

Thermochemical parameters of adducts of cadmium(II) halides with bidentate N- and O-ligands

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Abstract The adducts $[\text{CdX}_2(\text{L-L})]$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L-L} = 2,2'$ -bipyridine (bipy) or $2,2'$ -bipyridine N,N' -dioxide (bipyNO) have been synthesized and characterized by melting points, elemental analysis, thermal analysis, and IR spectroscopy. From calorimetric studies in solution, the standard enthalpies of formation of the adducts and several thermochemical parameters were determined. The mean standard enthalpies of the cadmium-nitrogen and cadmium-oxygen bonds have been estimated.

Keywords Cadmium(II) halides · Thermochemistry · Coordinated bond energies · Dissolution enthalpies · Calorimetry · Adducts

Introduction

The cadmium(II) halides have industrial or biological importance. They are very toxic reagents that are using in metal plating, battery industry, photography, dying, and printing industries [1]. As well as, complexes of $2,2'$ -bipyridine and $2,2'$ bipyridine N,N' -dioxide with ions of transition metals are reported in the literature [2–4]. The coordination takes place through the two nitrogen atoms or the two oxygen atoms, respectively, leading to the chelation of the metal ions. Cadmium(II) halides have interesting properties as their d^{10} configuration permits a wide variety of geometries and coordination numbers. Complexes of the type $[\text{CdX}_2(\text{L-L})]$ where L-L is a bidentate ligand are known [5]. In the last years, several studies on

the complexes formed by cadmium(II) halides have been made [4–21]. These included some thermodynamic studies. But relatively few researches have been made on the energetic of the cadmium(II)-donor atom bonds. In this article, it is described a study of the adducts formed by the ligands $2,2'$ -bipyridine and $2,2'$ -bipyridine N,N' -dioxide with cadmium(II) halides to determine several thermochemical parameters, including, the mean strength of the cadmium(II)-nitrogen and cadmium(II)-oxygen coordinated bonds to fill the uncompleted data [4] and find correlations between the thermochemical parameters. The thermodynamic characterization of the adducts is important to understand their properties and determine new potential applications.

Experimental

$2,2'$ -bipyridine (Aldrich Chemical Co Inc. 99 + %) was purified by recrystallization from ethanol according to the method described by Gallagher et al. [22]. $2,2'$ -bipyridine N,N' -dioxide was synthesized as described in the literature [2]. Cadmium(II) chloride and bromide were synthesized as described in the literature [23]. Cadmium(II) iodide (Aldrich Chemical Co Inc., 99%) was purified according Queiroz et al. [12].

Carbon, hydrogen, and nitrogen were determined by microanalytical procedures [24]. Halide analysis was made by gravimetry using standard $\text{N}/10 \text{ AgNO}_3$ solution, after the adducts were dissolved in water [25]. Cadmium content was determined by spectrophotometric titration with ethylenediaminetetraacetate (EDTA) [26].

Infrared spectra were obtained using samples of the adducts in a KBr matrix in the region $4000\text{--}400 \text{ cm}^{-1}$ using a Perkin Elmer 1600 series FTIR spectrophotometer.

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The TG/DTG and DSC measurements were obtained in an argon atmosphere in a Du Pont 951 analyzer with samples varying in mass from (7.16 to 13.92) mg (TG/DTG) and from (2.91 to 8.45) mg (DSC) and a heating rate of 10 K min⁻¹ in the 298–678 K (DSC) and 298–1248 K (TG/DTG) temperature ranges.

All the solution calorimetric measurements were carried out in a LKB 8700-1 precision calorimeter as described previously [27]. The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris(hydroxymethylamino)methane in 0.1 mol dm⁻³ hydrochloric acid. The result (-29.78 ± 0.03 kJ mol⁻¹) is in agreement with the value recommended by I.U.P.A.C. (-29.763 ± 0.003 kJ mol⁻¹) [28]. The uncertainty intervals are twice the standard deviations of the means of about 3–6 replicate measurements on each compound.

Results and discussion

All the adducts were solids. The yields range from (28 to 99%). The analytical data of the adducts are summarized in Table 1.

The more important IR bands are reported in Table 2. The IR spectra of the adducts of bipy show dislocation and splitting of some bands and the appearance of new bands when compared with the spectra of free bipy.

These are absent in the free bipy and are indicative of adduct formation [3]. The IR spectra of adducts of bipyNO show shifts in frequencies with respect to free bipyNO, of characteristic bands due to the stretching and bending vibration of the N–O bond (1265–1200 and 860–830 cm⁻¹), respectively. The observed average shift of the mid-point of the first vibration to lower frequencies after coordination is about 34–47 cm⁻¹. The second vibration is slightly dislocated to lower frequencies after complexation. These facts indicate the decrease of the N–O order after coordination of bipyNO [29]. Table 2 shows the main IR frequencies observed for the free ligands and the adducts.

The thermogravimetry of the adducts shows the loss of the ligand in two or three steps of mass loss followed by the loss of the salt, together in the last step of ligand loss or in another step of mass loss. The bipyNO adduct of CdI₂ left a residue that is part of the metal content. The DSC curves are consistent with the TG data. They present exothermic peaks due to the decomposition of the adduct. Table 3 presents the thermoanalytical data of the adducts.

The standard enthalpies of dissolution of cadmium(II) halides, ligands, and adducts were obtained as previously reported [27]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of the following reactions in solution:

Table 1 Analytical data (in mass/%) for the compounds (observed (calculated))

Compound	C	H	N	X	Cd
[CdCl ₂ (bipy)]	35.38 (35.47)	2.38 (2.35)	8.25 (8.13)	20.89 (20.80)	33.11 (33.01)
[CdBr ₂ (bipy)]	28.04 (28.24)	1.88 (1.93)	6.54 (6.45)	37.31 (37.19)	26.24 (26.14)
[CdI ₂ (bipy)]	22.99 (22.78)	1.54 (1.50)	5.36 (5.26)	48.59 (48.70)	21.52 (21.55)
[CdCl ₂ (bipyNO)]	32.33 (32.18)	2.17 (2.27)	8.25 (8.15)	19.09 (19.21)	30.26 (30.32)
[CdBr ₂ (bipyNO)]	26.09 (25.99)	1.75 (1.70)	6.08 (5.99)	34.71 (34.80)	24.41 (24.50)
[CdI ₂ (bipyNO)]	21.67 (21.79)	1.45 (1.40)	5.05 (4.98)	45.78 (45.69)	20.27 (20.19)

Table 2 Main IR spectral data of compounds/cm⁻¹

Compound	ν_{NO}	γ_{NO}	$\nu_{(\text{C}-\text{C})}$	Ring	$\phi_{(\text{C}-\text{C})}$	New bands
bipy			1578 s	993 m	757vs	
[CdCl ₂ (bipy)]			1577 m	1016 m	773vs	1317 m, 735 m
[CdBr ₂ (bipy)]			1571 m	1015 m	772vs	1313 m, 736 m
[CdI ₂ (bipy)]			1561 m	1015 m	770vs	1315 m, 734 m
bipyNO	1262vs, 1255vs	852 s, 840 s	1479 s	1022 m	769vs	
[CdCl ₂ (bipyNO)]	1224vs	831 s	1478 m	1029 m	767vs	
[CdBr ₂ (bipyNO)]	1222vs	838 s	1476 s	1033 m	774vs	
[CdI ₂ (bipyNO)]	1220vs, 1204vs	833 s	1475 s	1032 m	769vs	

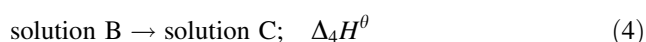
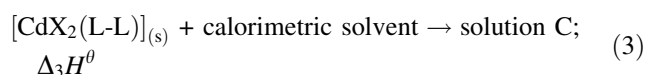
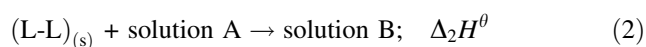
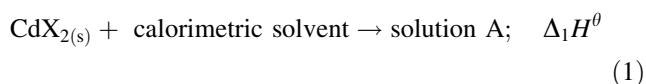
ν stretching, γ bending out of the plane, *Ring* ring breathing ϕ ring deformation out of the plane. Intensity of bands: vs very strong, s strong, m medium

Table 3 Thermoanalytical data of the compounds

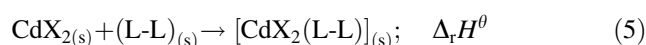
Compound	Mass loss/%		TG temperature range/°C	Species lost	DSC peak temperature/ °C	$\Delta H^\theta/\text{kJ mol}^{-1}$
	Calcd.	Obs.				
[CdCl ₂ (bipy)]	23.1	23.0	245–384	–0.5L	155	–270.30
	23.1	20.1	384–529	–0.5L		
	54.0	55.0	529–741	–CdCl ₂		
[CdBr ₂ (bipy)]	18.2	19.0	176–381	–0.5L	156	–251.05
	18.2	20.1	381–481	–0.5L		
	63.5	60.2	481–634	–CdBr ₂		
[CdI ₂ (bipy)]	23.9	24.2	293–329	–0.8L	299	0.84
	76.1	76.6	329–473	–0.2L–CdI ₂		
[CdCl ₂ (bipyNO)]	8.7	8.8	332–329	–0.17L	155	–186.60
	19.0	18.6	329–445	–0.37L		
	73.0	71.2	445–970	–0.46L –CdCl ₂		
[CdBr ₂ (bipyNO)]	16.4	16.4	94–310	–0.40L	155	–447.24
	18.4	18.2	310–418	–0.45L		
	65.3	65.6	418–970	–0.15L–CdBr ₂		
[CdI ₂ (bipyNO)]	23.8	23.7	285–305	–0.7L		
	71.2	71.0	305–507	–0.3L–I ₂ –0.75Cd		
		5.3 ^a				

^a Residue at 970 °C**Table 4** Enthalpies of dissolution at 25.00 °C

Compound	Calorimetric solvent	Number of experiments	$\Delta_i H^\theta/\text{kJ mol}^{-1}$
CdCl _{2(s)}	4.2 M HCl	6	3.82 ± 0.13
bipy _(s)	1:1 CdCl ₂ –4.2 M HCl	4	–21.04 ± 0.19
[CdCl ₂ (bipy)] _(s)	4.2 M HCl	3	39.31 ± 2.35
CdBr _{2(s)}	4.2 M HCl	7	14.07 ± 0.52
bipy _(s)	1:1 CdBr ₂ –4.2 M HCl	4	–19.61 ± 0.68
[CdBr ₂ (bipy)] _(s)	4.2 M HCl	5	28.61 ± 1.53
CdI _{2(s)}	4.2 M HCl	5	30.81 ± 0.22
bipy _(s)	1:1 CdI ₂ –4.2 M HCl	6	–19.07 ± 0.69
[CdI ₂ (bipy)] _(s)	4.2 M HCl	5	34.17 ± 0.46
bipyNO _(s)	1:1 CdCl ₂ –4.2 M HCl	4	0.98 ± 0.07
[CdCl ₂ (bipyNO)] _(s)	4.2 M HCl	5	7.71 ± 0.68
bipyNO _(s)	1:1 CdBr ₂ –4.2 M HCl	6	0.61 ± 0.06
[CdBr ₂ (bipyNO)] _(s)	4.2 M HCl	5	22.12 ± 1.57
bipyNO _(s)	1:1 CdI ₂ –4.2 M HCl	5	2.54 ± 0.06
[CdI ₂ (bipyNO)] _(s)	4.2 M HCl	4	47.27 ± 2.42



The application of the Hess' law to the series of reactions (1)–(4) gives the standard enthalpies of acid/base reaction ($\Delta_r H^\theta$) according to the reaction:



where $\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$. Table 4 gives the values obtained for the enthalpies of dissolution of CdX₂ ($\Delta_1 H^\theta$), (L-L) into the solution of CdX₂ ($\Delta_2 H^\theta$) and of the

Table 5 Summary of the thermochemical results for the compounds/kJ mol⁻¹

Compound	$\Delta_f H^\theta$	$\Delta_r H^\theta$	$\Delta_s^\theta H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta/g$	$\bar{D}_{(Cd-N/O)}$
CdCl _{2(s)}	-391.5 ^a	181.2 ^b					
CdBr _{2(s)}	-316.2 ^a	151.2 ^c					
CdI _{2(s)}	-203.3 ^a	137.7 ^c					
Bipy _(s)	216.4 ± 7.4 ^d	81.93 ± 0.33 ^d					
BipyNO _(s)	16.6 ± 5.2 ^e	80 ± 10 ^e					
[CdCl ₂ (bipy)] _(s)	-56.53 ± 2.36	-231.6 ± 8.0	81.93 ± 8.19 ^f	-319.7 ± 2.6	138.26 ± 2.38	-237.7 ± 8.6	128.9 ± 4.3
[CdBr ₂ (bipy)] _(s)	-34.15 ± 1.75	-134.0 ± 7.7	81.93 ± 8.19 ^f	-267.3 ± 2.0	116.08 ± 1.78	-185.4 ± 8.4	92.7 ± 4.2
[CdI ₂ (bipy)] _(s)	-22.43 ± 0.86	-9.33 ± 7.52	81.93 ± 8.19 ^f	-242.1 ± 2.2	104.36 ± 0.92	-160.1 ± 8.5	80.1 ± 4.3
[CdCl ₂ (bipyNO)]	-2.91 ± 0.70	-377.8 ± 5.6	180 ± 28 ^f	-364 ± 10	183 ± 10	-184 ± 30	92 ± 15
[CdBr ₂ (bipyNO)]	-7.44 ± 1.65	-307.0 ± 5.5	180 ± 28 ^f	-339 ± 10	187 ± 10	159 ± 30	80 ± 15
[CdI ₂ (bipyNO)]	-13.92 ± 2.43	-200.6 ± 5.8	180 ± 28 ^f	-332 ± 11	194 ± 10	-152 ± 30	76 ± 15

^a [30], ^b [31], ^c [32], ^d [33], ^e [4], ^f [34]

Table 6 Auxiliary data and enthalpy changes of the ionic complex formation process in the gaseous phase/kJ mol⁻¹

Compound	$\Delta_r H^\theta$	$\Delta_r H^\theta/g$	$\Delta_f H^\theta$
Cl _(g) ⁻	-233.13 ^a		
Br _(g) ⁻	-219.07 ^a		
I _(g) ⁻	-197 ^a		
Cd _(g) ²⁺	2623.54 ^a		
[CdCl ₂ (bipy)] _(g)	-	-237.7 ± 8.6	-2605.3 ± 13.9
	149.7 ± 11.4		
[CdBr ₂ (bipy)] _(g)	-52 ± 11	-185.4 ± 8.4	-2536 ± 14
[CdI ₂ (bipy)] _(g)	72.6 ± 11.4	160.1 ± 8.5	-2455 ± 34
CdCl ₂ (bipyNO) _(g)	-197 ± 33	-184 ± 30	-2551 ± 34
[CdBr ₂ (bipyNO)] _(g)	-127 ± 32	-159 ± 30	-2509 ± 34
[CdI ₂ (bipyNO)] _(g)	-21 ± 32	-152 ± 30	-2448 ± 34

^a [30]

adducts ($\Delta_s H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the means of 3–6 replicate measurements.

From the values obtained for the standard enthalpies of the reaction (5) and by using appropriate thermochemical cycles [27], the following thermochemical parameters for the adducts were determined: the standard enthalpies of formation ($\Delta_f H^\theta$), the standard enthalpies of decomposition ($\Delta_D H^\theta$), the standard lattice enthalpies ($\Delta_M H^\theta$) and the standard enthalpies of the reaction in the gaseous phase ($\Delta_r H^\theta(g)$). The standard enthalpies of the Cd(II)-N or Cd(II)-O bonds are equal to $\bar{D}_{(Cd-N/O)} = (-\Delta_r H^\theta(g)/2)$ [27]. Table 5 lists the values obtained for these enthalpies.

The enthalpies for the process of adduct formation in the gaseous phase, from cadmium(II), halide ions and ligand molecules can be evaluated:

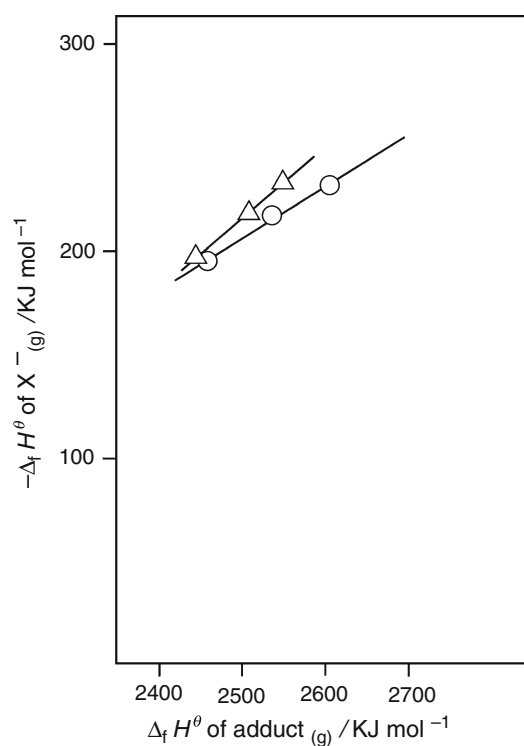
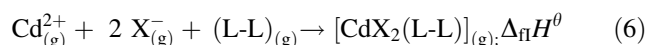


Fig. 1 Plot of the enthalpy changes of the halide gaseous formation against the enthalpy changes of the respective adduct formation in the gaseous phase (Δ = bipyNO; O = bipy)



where $\Delta_f H^\theta = \Delta_f H^\theta(\text{adduct}_{(g)}) - \Delta_f H^\theta(\text{Cd}_{(g)}^{2+}) - 2 \Delta_f H^\theta(\text{Br}_{(g)}^{-}) - \Delta_f H^\theta((\text{L-L})_{(g)})$

Table 6 lists the values obtained for these enthalpy values.

The correlation between the formation enthalpies of X⁻ gaseous ions with the formation enthalpies of the respec-

tive adduct (bipy or bipyNO) in the gaseous phase is linear. It is showed in Fig. 1.

Conclusions

Based on the $\Delta_r H^\theta$ values for the adducts, the acidity order of the salts can be obtained: $\text{CdCl}_2 > \text{CdBr}_2 > \text{CdI}_2$ (for bipy) and $\text{CdI}_2 > \text{CdBr}_2 > \text{CdCl}_2$ (for bipyNO). Using the $\bar{D}_{(\text{Cd}-\text{N/O})}$ values, the order is $\text{CdCl}_2 > \text{CdBr}_2 > \text{CdI}_2$ (for bipy) and $\text{CdCl}_2 > \text{CdBr}_2 > \text{CdI}_2$ (for bipyNO). The expected order on the basis of an inductive effect of the electronegative values of the halogen atoms would be: $\text{CdCl}_2 > \text{CdBr}_2 > \text{CdI}_2$. Comparing the $\Delta_r H^\theta$ or $\bar{D}_{(\text{Cd}-\text{N/O})}$ values for adducts with the same halide, the basicity order of the ligands can be obtained: $\text{bipy} > \text{bipyNO}$.

References

- Diesnis M. The determination of the critical hygrometric state. *Ann Chim.* 1937;7:5–69.
- Simpson PG, Vinciguerra A, Quagliano JV. The donor properties of 2, 2'-bipyridine N, N'-dioxide. *Inorg Chem.* 1963;2:282–6.
- Sinha SP. 2, 2'-Dipyridyl complexes of rare earths. I. Preparation and infrared and some other spectroscopic data. *Spectrochim Acta.* 1964;20:879–86.
- Silva MLCP, Chagas AP, Airoidi C. Heterocyclic N-oxide ligands: a thermochemical study of adducts with zinc, cadmium and mercury chlorides. *J Chem Soc Dalton Trans* 1988;2113–6.
- Bailey RD, Pennington WT. Cadmium(II) halide complexes of pyrazine. *Polyhedron.* 1997;16(3):417–22.
- Morioka Y, Nakagawa I. Far-i.r. reflection spectra and lattice vibrations of cadmium chloride, bromide and iodide crystals. *Spectrochim Acta A.* 1978;34:5–8.
- Simoni JA, Airoidi C, Chagas AP. Thermochemistry of dichlorobis(NN-dimethylacetamide)-zinc(II) and dichloro(NN-dimethylacetamide)-cadmium(II) and mercury(II). *J Chem Soc.* 1980; 11:156–8.
- Ahrland S, Bjork NO, Person I. Metal halide and pseudohalide complexes in dimethylsulfoxide solution. X. Equilibrium and enthalpy measurements on halide systems of zinc(II), cadmium(II) and mercury(II) in 0.1 M ammonium perchlorate. *Acta Chem Scan A.* 1981;35:67–75.
- Airoidi C, Chagas AP, Namora Filho M. Thermochemistry of dihalide (diacetamide)zinc(II), cadmium(II) and dihalide bis (diacetamide)-mercury(II). *Inorg Chem.* 1981;43:89–93.
- Rath SC, Das PB. Thermodynamics of CdCl_2 and CdBr_2 in aquo-organic solvents from conductance data. *Thermochim Acta.* 1983;60:77–86.
- Rath SC, Das PB. Thermodynamics of CdCl_2 and CdBr_2 in mixed solvents from viscosity data. *Thermochim Acta.* 1983;63:369–75.
- Queiroz JC, Airoidi C, Chagas AP. Thermochemical data for adducts of zinc, cadmium and mercury halides with hexamethylphosphoramide. *J Chem Soc Dalton Trans* 1985;1103–5.
- Queiroz JC, Airoidi C, Chagas AP. A thermochemical study involving adducts $\text{MX}_2 \cdot \text{P}(\text{C}_6\text{H}_5)_3\text{O}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}; \text{x} = \text{Br}, \text{I}$). *J Chem Thermodynamics.* 1986;18:709–14.
- Santos MRMC, Airoidi C. Thermochemical study of adducts of urea with zinc, cadmium and mercury: some correlations for urea derivatives. *Thermochim Acta.* 1988;125:295–305.
- Graddon DP, Khoo CS. Thermodynamics of metal-ligand bond formation-XXXVI. Formation of complex zinc and cadmium halides in acetonitrile solution. *Polyhedron.* 1988;7(21):2129–33.
- Skudlarski K, Dudek J, Kapala J. Thermodynamics of $\{\text{x}\text{CdBr}_2 + (1-\text{x})\text{CdI}_2\}(\text{s})$ investigated by mass spectrometry. *J Chem Thermodynamics.* 1989;21:785–8.
- Saito M, Nakajima M, Hashimoto S. Enantioselective conjugate addition of thiols to cyclic enones and enals catalyzed by chiral N,N'-dioxide-cadmium iodide complex. *Tetrahedron.* 2000;56: 9589–94.
- Farias RF, Airoidi C. Calorimetric study of the adducts $\text{CdBr}_2 \cdot \text{nL}$ ($\text{n} = 1$ and 2 ; $\text{L} = \text{ethyleneurea}$ and propyleneurea). *Thermochim Acta.* 2002;390:213–5.
- Zhao J, Zhang Y, Kan Y, Zhu L. Theoretical studies on vibrational spectra of some halides of group IIB elements. *Spectrochim Acta A.* 2004;60:679–88.
- Silva UG Jr, Oliveira OA, Farias RF. Synthesis, characterization and calorimetric study of zinc group halide adducts with aniline. *Thermochim Acta.* 2006;450:2–4.
- Yu JH, Ye L, Bi MH, Hon Q, Zhang X, Xu JQ. Structural characterization of several cadmium halides with N-donor ligands. *Inorg Chim Acta.* 2007;360:1987–94.
- Gallagher MJ, Graddon DP, Sheik AR. Reaction of antimony(III) halides with Lewis bases. *Thermochim Acta.* 1978;27:269–80.
- Hamilton RT, Butler JA. The preparation of pure zinc chloride. *J Chem Soc* 1932; 2283–4.
- Niederl JB, Sozzi JA. *Microanálisis elemental orgánico.* 1st ed. Buenos Aires: Methopress; 1958.
- Kolthoff IM, Sandall EB. *Tratado de química analítica cuantitativa.* 3rd ed. Buenos Aires: Librería y editorial Nigar S.R.L; 1956.
- Schwarzenbach G, Flaschka HA. *Complexometric titration.* 3rd ed. London: Methuen; 1969.
- Dunstan PO. Thermochemical parameters of α -picoline N-oxide adducts of some divalent transition metal bromides. *J Therm Anal Cal.* 2005;79:355–9.
- Henrington EF. Recommended reference materials for the realization of physicochemical properties (recommendation approved 1974). *Pure Appl Chem.* 1974;40:391–450.
- Kida S, Quagliano JV, Walmsley JA, Tyree SY. Zn(II), Al(III), Cr(III), Fe(II), Fe(III) and Sn(IV) complexes in the 3–15- μ region. *Spectrochim Acta.* 1963;19:189–99.
- Wagman DD, Evans WH, Parker VB, Schumm RH, Hallow I, Churney SM, Nuttall RL. The NBS table of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units. *J Phys Chem Ref Data.* 1982;2: 144–5.
- Keneshea FJ, Cubicciotti DD. Vapor pressure of cadmium chloride and thermo-dynamic data for CdCl_2 gas. *J Chem Phys.* 1964;40:1778–9.
- Kubaschewski O, Evans EL, Alcock CB. *Metallurgical thermochemistry.* 4th ed. London: Pergamon; 1967.
- Dunstan PO. Thermochemistry of adducts of nickel(II) acetylacetonate chelate with heterocyclic bases. *Thermochim Acta.* 1998;317:165–74.
- Burkinshaw PM, Mortimer CT. Enthalpies of sublimation of transition metal complexes. *J Chem Soc Dalton Trans* 1984;75–7.