Potentiometric Study of Lanthanide Salicylaldimine Schiff Base Complexes

Małgorzata T. Kaczmarek · Renata Jastrząb · Wanda Radecka-Paryzek

Received: 13 October 2011/Accepted: 19 March 2012/Published online: 11 January 2013 © Springer Science+Business Media New York 2013

Abstract Formation of complexes between the lanthanide ions and *N*,*N'*-bis(salicylidene)-4-methyl-1,3-phenylenediamine ligand was studied in solution by pH potentiometry. The potentiometric titration was performed at 25.00 °C in 0.1 mol·dm⁻³ NaClO₄ ionic strength and in DMSO:water (30:70 v:v) solvent mixture. *N*,*N'*-bis(salicylidene)-4-methyl-1,3-phenylenediamine ligand (H₂L) occurs in three forms: fully or partially deprotonated and unionized. Computer analysis of potentiometric data indicated that in solution the lanthanide (Ln) complexes exist as LnL₂, Ln(HL)₂ and Ln(H₂L)₂ species. This observation appears to be in contrast to the solid-state behavior of these complexes prepared in a self-assembly process and structurally defined. Stability constants for La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺ (Ln³⁺) complexes were determined. The order of stabilities of LnL₂ species in terms of metal ions is La³⁺ > Eu³⁺ \approx Gd³⁺ = Tb³⁺ < Ho³⁺ < Lu³⁺ with a prominent "gadolinium break".

Keywords Schiff base complexes · Lanthanides · Salicylaldimines · Potentiometry · Gadolinium break

1 Introduction

Schiff bases of the salen-type, derived from salicylaldehyde and diamines, are well known as polydentate ligands that can coordinate metal ions in both protonated [1-3] and deprotonated forms [4–6]. These compounds are often called "privileged ligands" because they are easy to obtain and have numerous applications such as fluorgenic agent, pesticides, herbicidal agents [7, 8], and as ionoselective electrodes for the determination of anions in analytical samples [9]. Interest in Schiff base ligands has increased recently because of their antitumor, antibacterial, antivirus as well as antifungal activities, which are increased by coordinating the ligands to a metal ion [10, 11]. Transition metal complexes of salen-type ligands have been applied in heterogenous and homogenous catalysis

M. T. Kaczmarek (🖂) · R. Jastrząb · W. Radecka-Paryzek

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland e-mail: gosiat@amu.edu.pl

[12–14], diagnostic pharmaceuticals, and laser technology [15]. X-ray structural data reveal that in the metal complexes of salen-type ligands, the Schiff bases generally act as deprotonated tetradentate ligands with the N₂O₂ set of donor atoms capable of effective coordination in a planar arrangement [16–20]. However, our recent findings extend the unique series of structurally defined salen-type lanthanide complexes and provide relatively rare examples of complexes in which the salicylaldimine Schiff base acts as a neutral undeprotonated ligand [21–24]. Having in mind that the solid-state characteristics of the complexes are not necessarily reflected in their solution behavior, we have decided to examine the formation of complexes between lanthanide ions and a salicylaldimine ligand by using pH potentiometry in solution. This paper describes potentiometric studies of the Schiff base lanthanide complexes formed between La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺ ions and *N*,*N*'-bis(salicylidene)-4-methyl-1,3-phenylenediamine.

2 Experimental

2.1 Chemicals Used

Lantanum(III), europium(III), gadolinium(III), terbium(III), holmium(III) and lutetium(III) nitrates, salicylaldehyde, and 4-methyl-1,3-phenylenediamine were obtained from Aldrich Chemical Company. 4-Methyl-1,3-phenylenediamine was purified by recrystallization from *n*-heptane.

2.2 Physical Measurements

IR spectra were recorded using KBr pellets in the range of 4,000–400 cm⁻¹ on a Bruker IFS 66v/S spectrophotometer. Mass spectra were measured using fast atom bombardment (FAB) and electrospray ionization (ESI) techniques. FAB-mass spectra were obtained on a AMD-604 mass spectrometer with nitrobenzyl alcohol as matrix. Electrospray mass spectra were determined in methanol using a Waters Micromass ZQ spectrometer. The concentrations of the compounds were about 10^{-4} mol·dm⁻³. Sample solutions were introduced into the mass spectrometer source with syringe pump at a flow rate of 40 μ L·min⁻¹ with a capillary voltage of +3 kV and desolvation temperature of 300.00 °C. The source temperature was 120.00 °C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation. Scanning was performed from m/z = 200 to 1,000 in 6 s, and 10 scans were summed to obtain the final spectrum. 13 C NMR and 1 H NMR spectra were recorded in DMSO-d₆ on a Varian Gemini 300 spectrometer with chemical shift (ppm) reported relative to TMS as an internal reference. Electronic absorption spectra were measured on a JASCO V-550 spectrophotometer in ethanol and DMSO. Microanalyses (CHN) were obtained using a Perkin-Elmer 2400 CHN microanalyzer.

2.3 Preparation of N,N'-Bis(salicylidene)-4-methyl-1,3-phenylenediamine (H₂L)

To a solution of salicylaldehyde (24 mg, 0.2 mmol) in ethanol (10 mL), 4-methyl-1,3phenylenediamine (12 mg, 0.1 mmol) in ethanol (10 mL) was added dropwise with stirring. The reaction was carried out for 24 h at 60 °C. The yellow solution volume was then reduced to 5 mL by roto-evaporation and yellow crystals formed. After 2 days at room

temperature, yellow crystals suitable for X-ray were isolated and dried in air. Yield $[C_{21}H_{18}N_2O_2 + H]^+$. MS 89 %. MS (ESI+): m/z = 331(FAB): m/z = 331 $(C_{21}H_{18}N_2O_2 + H)^+$. IR (KBr): $\overline{v} = 3490$, 3448 (O–H), 2712 (O–H...N), 1619 (C=N), 1,499, 760, 747 (C=C), and 1282 (C–O) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ = OH: 13.28, 13.14 (two s, 2H); two HC = N: 9.06, 9.03 (two s, 2×1 H); aryls: 7.69 (d, J = 7.96 Hz, 2H), 7.48 (d, J = 7.96 Hz, 2H), and 6.99 (t, J = 7.96 Hz, 4H); phen-H: 7.42 $(d, J = 6.6 \text{ Hz}, 2\text{H}), 7.32 \text{ (s, 1H)}, \text{ and } 7.07 \text{ (d, } J = 6.6 \text{ Hz}, 2\text{H}); \text{ phen-CH}_3: 2.37 \text{ (s, 3H)}.$ ¹³C NMR (300 MHz, DMSO-d₆): δ = 163.74, 163.16, 160.41, 160.00, 147.77, 147.12, 133.43, 133.25, 132.68, 132.51, 131.34, 130.66, 119.68, 119.35, 119.26, 119.16, 116.63, 116.51, 111.13, and 17.45. UV–Vis (EtOH): λ_{max} (ϵ , L·mol⁻¹·cm⁻¹): 211 (27,075), 233 (20,051), 270 (17,147), 302 (13,294), and 344 (16,668) nm. UV–Vis (DMSO); λ_{max} (ε , $L \cdot mol^{-1} \cdot cm^{-1}$): 274 (6,381), 306 (5,402), and 346 (6,375) nm. $C_{21}H_{18}N_2O_2$ (330) calculated: C 75.93, H 5.10, N 8.86; found C 75.79, H 5.05, N 8.82.

2.4 Potentiometric Measurements

All experiments were carried out using DMSO:water 30:70 (v/v) solvent mixtures (demineralized carbonate-free water was used). The concentrations of metal ions were determined by inductively coupled plasma optical emission spectrometry (ICP OES). The potentiometric titrations were carried out using a Titrino 702 Metrohm equipped with an autoburette with a Metrohm Solvotrode combination pH glass electrode specially designed for use with nonaqueous acid-base titrations, calibrated prior to each titration [25]. Prior to each measurement series, a correction to the pH-meter reading was made and two standard buffers were applied (pH = 4.002 and pH = 9.225). All potentiometric titrations were made in an atmosphere of inert gas (helium) at the constant ionic strength (0.1 mol·dm⁻³ LiNO₃), at 25.00 \pm 0.5 °C, using CO₂-free NaOH as a titrant at a concentration of 0.1799 mol dm⁻³. The concentration of the ligand was 1×10^{-3} mol dm⁻³, and the metal-to-ligand ratio investigated was 1:2 because solid complexes are formed only at this ratio. The determined pK_w for DMSO:water (30:70 v/v) is 14.501 [26]. The protonation constants of N,N'-bis(salicylidene)-4-methyl-1,3-phenylenediamine, as well as the stability constants of the complexes, were determinated using HYPERQUAD software [27] and the corresponding distribution of respective forms was obtained by using the HALTFALL program [28]. The calculations were performed using 150–350 points for each analysis, taking into account only the part of the titration curves where no precipitate occurred. Precipitation was observed above pH = 7 for all studied systems. In all cases the testing began with the simplest hypothesis and then in the following steps the models were expanded to include progressively more species, and the results were scrutinized to eliminate the species that were rejected in the refinement procedures. The criteria used for verification of results were given in an earlier paper [29].

3 Results and Discussion

The N,N'-bis(salicylidene)-4-methyl-1,3-phenylenediamine ligand (H₂L) (Fig. 1) was obtained by the condensation reaction of salicylaldehyde and 4-methyl-1,3-phenylenediamine in a 2:1 molar ratio. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

The crystal structure of the ligand N,N'-bis(salicylidene)-4-methyl-1,3-phenylenediamine (H₂L) (Fig. 1) has four symmetry-independent molecules. Hydrogen bonds are



Fig. 1 Formula and crystal structure of ligand H₂L

observed between the nitrogen atom on the imine group and oxygen atom of the hydroxy group. Additionally, weak interactions are observed between C–H and the aromatic rings [23, 30].

The formation of complexes between N,N'-bis(salicylidene)-4-methyl-1,3-phenylenediamine (H₂L) ligand and La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺ ions (Ln³⁺) was studied by pH potentiometry in low water fraction solutions. Due to the insolubility of the ligand in water, the potentiometric titrations were performed in a DMSO:water 30:70 (v/v) solvent mixture ($pK_w = 14.501$). For N,N'-bis(salicylidene)-4-methyl-1,3-phenylenediamine, three protonation constant were determined from computer analysis of the titration data: $\log_{10} K_1 = 8.54$ (7), $\log_{10} K_2 = 6.36$ (7) (protonation of the phenolic units) and $\log_{10} K_3 = 4.52$ (4) (protonation of an imine nitrogen) [31, 32].

Results of the computer analysis of the potentiometric titration data for the Ln^{3+}/H_2L systems are listed in Table 1. The assumed model was verified by analysis of the standard deviations, while the convergence of the experimental data with the curve obtained for the model was evaluated by the Hamiltonian test and the Chi squared test.

Complex formation starts at pH = 2.5 for the Eu³⁺ and Gd³⁺ systems and at pH = 3.0 for the La³⁺, Tb³⁺, Ho³⁺ and Lu³⁺ systems. Complexes of the Ln(H₂L)₂, Ln(HL)₂ and LnL₂ types are observed for all of the lanthanide ions (Fig. 2). All of these species exist in solution up to pH = 7. Precipitation occurs above this pH value.

Ln(H₂L)₂ complexes with two fully protonated ligands start to form at pH = 2.5 for La³⁺, Eu³⁺ and Gd³⁺ and at pH = 3.0 for Tb³⁺, Ho³⁺ and Lu³⁺. The stability constants of Ln(H₂L)₂ formation, determined using HYPERQUAD software, are 36.80, 37.39, 37.28, 36.39, 36.32 and 36.74 for La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺, respectively. The equilibrium constants of Ln(H₂L)₂ formation, calculated according to the formula log₁₀ $K_{\text{Ln(H2L)2}} = \log_{10} \beta_{\text{Ln(H2L)2}} - 2\log_{10} \beta_{\text{H2L}}$, are 7.00, 7.59, 7.48, 6.59, 6.52, and 6.91 for La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺, respectively (Table 1).

Table 1 Stability constants $(\log_{10} \beta)$ and equilibrium constants $(\log_{10} K_e)$ of complexes formed in the Ln^{3+}/H_2L systems

		La(III)	Eu(III)	Gd(III)	Tb(III)	Ho(III)	Lu(III)
Ln(H ₂ L) ₂	$\log_{10} \beta$	36.80 (3)	37.39 (6)	37.28 (3)	36.39 (8)	36.32 (8)	36.74 (8)
	$\log_{10} K_e$	7.00	7.59	7.48	6.59	6.52	6.91
Ln(HL) ₂	$\log_{10} \beta$	27.89 (2)	28.05 (5)	27.91 (3)	27.46 (5)	27.54 (6)	27.97 (6)
	$\log_{10} K_e$	10.81	10.97	10.83	10.38	10.46	10.89
LnL ₂	$\log_{10} \beta$	17.72 (2)	17.19 (7)	17.30 (6)	17.30 (4)	17.53 (6)	18.26 (5)
	$\log_{10} K_e$	17.72 (2)	17.19 (7)	17.30 (6)	17.30 (4)	17.53 (6)	18.26 (5)



Fig. 2 Distribution diagram for the lanthanide/H₂L systems; $C_{Ln} = 0.001 \text{ mol} \cdot \text{dm}^{-3}$ and $C_{H2L} = 0.002 \text{ mol} \cdot \text{dm}^{-3}$

 $Ln(HL)_2$ species with two monoprotonated ligands are formed at pHs at which the ligand H_2L is partly deprotonated and the lanthanide(III) ion is connected to this form, according to $H_2L \rightleftharpoons HL + H$ and $2HL + Ln \rightleftharpoons Ln(HL)_2$ equilibria, respectively.

Coordination to form this type of complexe begins at pH = 3.5 for Eu³⁺ and Lu³⁺ and at pH = 3.75 for La³⁺, Gd³⁺, Tb³⁺ and Ho³⁺. The stability constants of Ln(HL)₂ formation determinate using HYPERQUAD software are 27.89, 28.05, 27.91, 27.46, 27.54 and 27.97 for La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺, respectively. The equilibrium constants of formation of Ln(HL)₂, calculated according to the formula log₁₀ $K_{\text{Ln(HL)2}} = \log_{10} \beta_{\text{Ln(HL)2}} - 2\log_{10} \beta_{\text{HL}}$, are 10.81, 10.97, 10.83, 10.38, 10.46 and 10.89 for La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺, respectively, indicating similar stability of these complex species with a slight decrease in stability for the complexes of Tb³⁺ and Ho³⁺ (Table 1). The LnL₂ complexes form by the result of total ligand deprotonation according to $HL \rightleftharpoons L + H$ and $2L + Ln \rightleftharpoons LnL_2$ equilibria. They start to form at pH = 4.0 for the Lu^{3+} complex, pH = 4.25 for the La^{3+} complex, and pH = 4.5 for the Eu^{3+} , Gd^{3+} , Tb^{3+} and Ho^{3+} complexes. The stability constants for LnL₂ formation, determined using HYPER-QUAD software, are 17.72, 17.19, 17.30, 17.30, 17.53 and 18.26 for La³⁺, Eu^{3+} , Gd^{3+} , Tb^{3+} , Ho^{3+} and Lu^{3+} , respectively. A decrease in the stability constants of the LnL₂ complex species is observed around Eu^{3+} . It is worth noting that the stability constants of lanthanide complexes generally increase monotonically with increasing atomic number of the lanthanide s due to the lanthanide contraction (i.e. decrease in ionic radii). However, for many lanthanide complexes there is a marked deviation from the expected linear relation around gadolinium. This phenomenon is known as the "gadolinium break" [33–40]. Our findings are in accord with this behavior. The order of stabilities of the LnL₂ complexes in terms of metal ions is $La^{3+} > Eu^{3+} \approx Gd^{3+} = Tb^{3+} < Ho^{3+} < Lu^{3+}$ with an evident "gadolinium break".

Recently, we reported the synthesis, spectral characterization and definitive structural identification of lanthanide complexes containing *N*,*N*'-bis(salicylidene)-4-methyl-1,3-phenylenediamine [23, 24]. These complexes of formula $Ln(H_2L)_2(NO_3)_3$, where $Ln^{3+} = La^{3+}$, Eu^{3+} , Gd^{3+} and Lu^{3+} , were formed in a self-assembly process involving the condensation reaction between salicylaldehyde and 4-methyl-1,3-phenylenediamine in the presence of lanthanide nitrates acting as template agents [23]. The Eu^{3+} and Gd^{3+} complexes were isolated as crystals, whereas the La^{3+} and Lu^{3+} complexes formed powder solids. Contrary to the solution behavior of these complexes, in all of the solid complexes the two salicylaldimine ligands remain un-deprotonated and exist exclusively in the neutral form. Interestingly, comparison of the equilibrium constants observed for the same lanthanide ions along the $Ln(H_2L)_2$ series in solution (Fig. 3a) reveals that the highest values



Fig. 3 Comparison of equilibrium constants of complexes studied for a Ln(H₂L)₂, b Ln(HL)₂, c LnL₂

are for complexes of La^{3+} and Gd^{3+} that are able to form well defined crystals. The analogous La^{3+} and Lu^{3+} complexes, isolating as solid powders, correspond to lower equilibrium constants in solution. The lowest values of the equilibrium constants are for Tb^{3+} and Ho^{3+} , which accounts for the existence of their complexes in solution but not in the solid phase.

4 Conclusions

Our potentiometric study reveals that, in solution, complexes of N,N'-bis(salicylidene)-4methyl-1,3-phenylenediamine with lanthanide ions (La³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Ho³⁺ and Lu³⁺) appear to have 1:2 lanthanide ion-to-ligand stoichiometry. In contrast to the existence of exclusively neutral unionized ligands in the well-defined complexes in the solid state, they form three different types of species in solution: with two neutral undeprotonated salicylaldimine ligands, with two monodeprotonated ligands and with two fully deprotonated ligands, depending on pH. The stability constants of the complexes with two fully deprotonated ligands display a minimum around europium and gadolinium as a manifestation of the "gadolinium break". This discontinuity around gadolinium, observed in a number of physicochemical properties of the lanthanide complexes with various ligands, may be attributed to the half-filled 4f orbitals of the gadolinium ion.

These results, along with our earlier findings, confirm that the solid-state characteristics of the complexes are not necessarily reflected in their solution behavior.

Acknowledgments This work was partially supported by the Polish Ministry of Science and Higher Education (Grant N N204 127 039).

References

- 1. Xie, W.: Formation and crystal structure of a polymeric La(H₂salen) complex. Inorg. Chem. **38**, 2541–2543 (1999)
- Gao, T., Yan, P.-F., Li, G.-M., Hou, G.-F., Gao, J.-S.: Ion size dominated 1D and 2D Salen lanthanide coordination complexes and their luminescence. Polyhedron 26, 5382–5388 (2007)
- Bullock, J., Tajmir-Riahi, H-A.: Schiff-base complexes of the lanthanoids and actinoids. Part 1. Lanthanoid(III) halide complexes with the un-ionized form of NN[']-ethyl-enebis(salicylideneimine) and related bases. J. Chem. Soc. Dalton Trans. 1, 36–39 (1978)
- Yang, X., Jones, R.A., Wong, W.-K.: Anion dependant self-assembly and the first X-ray structure of a neutral homoleptic lanthanide salen complex Tb₄(salen)₆. Chem. Commun. 28, 3266–3268 (2008)
- Yang, X., Jones, R.A.: Anion dependent self-assembly of "tetra-decker" and "triple-decker" luminescent Tb(III) salen complexes. J. Am. Soc. Chem. 127, 7686–7687 (2005)
- Lu, Z., Yuan, M., Pan, F., Gao, S., Zhang, D., Zhu, D.: Syntheses, crystal structures, and magnetic characterization of five new dimeric manganese(III) tetradentate Schiff base complexes exhibiting single-molecule-magnet behavior. Inorg. Chem. 45, 3538–3548 (2006)
- Rehman, W., Saman, F., Ahmad, I.: Synthesis, characterization, and biological study of some biologically potent Schiff base transition metal complexes. Russ. J. Coord. Chem. 34, 678–682 (2008)
- Cozzi, P.G.: Metal-salen Schiff base complexes in catalysis: practical aspects. Chem. Soc. Rev. 33, 410–421 (2004)
- Naeimi, H., Safari, J., Heidarnezhad, A.: Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine. Dyes Pigm. 73, 251–253 (2007)
- Eshtiagh-Hosseini, H., Housaindakht, M.R., Beyramabadi, S.A., Beheshti, S., Esmaeili, A.A., Khoshkholgh, M.J., Morsali, A.: Synthesis, experimental and theoretical characterization of tetra dentate N, N'-dipyridoxyl (1, 3-propylenediamine) salen ligand and its Co(III) complex. Spectrochim. Acta Part A 71, 1341–1347 (2008)

- Neelakantan, M.A., Rusalraj, F., Dharmaraja, J., Johnsonraja, S., Jeyakumar, T., Sankaranarayana Pillai, M.: Spectral characterization, cyclic voltammetry, morphology, biological activities and DNA cleaving studies of amino acid Schiff base metal(II) complexes. Spectrochim. Acta Part A 71, 1599–1609 (2008)
- 12. Rajabi, F.: A heterogeneous cobalt(II) Salen complex as an efficient and reusable catalyst for acetylation of alcohols and phenols. Tetrahedron Lett. **50**, 395–397 (2009)
- Kleij, A.W.: Nonsymmetrical salen ligands and their complexes: Synthesis and applications. Eur. J. Inorg. Chem. 2, 193–205 (2009)
- Lima, L.F., Corraza, M.L., Cardoza-Filho, L., Màrquez-Alvarez, H., Antunes, O.A.C.: Oxidation of limonene catalyzed by metal(salen) complexes. Braz. J. Chem. Eng. 23, 83–92 (2006)
- Papadopoulos, C., Kantiranis, N., Vecchio, S., Lalia-Kantouri, M.: Lanthanide complexes of 3-methoxy-salicylaldehyde thermal and kinetic investigation by simultaneous TG/DTG–DTA coupled with MS. J. Therm. Anal. Calorim. 99, 931–938 (2010)
- Benisvy, L., Kannappan, R., Song, Y-F., Milikisyants, S., Huber, M., Mutikainen, I., Turpeinen, V., Gamez, P., Bernasconi, L., Baerends, E.J., Hartl, F., Reedijk, J.: A square-planar nickel(II) monoradical complex with a bis(salicylidene)diamine ligand. Eur. J. Inorg. Chem. 5, 637–642 (2007)
- He, J., Yin, Y.-G., Huang, X.-C., Li, D.: Solid structure and photoluminescence of zinc(II) multiplex with heptadentate salicylideneamine as primary ligand. Inorg. Chem. Commun. 9, 205–207 (2006)
- Chantarasini, N., Ruangpornvisuti, V., Munangsin, N., Detsen, H., Mananunsp, T., Batiya, C., Chaichit, N.: Structure and physico-chemical properties of hexadentate Schiff base zinc complexes derived from salicylaldehydes and triethylenetetramine. J. Mol. Struct. **701**, 93–103 (2004)
- Howell, R.C., Spence, K.V.N., Kahwa, I.A., Williams, D.J.: Structure and luminescence of the neutral dinuclear lanthanide(III) complexes [{Ln(api)}2] {H₃api = 2-(2-hydroxyphenyl)-1,3-bis[4-(2hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}. J. Chem. Soc. Dalton Trans. 16, 2727–2734 (1998)
- Liu, Q., Meermann, C., Görlitzer, H.W., Runte, O., Herdtweck, E., Anwander, P.: Cationic rare-earth metal salen complexes. Dalton Trans. 44, 6170–6178 (2008)
- Kaczmarek, M.T., Pospieszna-Markiewicz, I., Kubicki, M., Radecka-Paryzek, W.: Novel lanthanide salicyaldimine complexes with unusual coordination mode. Inorg. Chem. Commun. 7, 1247–1249 (2004)
- Radecka-Paryzek, W., Pospieszna-Markiewicz, I., Kubicki, M.: Self-assembled two-dimensional salicylaldimine lanthanum(III) nitrate coordination polymer. Inorg. Chim. Acta 360, 488–496 (2007)
- Kaczmarek, M.T., Kubicki, M., Radecka-Paryzek, W.: Self-assembly as a route to dinuclear lanthanide complexes with rare coordination pattern of salen-type ligand. Struct. Chem. 21, 779–786 (2010)
- Kaczmarek, M.T, Kubicki, M., Mondry, A., Janicki, R., Radecka-Paryzek, W.: Self-assembled lanthanide salicylaldimines with a unique coordination mode. Eur. J. Inorg. Chem. 14, 2193–2200 (2010)
- Irving, M.H., Miles, M.G., Petit, L.D.: The stability constants of some metal chelates of triethylenetetraminehexaacetic acid (ttha). Anal. Chim. Acta 38, 475–488 (1967)
- Stańczak, P., Łuczkowski, M., Juszczyk, P., Grzonka, Z., Kozłowski, H.: Interactions of Cu²⁺ ions with chicken prion tandem repeats. Dalton Trans. 14, 2102–2107 (2004)
- Gans, P., Sabatini, A., Vacca, A.: Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs. Talanta 43, 1739–1753 (1996)
- Ingri, N., Kakolowicz, W., Sillen, L.G., Warqvist, B.: High-speed computers as a supplement to graphical methods-V1: haltafall, a general program for calculating the composition of equilibrium mixtures. Talanta 14, 1261–1286 (1967)
- Łomozik, L., Jaskólski, M., Wojciechowska, A.: A multistage verification procedure for the selection of models in the studies of complex formation equilibria. Pol. J. Chem. 65, 1797–1807 (1991)
- Alcock, N.W., Clase, H.J., Willey, G.R., Daly, L.T.: Packing of four independent molecules: 1-methyl-N, N'-bis(salicylidene)-2, 4-phenylenediamine. Acta Cryst. C52, 2340–2343 (1996)
- Kaczmarek, M.T., Jastrząb, R., Hołderna-Kędzia, E., Radecka-Paryzek, W.: Self-assembled synthesis, characterization and antimicrobial activity of zinc(II) salicylaldimine complexes. Inorg. Chim. Acta 362, 3127–3133 (2009)
- 32. Hernandez-Molina, R., Mederos A., Gili, P., Dominguez S., Lloret F., Cano J., Julve M., Ruiz-Prerz C., Solans X.: Dimer species in dimethyl sulfoxide–water (80:20 w/w) solution of N,N'-bis(salicylideneimine)-m-phenylenediamine (H₂sal-m-phen) and similar Schiff bases with Cu^{II}, Ni^{II}, Co^{II} and Zn^{II}. Crystal structure of [Co₂(sal-m-phen)₂]·CHCl₃. J. Chem. Soc., Dalton Trans. **22**, 4327–4334 (1997)
- Toraishi, T., Nagasaki, S., Tanaka, S.: Polynuclear complex formation of trivalent lanthanides by 5-sulfosalicylate in an aqueous system—Potentiometric, 1H NMR, and TRLIFS studies. Inorg. Chim. Acta 360, 15751583 (2007)
- Gałęzowska, J., Janicki, R., Mondry, A., Burgada, R., Bailly, T., Lecouvey, M., Kozłowski, H.: Coordination ability of *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*',*N*'-tetrakis(methylenephosphonic acid) towards lanthanide(III) ions. J. Chem. Soc., Dalton Trans., 4384–4394 (2006)

- Dash, B.C., Tripathy, P.K., Kanungo, B.K.: Mixed chelates of some trivalent lanthanide ions containing (trans-1, 2-cyclohexylenedinitrilo)tetra-acetate and norleucinate. Monatsh. Chem. 122, 341–348 (1991)
- Pardeshi, R.K., Palaskar, N.G., Chondhekar, T.K.: Potentiometric study of lanthanide(III) ion complexes with some Schiff base. J. Indian Chem. Soc. 79, 958–959 (2002)
- Pashchevskaya, N.V., Bolotin, S.N., Sokolov, M.E., Sklyar, A.A., Panyushkin, V.T.: Potentiometric study of reactions of rare-earth elements with 3-allylpentanedione in a water–dioxane medium. Russ. J. Gen. Chem. 76, 1011–1014 (2006)
- Mahalakshmi Sita, N.: Equilibrium studies of lanthanide(III) complexes of 1-phenyl-3-methyl-4-benzoyl pyrazolone-5 (BMBP) and 1-phenyl-3-methyl-trifluoroacetylpyrazolone-5 (PMTFP). Indian J. Chem. Sec. A, 36A, 118–120 (1997)
- Spedding, F.H., Jones, K.C.: Heat capacities of aqueous rare earth chloride solution at 25°. J. Phys. Chem. 70, 2450–2455 (1966)
- Spedding, F.H., Csejka, D.A., DeKock, C.W.: Heat of dilution of aqueous rare earth chloride solution at 25°. J. Phys. Chem. 70, 2423–2429 (1966)