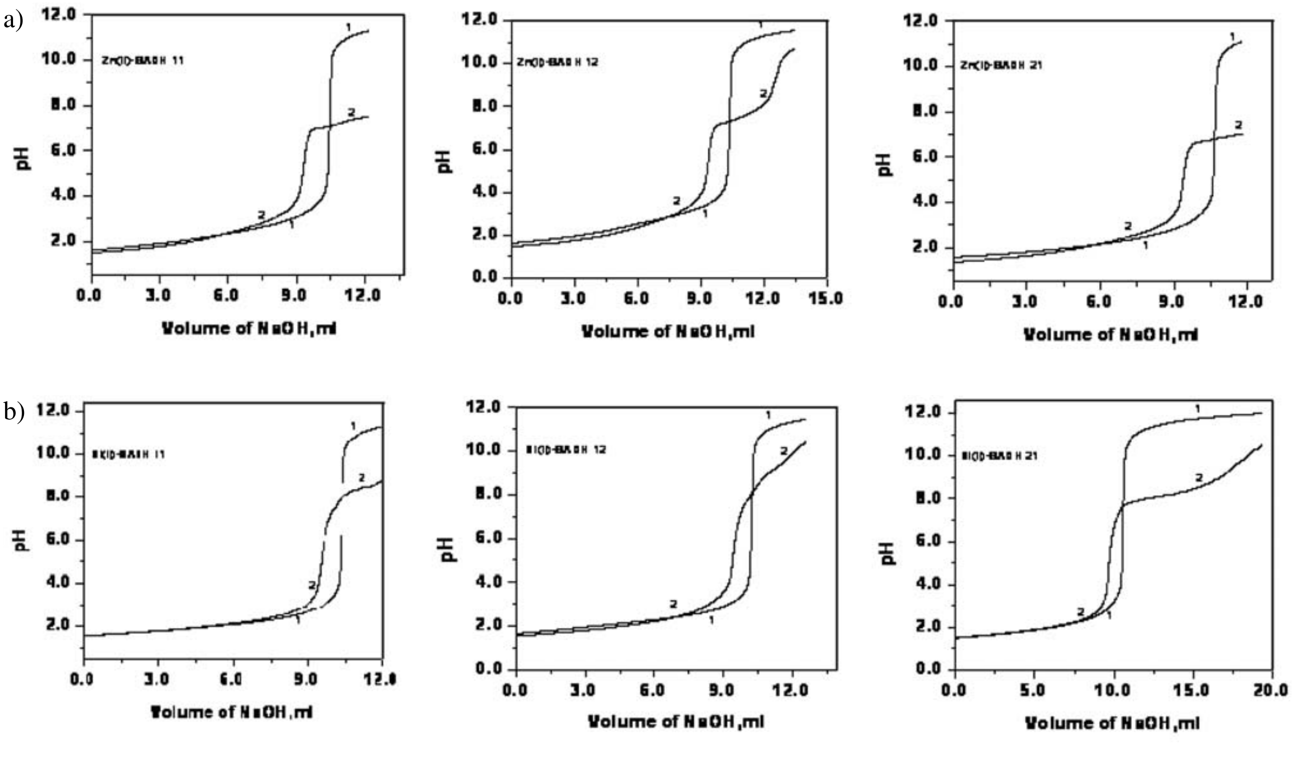

Figure 3. Simulated and experimental titration curves for (a) Zn(II)-SADH and (b) Ni(II)-SADH systems for 1:1, 1:2 and 2:1 compositions. (1.Simulated titration curve 2. Experimental titration curve)

Table 2. Best-Fit models for SADH- METAL ION SYSTEMS (Temp. 30 ± 1 °C and ionic strength, *I* = 0.1 mol dm^{-3})

Concentration Ratio M:L	**Species *mlh***	***log β_{mlh}* (SD*)**				
		Mn(II)	**Co(II)**	**Ni(II)**	**Cu(II)**	**Zn(II)**
1:1	111	6.57 (5)	7.03 (5)	7.11 (3)	8.22 (8)	7.80 (9)
	110	3.30 (4)	3.99 (4)	4.78 (1)	5.72 (6)	4.38 (8)
	11–1	–	–4.77 (5)	–4.39 (8)	–	–
	11–2	–14.87 (5)	–	–12.95 (3)	–5.35 (9)	–10.57(7)
1:2	111	6.57	7.03	7.11	8.22	–
	11–1	–	–4.77	–4.39	–	–
	11–2	–	–	–12.95	–5.35 (9)	–10.57
	122	–	13.61 (9)	14.39 (2)	16.66 (8)	13.60 (3)
	121	8.92 (7)	10.45 (7)	11.95(1)	14.06 (5)	–
	120	5.85 (2)	7.42 (6)	8.36 (2)	–	7.13 (2)
	12–1	–	–1.40 (8)	–0. 835 (5)	–	–0.219 (7)
	12–2	–12.45 (3)	–	–	–	–8.17 (4)
2:1	111	6.57	7.03	7.11	8.22	7.80
	11–1	–	–4.77	–	–	–
	210	4.81 (9)	6.49 (2)	7.04 (4)	8.06(0.0)	6.67 (4)
	21–1	–	–2.27 (1)	–	–	–0.406 (4)
	21–2	–13.10 (7)	–	–9.13 (4)	–1.61 (5)	–

(*SD = Standard deviation in the least significant digit)

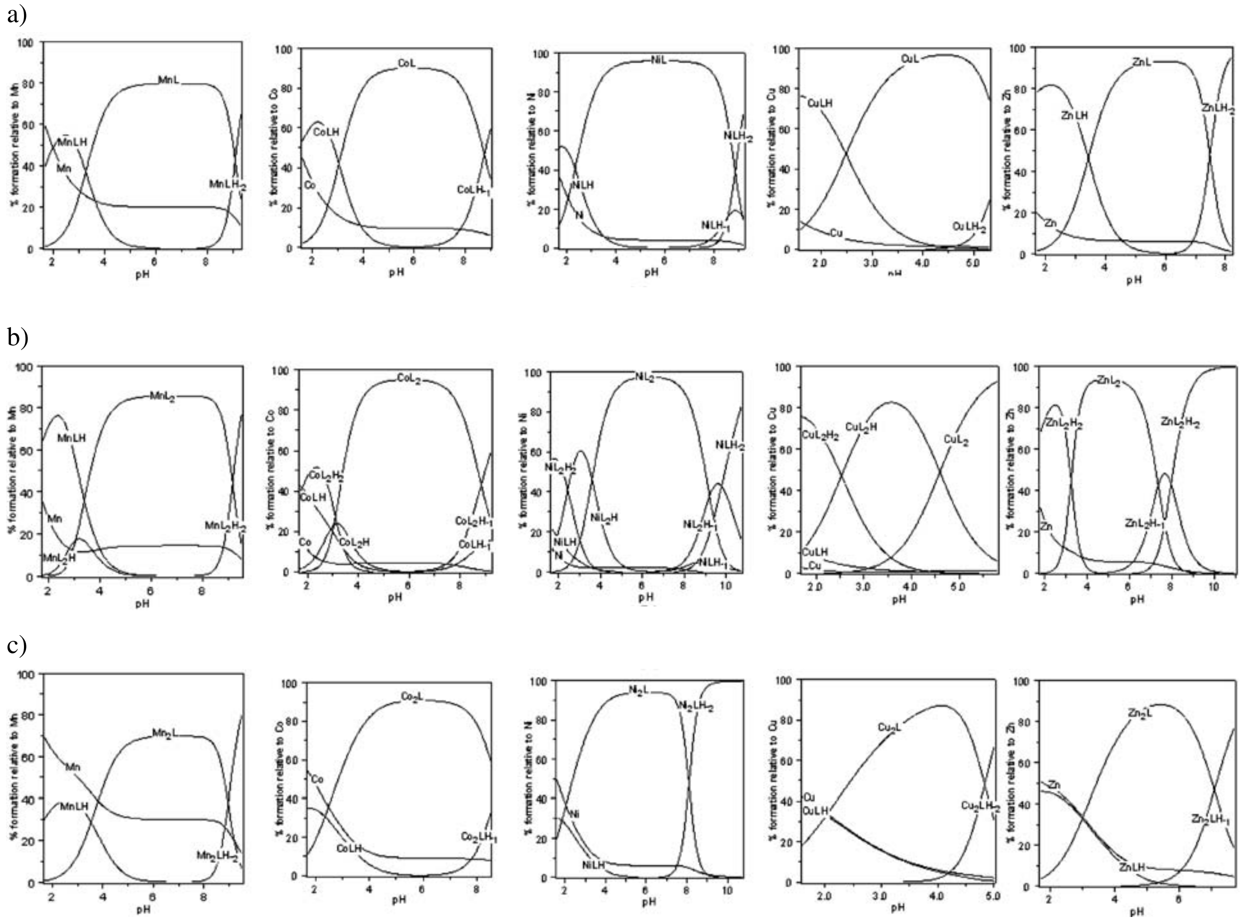

Figure 4. Species distribution diagrams of M(II)-SADH systems (M = Mn, Co, Ni, Cu and Zn) (a) 1:1 (b) 1:2 and (c) 2:1, M:L concentration ratios

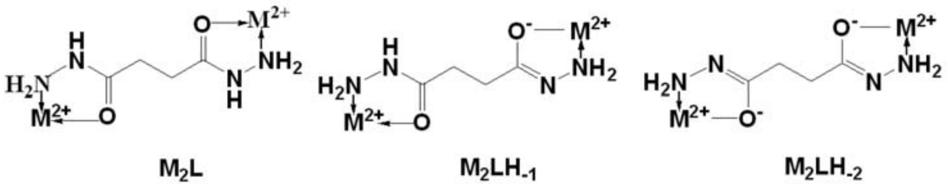

Figure 5. Homo binuclear species of metal-SADH systems

The formation constants for different metal ions were found to obey the Irving-William order.[34,35] The species distribution diagrams for metal- ligand systems (Fig. 4) give the percentage of formation of various species as a function of pH. For 1:1 and 1:2 compositions at low pH i.e 1.5 to 4.0, the protonated species MLH, ML_2H and ML_2H_2 are prevalent for all metals ions under study. In the case of protonated species MLH and ML_2H_2 probably only one of the hydrazide groups of the SADH (L) is involved in bonding as a bidentate through carbonyl oxygen and terminal nitrogen.[36,37] The other hydrazide group is protonated at the terminal nitrogen and is non-bonding. The species ML_2H_2 loses a proton with increase in pH on non-bonding side and forms ML_2H. Beyond pH 4.0 the neutral form of SADH participates in complexation and simple complexes like ML and ML_2 appear in solutions of compositions 1:1 & 1:2 (M: L). The percentage of formation of these species reaches 85–97%. With increase in pH these species lose protons and form deprotonated species like MLH_{-1}, MLH_{-2}, ML_2H_{-1}, ML_2H_{-2} etc. The formation of these species may be due to the participation of deprotonated enolic form (Fig.1) of the ligand in bonding.

In the case of 2:1 metal to ligand concentration ratio, all the metal-SADH systems exhibit the formation of homo binuclear complexes, in which SADH acts as a ditopic ligand and is attached to two metal ions (Fig. 5) either in neutral or deprotonated enolic form. The coordination of a metal ion by one unit of the ligand may affect the coordination at the other unit. This leads to the formation of unsymmetrical complexes where the mode of coordination is different at the two structurally identical units of the same ligand. In M_2LH_{-1} type of species one metal ion is coordinated to hydrazide group in the neutral form whereas the other to deprotonated enolic form. The extent of formation of M_2L ranges from 70–95% for different metal ions in the pH range ~4.0 to 8.0. Beyond this range deprotonation of M_2L takes place leading to the formation of M_2LH_{-1} and M_2LH_{-2} species.

3. Conclusion

Succinic acid dihydrazide possesses number of potential donor atoms and exhibit versatile behavior in metal coordination. The solution phase speciation study indicated the formation of a variety of species in which the ligand exists in protonated, unprotonated and deprotonated forms. Homo binuclear unprotonated and deprotonated species were also observed in 2:1 (M:L) composition, in which two metal ions are bonded to adjacent coordination pockets of the same ligand.

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5. References

1. B. Singh, U. R. Singh, *Transition. Met. Chem.* **1995,** 20, 100
2. A. M. Tomuta, Xavier Ramis, Francesc Ferrando, Angels Serra, *Progress in Organic Coatings* **2012**, *74*, 59–66.
3. M. A. Amin, H. Shokry, E. M. Mabrouk, *Corrosion (Houston, TX, United States)* **2012** *68(8)*, 699–712.
4. M. Abdallah, M. El Nagar, H. E. Megahed, D. Radwan, E. M. Mabrouk, *Corrosion Prevention & Control* **2003**, *50(4),* 173–180.
5. B. Tomitta, Hideaki Osawa, Y. H. S. E. Chung, E. M. George, *Mokuzai Gakkaishi* **1989**, *35(5)*, 455.
6. Hitachi Chemical Co. Ltd. Jpn., *Kokai Tokkyo Koho,* Patent Number JP 59,172,571, date of patent 1984; *Chem. Abstr.* **1986,** 105:44290k.
7. M. L.Ciompi, A. Lucacchini, D. Segnini, M. R. Mazzoni, Adv. *Exp. Med. Biol*. **1980**, *122b*, 395.
8. B. Singh, R. Srivastava, K. K. Narang, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **2000,** *30*, 1175.
9. Z. Muhi-Eldeen, K. Al-Obidi, M. Nadir, F. Rochev, *Eur. J. Med. Chem.* **1992,** *27*, 101.
10. K. K.Narang, V. P.Singh, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1993,** *23*, 971.
11. C. G.Kumbhar, N. Sadasivan, *Journal of Armament Studies* **1976,** *12(2)*, 135.
12. Ahmed A Dutta, Chaudhuri N Ray, *J. Inorg. Nucl. Chem.* **1969**, *31(8)*, 2545–56.
13. R. I.Machkhoshvili, N. N. Vekua, P. V. Gogorishvili, Kharitonov Yu. Ya, A. E. Shvelashvili, *Koordinatsionnaya Khimiya* **1977**, *3(3),* 332–41.
14. K. S. Patel, A. A. Adeniyi, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1991**, *21(9),* 1351–1364.

15. A. A. Adeniyi, K. S. Patel, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1993,** *23(2)*, 199–211.
16. A. A. Adeniyi, K. S. Patel, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1999,** *29(6)*, 1063–1075.
17. F. Krivis Alan, G. R. Supp, Doerr, L. Richard , *Anal. Chem.* **1966**, *38(7)*, 936–8.
18. G. R.Supp, *Anal. Chem.* **1968**, *40(6),* 981
19. L. D. Tsitsishvili, T. I. Tsutsunava, Kharitonov Yu Ya, *Koordinatsionnaya Khimiya* **1982**, *8(5)*, 674.
20. Jayanthi Narayanan, Alejandro Solano-Peralta, Výctor Manuel Ugalde-Saldivar, Roberto Escudero, Herbert Hopfl, Martha Elena Sosa Torres, *Inorg. Chim. Acta.* **2008**, *361*, 2747–2758.
21. Adrian-Mihail Stadler, Jack Harrowfield, *Inorg. Chim. Acta.* **2009**, *362*, 4298–4314
22. T. A. Kaden, *Coordination Chemistry Reviews* **1999**, *190*, 371–389.
23. E. K. Van den Beuken, B. L. Feringa, *Tetrahedron* **1998**, *54*, 12985–13011.
24. H. Steinhagen, G. Helmchen, "Asymmetric Two-Center Catalysis: Learning from Nature", *Angew. Chem. Int. Ed.* **1996**, *35*, 2339–2342.
25. G. Gran, *Analyst* **1952**, *77*, 661
26. G. Gran, *Acta. Chem. Scand.* **1950,** *4*, 559.
27. Giuseppe Arena, Enrico Rizzarelli, Silvio Sammartano, Carmelo Rigano, *Talanta* **1979**, *26*, 1.
28. H. M. Irving, H. S. Rossotti, "Methods for computing successive stability constants from experimental formation Curves", *J. Chem. Soc*. **1953**, 3397–3405.
29. H. M. Irving, H. S. Rossotti, *J. Chem. Soc*. **1954**, 2904–2910
30. P. Gans, A. Sabatini, A. Vacca, *Inorg. Chem. Acta* **1976**, *18*, 1237.
31. L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coord. Chem. Rev.* **1999**, *184*, 311–318.
32. E. V. Titov, N. G. Korzhenevskaya, V. I. Rybachenko, *Ukr. Khim. Zh.* **1968**, *34*, 1253.
33. R. Sambasiva Rao, A. Satyanarayana, P. V. Krishna Rao, Proc. Summ. Simul. Conf. **1984**, 563.
34. H. M. Irving, R. J. P. Williams, *Nature (London)* **1948**, *162*, 746.
35. H. M. Irving, R. J. P. Williams, *J. Chem. Soc*. **1953,** *167*, 3192.
36. Y. V. Temerk, M. M. Ghoneim, J. Y. Maghrabi, *Journal fur praktische chemie* **1978,** *320*, 1029–35
37. B. B. Swarnali, Tushari S. B. B, E. Rivarola, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* **1991,** *29*, 215–231.

Povzetek

Raziskovali smo interakcije dihidrazida sukcinične kisline z Mn(II), Co(II), Ni(II), Cu(II) in Zn(II) v vodi pri 303K in ionski moči 0.1 mol dm^{-3}. Potenciometrično smo določili konstante stabilnosti kompleksov. Predpostavili smo prisotnost mononuklearnih in homo binuklearnih specieseov v različnih protoniranih in deprotoniranih stanjih ter zanje z uporabo MINIQUAD-75 programa izračunali konstante stabilnosti. S HYSS programom smo na osnovi statističnih parametrov predvideli najbolj verjetno porazdelitev prisotnih kompleksov v raztopini.