J Therm Anal Calorim (2011) 103:1063–1072
DOI 10.1007/s10973-010-1043-y

Thermodynamic properties of spin crossover 3d-metal coordination compounds

G. A. Berezovskii · L. G. Lavrenova

Received: 5 August 2010 / Accepted: 7 September 2010 / Published online: 25 September 2010

Abstract Thermodynamic studies are necessary to understand the mechanism of such an interesting phenomenon as spin crossover in complex compounds. A number of reviews have already covered spin crossover in mononuclear complexes, so the suggested review considers in more detail the problems of obtaining thermodynamic data for polynuclear complex compounds of iron (II) with 4-substituted 1,2,4-triazole derivatives. The composition of trinuclear and polynuclear complexes of iron (II) with 1,2,4-triazoles was studied in terms of its effect on $C_p(T)$ dependence; magnetochemical and thermodynamic data are also confronted with each other.

Keywords Spin crossover · Complexes · Heat capacity · Entropy · Enthalpy · Phase transition

List of Abbreviations and Symbols

acpa	Hacpa = *N*-(1-acetil-isopropylidene) (2-pyridylmethyl) amine
bpy	2,2′-Bipyridine
bpym	2,2′-Bipyrimidine
bt	2,2′-Bi-2-thiazoline
btr	4,4′-bis(1,2,4-triazole)
bts	2,2′-Bi(5-methyl thiazoline)
depe	1,2-Bis(diethylphosphino)ethane
3EtO-salenAPA	3EtO-salenAPA is the Schiff base condensed from 1 mol of 3-ethoxysalicylaldehyde with 1 mol of *N*-aminopropylaziridine
Htrz	1,2,4-Triazole
NH_2trz	4-Amino-1,2,4-triazole
phen	1,10-Phenanthroline
phy	1,10-Phenanthroline-2-carbaldehyde phenylhydrazone
2-pic	2-Aminomethylpyridine or 2-picolylamine
prtrz	4-Propyl-1,2,4-triazole
py	Pyridine
pytrz	4-(pyridyl-2)-1,2,4-triazole
Cl*thsa*	Chlorinated thiosemicarbazone salicylaldehyde of iron(III)
AVC	Adiabatic vacuum calorimeter
DSC	Differential scanning calorimeter
SCO	Spin crossover
HS	High-spin state
LS	Low-spin state

Introduction

Spin transition (spin crossover, SCO) in metal complexes of the first transition series with d^4–d^7 configuration in the octahedral ligand field is among the most interesting phenomena in coordination chemistry. A reversible transition from a low-spin (LS) state to a high-spin (HS) state can be due to the effect of temperature, pressure, or light of a certain wavelength. "Bistable" complexes are of particular interest for molecular electronics [1, 2]. Spin transition is observed when a certain ratio is reached between splitting parameters for low (Δ_{LS}) and high (Δ_{HS}) spin forms of the complex and the spin coupling energy. Thus, SCO is possible only at an appropriate value of ligand field strength. Most frequently, spin transitions due to the

G. A. Berezovskii (✉) · L. G. Lavrenova
Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Akad. Lavrentiev Ave 3, Novosibirsk, Russia 630090
e-mail: berez@niic.nsc.ru

change of external conditions could be observed for the complexes of iron (II) and iron (III) with nitrogen-containing ligands and FeN_6 coordination core. SCO has been a subject of much research (e.g., see reviews [3–11] and a monograph [12]).

Transformations associated with spin multiplicity change are evaluated by such factors as abruptness of SCO, hysteresis observed in $\mu_{eff}(T)$ curves, the completeness of transition. The presence of water molecules in the structure of complexes is also of essential importance [13]. Dehydration usually results in T_c change which can be rather substantial to reach dozens degrees, T_c increasing or decreasing [13, 14].

Abruptness, or the slope of $\mu_{eff}(T)$ curve, is the major property of SCO. There are two extreme cases of an abrupt SCO within a narrow temperature range (about several degrees) and a gradual transition within a wide temperature range (up to hundred degrees and more). An abrupt transition, unlike a gradual one, is associated with temperature hysteresis in $\mu_{eff}(T)$ curve and thermodynamic properties of first-order phase transition. The latter case has two transition temperatures, $T_c\uparrow$ on heating and $T_c\downarrow$ on cooling, the width of a hysteresis loop being $\Delta T = T_c\uparrow - T_c\downarrow$. The SCO temperature is defined either as inflection points in $\mu_{eff}(T)$ curve or as point of equal contributions from a high-spin α_{HS} and a low-spin α_{LS} states.

A transition is considered to be complete when $\alpha_{HS} \rightarrow 0$ and $\alpha_{LS} \rightarrow 1$ at low temperatures, and $\alpha_{LS} \rightarrow 0$ and $\alpha_{HS} \rightarrow 1$ at high temperatures.

Abrupt transitions with hysteresis in μ_{eff} (T) curves are associated with strong cooperative interactions between SCO-centers in the solids. Such interactions in mononuclear compounds could be caused either by a branched system of hydrogen bonds or by π–π stacking. Cooperative interactions in multinuclear complexes are caused by ligand coordination in a bidentate bridging manner which makes it possible to synthesize compounds with structures of various dimensions. Some compounds, such as complexes of iron (II) with 1,2,4-triazoles and tetrazoles, SCO is accompanied by thermochromism which is a change of color reversible on heating and cooling. The fact is of scientific and practical interest in itself [15]. The complexes can be used to construct displays and memory systems [2].

SCO complexes demonstrate the phenomenon of light-induced excited spin state trapping (LIESST) [16–18] which means that the transition to the long-life high-spin state takes place at temperatures much lower than thermoinduced SCO temperature. LIESST is induced by exposure to 540–550 nm wavelength light corresponding to $^1A_1 \rightarrow {}^1T_1$ d–d transition. The reverse transition takes place at heating or exposing to ~850 nm wavelength light that corresponds to $^5T_2 \rightarrow {}^5E$ transition. Thus, the SCO complexes could be used as thermal and optical sensors [19, 20].

Spin transition complexes are studied with various techniques such as static magnetic susceptibility, X-ray phase and structural analyses, and spectroscopic methods (electronic, IR, Moessbauer, and EXAFS). Thermodynamic studies are much rarer though they are vital for model making and verification and are contributive to understanding the nature of the phenomenon.

Thermodynamic studies of SCO complexes imply the use of adiabatic vacuum calorimeters (AVC) or differential scanning calorimeters (DSC). The first technique is more preferable since it allows one to measure $C_p(T)$ dependence over the temperature range from 5 K to 300–360 K, it provides high accuracy thermodynamic parameters of the transition and detailed description of heat capacity anomaly. However, the technique is rather complicated and laborious and implies that a self-made device is used. A differential scanning calorimeter, on the contrary, is a shop-assembled device with a measurement technique rather simple in operation. It is an express method to obtain thermodynamic data as well. DSC makes possible measurements at high temperatures (up to 1000 K) but the lower limit is only 80 K. Both the heating and cooling modes are possible which allows one to register hysteresis. However, the accuracy of DSC measured heat quantities is by an order lower than those measured by AVC. Moreover, it is rather difficult to obtain a detailed description of heat capacity anomaly using DSC.

Adiabatic vacuum calorimetry is a direct method to judge the presence and the type of a phase transition. Heat capacity, C_p, is usually measured at constant pressure. It is defined as enthalpy change H needed to raise the temperature of 1 mol of a substance by 1°. The enthalpy change H and the entropy S are found as

$$H = \int C_p \mathrm{d}T \text{ and } S = \int \left(C_p/T\right)\mathrm{d}T.$$

From H and S obtain the estimation for Gibbs energy $G = H - TS$. Heat capacity is a very important physical quantity since all the three fundamental thermodynamic quantities (H, S, and G) are found solely from C_p measurements.

Both the first-order and second-order phase transitions are accompanied by heat effect. In solids the effect is revealed as an anomaly of heat capacity near the transition temperature. Enthalpy $\Delta_{trs}H$ is found by integration of the anomalous contribution of heat capacity $\Delta C_p = C_p$ (total) $- C_p$ (regular) or from a special experiment. In both cases, the inaccuracy of the regular (or lattice) contribution of heat capacity can cause a considerable error in ΔC_p calculation. C_p (regular) value in the vicinity of the anomaly is determined by extrapolating to T_{trs} those values of heat capacities which are far from the transition; $\Theta_D(T)$ dependences and calculations from IR spectra are also used [21].

Here, we make an attempt to survey data published on issues related to thermodynamic properties of spin transition complexes. The latter are mostly Fe(II) and Fe(III) complexes or compounds with iron ions partially replaced by ions of some other metal. The first article on measuring heat capacity of Fe(II) complexes was published by Sorai and Seki [22], Fe [III] complex was first studied by Zelentsov et al. [23].

Mononuclear complexes

Iron (II) complexes

All AVC thermodynamic studies of mononuclear complexes of Fe(II), Fe(III), and Cr(II) were carried out by Sorai with colleagues. The results of the studies are presented in review [24]. SCO parameters for these complexes are shown in Table 1 of this review.

First SCO studies by means of AVC technique were carried out with such samples as [Fe(phen)A_2], where $A = \mathrm{NCS}^{-\bullet}$ or $\mathrm{NCSe}^{-\bullet}$ [21, 22]. Heat capacity C_p was measured from 13 to 375 K. The temperatures of maxima of heat capacity anomalies (T_{tr}) were in a good agreement with transition temperatures T_c obtained from magnetochemical measurements. The authors note that a transition is associated with a change in metal-to-ligand distance in the octahedral polyhedron: the distance for the low-spin form is 0.2 Å shorter than for the high-spin state. It was first discovered that transition entropy $\Delta_{trs}S$ obtained from C_p measurements substantially exceeds electronic entropy $\Delta_{el}S$ expected for the transition from the LS state singlet to the HS-state quintet. The authors attribute the excess entropy (above the contribution from multiplicity change) to contribution from phonons, believing the transition to be caused by the entropy change. The authors have also proposed a domain SCO model for mononuclear complexes. The substitution of thiocyanate ion by selenocyanate ion in the structure of the complex such as [Fe(phen)$_2$A$_2$] results in significant change of the temperature and other SCO parameters. Thus, the character of transition in the solid is very sensitive to the variation of both chemical and physical factors.

References [24–27] deal with such complexes as [Fe(2-pic)$_3$]Cl$_2$ (solv), where solv = C_2H_5OH, CH_3OH, H_2O, and $2H_2O$. Heat capacities were measured with AVC technique from 13 to 300 K. Interesting results were obtained in the studies of a crystallization solvent effect on the spin transition. Mossbauer spectroscopic investigation allowed the authors to reveal temperature dependences of the HS form contribution for the complexes with various solvent molecules. SCO was more abrupt for ethanol and became more gradual when ethanol was substituted by methanol. The spin transition was observed at 295 K on

Table 1 Thermodynamic quantities associated with spin crossover phenomena [24]

Ion	Compounds	T_{trs}/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔC_p(normal)/ J K^{-1} mol^{-1}	Spin entropy/ J K^{-1} mol^{-1}
Fe^{2+}	[Fe(NCS)$_2$(phen)$_2$]	176.29	8.60 ± 0.14	48.8 ± 0.7	18.7	R ln (5/1) = 13.38
S(LS) = 0	[Fe(NCSe)$_2$(phen)$_2$]	231.26	11.60 ± 0.44	51.2 ± 2.3	45.0	
S(HS) = 2	[Fe(2-pic)$_3$]Cl$_2$ (solv)					
	solv = C_2H_5OH	114.04, 122.21	6.14	50.6	7.8	
	solv = CH_3OH	Around 150	8.88	59.5		
	solv = H_2O	280	17.1	59.4		
Fe^{3+}	[Fe(acpa)$_2$PF$_6$	Around 190	7.03	36.2		R ln (6/2) = 9.13
S(LS) = 1/2	[Fe(3MeO-salenEt)$_2$]PF$_6$					
S(HS) = 5/2	As-prepared sample	161.12, 162,02	5.89	36.6	29.9	
	Perturbed sample	161.17	4.94	31.1	21.4	
	Recrystallized sample	162.31	5.94	36.7	28.2	
	[Fe(3EtO-salenAPA)$_2$]ClO$_4$ (solv)					
	solv = C_6H_6	187	7.08 ± 0.35	34.8 ± 1.5		
	solv = C_6H_5Cl	188	6.34	36.1		
	solv = C_6H_5Br	Around 165	7.99	40.4		
	solv = o-$C_6H_4Cl_2$	Around 150	5.38	39.5		
Cr^{2+}						
S(LS) = 1	[CrI$_2$(depe)$_2$]	171.45	6.69 ± 0.03	39.5 ± 0.2		R ln (5/3) = 4.25
S(HS) = 2						

heating [Fe(2-pic)$_3$]Cl$_2$·H$_2$O complex, and at 204 K on cooling, hysteresis loop thus reaching 94 K. The authors related such strong hysteresis to the formation of metastable LS and HS-states of the complex. The thermodynamic studies revealed two distinctly pronounced anomalies on the curve of $C_p(T)$ dependence for ethanol complex. Therefore, this is a kind of two-stage transition. When methanol molecule is introduced, a smooth anomaly appears on the $C_p(T)$ curve between 100 and 250 K, as should be expected for gradual SCO. For a complex with a single water molecule a narrow $C_p(T)$ anomaly is observed with maximum at 280 K. Interestingly, no SCO is observed when two water molecules are present in the complex.

Several mononuclear complexes of iron (II) were studied with DSC technique [28–34] (Table 2).

[Fe(bt)$_2$(NCS)$_2$]

Temperatures on DSC curves are $T_c\uparrow = 181.9$ K on heating and $T_c\downarrow = 172.3$ K on cooling. In order to calculate $\Delta_{trs}S$ the transition temperature was taken as simple average $T_c = (T_c\uparrow + T_c\downarrow)/2 = 175.95$ K. The transition enthalpy $\Delta_{trs}H$ was determined from the peak area on the DSC curve. $C_p(T)$ dependence with an anomaly corresponding to SCO was derived from the same curve. A heat capacity jump $\Delta C_p = 45 \pm 8$ J K^{-1} mol^{-1} has been observed at the transition temperature. "The first-order character of the transition follows from the observation of thermal hysteresis effects and the associated crystallografic phase change." [28].

In a later work Kulshreshtha et al. [29] reported DSC heat capacity measurements for [Fe(bt)$_2$(NCS)$_2$], [Fe(bt)$_2$(NCSe)$_2$], and [Fe(bts)$_2$(NCS)$_2$]. Strong anomalies of C_p were observed for the two-first complexes, maximum anomalies registered at 183 and 223 K, respectively. The authors refer to the spin transition to be the first-order phase transition. The third complex shows a broad anomaly in $C_p(T)$ curve in the region of spin transition with maximum at 205 K.

[Fe(btr)$_2$(NCS)$_2$]·H$_2$O

The complex exhibits a very sharp spin transition (80% of the spin change occurs within 3 K) with a wide hysteresis of 24 K ($T_c\downarrow = 121$ K and $T_c\uparrow = 145$ K, $T_c\downarrow$ and $T_c\uparrow$ being the temperatures at which the HS fraction, n_{HS}, is equal to 0.5 in the cooling mode and the heating mode, respectively). The temperatures were obtained from magnetic measurements. Enthalpy and entropy of the transition were calculated the same way as in the previous study.

X-ray structure analysis revealed a two-dimensional network of the complex. It should be noted that [Fe(btr)$_2$(NCS)$_2$]·H$_2$O is the first two-dimensional compound known to exhibit a spin transition [30, 31].

The highest entropy of spin transition was registered for [Fe(phy)$_2$](BF$_4$)$_2$ [32].

Iron (III) and chromium (II) complexes

SCO is also observed for a number of octahedral Fe(III) complexes with 3d^5 electronic configuration. Both LS and HS forms are paramagnetic: $S_{LS} = 1/2$, $S_{HS} = 5/2$. Entropy contribution at the transition corresponding to the multiplicity change is $S_{el} = R\ln 6/2 = 9.13$ J K^{-1} mol^{-1}. These complexes were studied mostly by Sorai et al. with the use of an adiabatic vacuum calorimeter (Table 1).

However, the first measurement of C_p for complexes of iron (III) was made by Zelentsov with colleagues [23]. AVC technique was used to study two compounds with chloro substituted thiosemicarbazones of salicylic aldehyde: Al$_{0.33}$[Fe(5-Cl*thsa*)$_2$] (I) and H[Fe(5-Cl*thsa*)$_2$] (II). At 210–230 K magnetic moment of these compounds changes abruptly from 2.5 to 5.6 μ_B with no hysteresis observed. However, the behavior of heat capacity is unusual. A weak smooth peak of heat capacity ($T_{trs} = 228$ K) in the region of abrupt change of magnetic moment was registered for compound I and a sharp peak with pronounced fine structure for compound II ($T_{trs} = 223.5$;

Table 2 Thermodynamic quantities of mononuclear Fe(II) spin crossover compounds (DSC technique)

No.	Compounds	T_{trs}/K	$\Delta_{trs}H$/kJ mol^{-1}	$\Delta_{trs}S$/J K^{-1}/mol^{-1}	References
1	[Fe(bt)$_2$(NCS)$_2$]	180.9	9.55 ± 0.7	54.5 ± 4	[28, 29]
2	[Fe(bt)$_2$(NCSe)$_2$]	223	–	–	[29]
3	[Fe(bts)$_2$(NCS)$_2$]	205	–	–	[29]
4	[Fe(btr)$_2$ (NCS)$_2$]·H$_2$O	~140	10.2	76.4	[30, 31]
5	[Fe(phy)$_2$](BF$_4$)$_2$	282	24.2 ± 1	86 ± 5	[32]
6	[Fe(phy)$_2$](ClO$_4$)$_2$	244.6	15.7 ± 1	64 ± 4	[32]
7	[Fe(bpy)$_2$(NCS)$_2$]	212	10.1 ± 0.5	48 ± 4	[33]
8	[Fe(py)$_2$bpym(NCS)$_2$] · 0.25py	115	6.5 ± 0.5	56 ± 4	[34]
9	[Fe(py)$_2$phen(NCS)$_2$] · 0.5py	106	3.7 ± 0.5	37 ± 5	[34]

225.5 and 226.3 K). Experimental $\Delta_{trs}S$ values for the compounds are almost equal and make 16–18 J K^{-1} mol^{-1}.

The first calorimetric study of gradual SCO was carried out for iron (III) complex $Fe(acpa)_2]PF_6$ [24, 27]. An unusually wide C_p anomaly was observed at 120–280 K. A series of complexes such as $[Fe(3EtO\text{-}salenAPA)_2]ClO_4$ (solv) (solv = C_6H_6, C_6H_5Cl, C_6H_5Br, $o\text{-}C_6H_4Cl_2$) was studied in [24, 27, 35]. There are four nitrogen atoms and two oxygen atoms in the octahedral environment of iron ions. Magnetic measurements demonstrated very gradual SCO within a wide temperature range. Accordingly, very wide anomalies of heat capacity were registered. Transition temperatures range from 150 to 190 K, $\Delta_{trs}S$ values range from 35 to 40 J K^{-1} mol^{-1} for all these compounds. A gradual SCO on cooling down to ~160 K is also observed for $[Fe(3MeO\text{-}salenEt)_2]PF_6$ with the same coordination unit structure as in the compounds of $[Fe(3EtO\text{-}salenAPA)_2]ClO_4$ (solv) series. The transition is accompanied by black (HS form) ⇔ blue (LS form) color change.

Grinding of a polycrystalline sample decreases the abruptness of a transition and makes it incomplete. These effects are mainly caused by crystal structure defects. The effect of grinding on the transition character for this complex was also studied with adiabatic vacuum calorimetry technique [24]. There is a sharp anomaly with two maxima $T_1 = 161.12$ K, $T_2 = 162.07$ K observed on the $C_p(T)$ curve for a freshly prepared sample of the compound. After grinding, the anomaly with one maximum becomes more diffuse ($T_{trs} = 161.17$ K). The type of C_p anomaly also changes if the sample is dissolved in methanol and then dried up: it becomes less gradual, but no peak splitting returns. The transition entropy value for both initial and dried samples is 36.7 J K^{-1} mol^{-1}, and 15% lower for the ground one.

According to the studies, SCO depends considerably on the size of grains and crystal defects.

Sorai [24] studied $C_p(T)$ dependence for chromium (II) complex $[CrI_2(depe)_2]$. The coordination core in the octahedral polyhedron of chromium ion consists of four phosphorus atoms belonging to the ligands and two iodine atoms. For the LS state, the spin quantum number $S = 1$ and for the HS-state $S = 2$. The magnetic measurements demonstrated an abrupt SCO near 170 K. There is an anomaly within a narrow temperature range on $C_p(T)$ curve with maximum at 171.45 K. The total entropy for the transition is 39.5 J K^{-1} mol^{-1} which is much higher than the entropy caused by multiplicity change ($R\ln5/3 = 4.25$ J K^{-1} mol^{-1}). The dominant contribution is the phonon entropy change just as it is in the case of other transitions.

Polynuclear iron (II) complexes

A series of polynuclear complexes $FeL_3A_n{\cdot}mH_2O$ (A = Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, BF_4^-, ReO_4^-, $SiF_6SO_4^{2-}$, SiF_6^{2-} etc.; $n = 1, 2$; $m = 0$–5) of various iron (II) salts with 4-R-1,2,4-triazoles (R = H, NH_2, etc.) was first synthesized and studied in the Institute of Inorganic Chemistry of SB RAS. Most of the complexes demonstrate an abrupt $^1A_1 \Leftrightarrow {}^5T_2$ spin transition accompanied by termochromism (changing pink color (LS form) ⇔ white color (HS form)[8]. In these compounds, 1,2,4-triazoles are coordinated to Fe(II) through heterocyclic N (1), N (2) nitrogen atoms to make a polymeric chain structure. Each two iron atoms are bound through three bridge ligand molecules. The coordination polyhedron represents a slightly distorted octahedron with FeN_6 core. It was found that SCO parameters (the transition completeness, sharpness, the presence of hysteresis on the $\mu_{eff}(T)$ curves of the effective magnetic moment temperature dependence, as well as the temperatures values for direct ($T_c\uparrow$) and reverse ($T_c\downarrow$) transitions) substantially depend, among other factors, on ligand and anion nature and also on the presence of solvent molecules in the structure.

AVC technique was used to study thermodynamic properties of some Fe(II) complexes with 1,2,4-triazoles. An adiabatic vacuum calorimeter with periodic introduction of heat was used to measure the isobaric heat capacity C_p of the substances. The calorimetric ampoule was made of nickel, the effective volume and weight of the ampoule being 6 cm^3 and 22.4 g, respectively. The calorimeter was calibrated at 5–350 K; the mean deviation of the experimental heat capacities from the smoothed $C_p(T)$ curve was 0.1% with at 80–350 K and increased up to 0.5% below 20 K. Control measurements of the reference substance (benzoic acid) demonstrated a good agreement with standard data. Heat capacity measurements for the complexes were carried out using samples from 0.2 to 3 g in weight.

Table 3 shows the parameters of spin transitions for studied iron (II) complexes with 1,2,4-triazoles.

$Fe(NH_2trz)_3(NO_3)_2$ was the first compound to start systematical studies of heat capacity of iron (II) polynuclear SCO complexes. The measurements were carried out from 6 to 354 K [36, 37]. The C_p anomaly with the maximum at 343.0 K corresponds to the spin transition and is in good agreement with magnetic data [8]. Hysteresis in C_p behavior was observed on slow cooling of a ampoule with the sample from 355 down to 330 K. A strong hysteresis with $\Delta T_c = 32$ K was also found out during the measurement of magnetic susceptibility which is presumably associated with a first-order phase transition. The rise of heat capacity at the temperature higher than 350 K indicates the presence of another anomaly. This is qualitatively

Table 3 Thermodynamic quantities of polynuclear and trinuclear Fe(II) spin crossover compounds with 1,2,4-triazoles (AVC technique)

No.	Compound	T_{trs}/K	$\Delta_{trs}H$/kJ mol^{-1}	$\Delta_{trs}S$/J K^{-1}mol^{-1}	ref
Polynuclear complexes					
1	$Fe(NH_2trz)_3(NO_3)_2$	343.0 ± 0.6	22.8 ± 0.4	66.5 ± 1	[36, 37]
2	$Fe(NH_2trz)_3Br_2$	330.7 ± 0.2	22.35 ± 0.30	67.6 ± 0.7	[38]
3	$Fe(NH_2trz)_3I_2$	270.8 ± 1	10.3 ± 0.5	38.4 ± 2.0	[39]
4	$Fe(NH_2trz)_3SiF_6{\cdot}H_2O$	250.7 ± 0.2	11.43 ± 0.10	45.6 ± 0.4	[40]
5	$Fe(NH_2trz)_3(ReO_4)_2$	230.5 ± 0.5	7.30 ± 0.07	32.8 ± 0.3	[40]
6	$Fe(NH_2trz)_3(ClO_4)_2$	165 ± 1	4.43 ± 0.05	30.0 ± 0.3	[38]
7	$Fe(prtrz)_3Br_2{\cdot}4H_2O$	253.9 ± 0.05	18.8 ± 0.2	73.9 ± 0.7	[44]
8	$Fe(prtrz)_3(CF_3SO_3)_2{\cdot}5H_2O$	198.0 ± 0.5	11.2 ± 0.1	56.5 ± 0.5	[44]
9	$Fe(Htrz)_3(B_{10}H_{10}){\cdot}H_2O$	234.5 ± 0.5	10.1 ± 0.2	43.0 ± 0.8	[43]
10	$Fe(Htrz)_{0.3}(NH_2trz)_{2.7}SiF_6{\cdot}H_2O$	262 ± 1	7.08 ± 0.35	27.3 ± 1.4	[39]
Trinuclear complexes					
11	$[Fe_3(pytrz)_8(H_2O)_4](NO_3)_6$	~235	3.2	15	[46]
12	$[Fe_3(prtrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$	~190	2.5 ± 0.25	13.6 ± 1.4	[43]

supported by data of DSC studies. It should be also noted that there is a small ill-reproduced anomaly on the low-temperature slope (300–330 K) with maximum deviation of 5–10% from the regular $C_p(T)$ contribution.

Heat capacity of $Fe(NH_2trz)_3Br_2$ complex was measured from 8 to 347 K [38]. The maximum C_p anomaly is close to $T_c\uparrow = 328$ K found from magnetic measurements. The width of hysteresis loop in $\mu_{eff}(T)$ curve is 10 K. $C_p(T)$ behavior within the anomaly region and transition parameters for the complex is similar to those of $Fe(NH_2trz)_3](NO_3)_2$ (Table 3).

Heat capacity anomaly corresponding to $^1A_1 \Leftrightarrow {}^5T_2$ spin transition in $Fe(NH_2trz)_3I_2$ [39] is observed from 230 to 295 K with maximum at $T_{trs} = 270.8$ K. The time to reach thermal equilibrium in the experiments considerably (three times) increases in the vicinity of the anomaly maximum. It should be noted that there is a discontinuity of the regular heat capacity contribution at the transition point T_{trs}: $C_p \sim 60$ J mol^{-1} K^{-1}. The Debye temperature dependence $\Theta_D(T)$ far from the anomaly maximum was used to determine the regular C_p contribution in the region of anomaly and the integration limits to calculate the transition enthalpy. There are experimental data indicating that spin transition in $Fe(NH_2trz)_3I_2$ is a first-order phase transition, namely: (a) increased time to reach thermal equilibrium in the vicinity of T_{trs}; (b) different character of $\Theta_D(T)$ dependence in the regions higher and lower than T_{trs}; (c) hysteresis phenomena when measuring $C_p(T)$ in the anomaly region.

$C_p(T)$ for $Fe(NH_2trz)_3SiF_6{\cdot}H_2O$ was measured from 80 to 337 K [40]. Magnetic measurements demonstrated an abrupt SCO: $T_c\uparrow = 255$ K, $T_c\downarrow = 245$ K, $\Delta T_c = 10$ K. High magnetic moment for LS phase indicates that the transition is not complete, i.e. some part of HS-phase is not subject to transition as the temperature decreases. There are also some indications of a first-order phase transition such as a rather narrow temperature range in the anomaly region and high C_p values in the vicinity of the anomaly maximum. Moreover, the time to reach thermal equilibrium is two to threefold longer at the points near the anomaly maximum. There is one more heat capacity anomaly on $C_p(T)$ curve for $Fe(NH_2trz)_3SiF_6{\cdot}H_2O$ with the maximum at 323 K. Furthermore, there is also a singularity at this temperature on the $\mu_{eff}(T)$ dependence curve. One may assume that this anomaly is associated with a structural change of octahedral SiF_6^{2-} ion [41, 42].

The effect of substituting a part of (NH_2trz) ligands by (Htrz) was considered by example of $Fe(Htrz)_{0.3}(NH_2trz)_{2.7}SiF_6{\cdot}H_2O$ [39]. As compared to $Fe(NH_2trz)_3SiF_6{\cdot}H_2O$, the SCO temperature was 12 K higher, but the transition became gradual. Heat capacity anomaly was observed at 200–320 K. Transition entropy considerably decreases, no indications of a first-order phase transition are seen. In contrast to $Fe(NH_2trz)_3SiF_6{\cdot}H_2O$, only a small deviation of heat capacity from the regular $C_p(T)$ curve was observed in the vicinity of 320 K.

Heat capacity of $Fe(NH_2trz)_3(ReO_4)_2$ was studied from 80 to 323 K [40]. According to the results of $\mu_{eff}(T)$ measurements, spin transition occurs over a wide temperature range (~100 K), $T_c\uparrow = 228$ K, $T_c\downarrow = 223$ K, the hysteresis loop width is $\Delta T_c = 5$ K. Thermodynamic data are also in good agreement with magnetic measurements: C_p anomaly is gradual, SCO is registered over a wide temperature range. Moreover, there are no indications of a first-order phase transition (Fig. 1).

Temperature dependence of heat capacity for $Fe(NH_2trz)_3(ClO_4)_2$ was measured from 58 to 331 K [38]. Magnetochemical data indicate a gradual SCO and no hysteresis of $\mu_{\mathrm{eff}}(T)$. λ-type anomaly of heat capacity covers a wide temperature range from 80 to 200 K and thus supports the conclusion about a gradual character of the transition drawn from the data of magnetic measurements.

Thermodynamic properties of $Fe(Htrz)_3B_{10}H_{10}{\cdot}H_2O$ complex were investigated from 85 to 300 K [43]. The λ-type anomaly of heat capacity with maximum at T_{trs} = 234.5 K takes place within a wide temperature range, from 170 to 260 K. Such pattern is typical of gradual SCO. Meanwhile, HS-phase is subject to overcooling typical of first-order phase transitions. According to magnetochemical data, $T_c{\uparrow} = 246$ K, $T_c{\downarrow} = 233$ K for $Fe(Htrz)_3B_{10}H_{10}{\cdot}H_2O$, hysteresis amounts to 13 K, which is also indicative of a first-order phase transition. Thermodynamic properties of $Fe(prtrz)_3Br_2{\cdot}4H_2O$ complex were studied from 87 to 330 K [36]. According to calorimetric data, the time to reach thermal equilibrium substantially increased in the vicinity of anomaly maximum. The effect is typical of first-order phase transitions (Fig. 2). According to a magnetochemical study, the temperatures of direct and reverse SCO are $T_c{\uparrow} = 252$ and $T_c{\downarrow} = 247$ K, respectively [37].

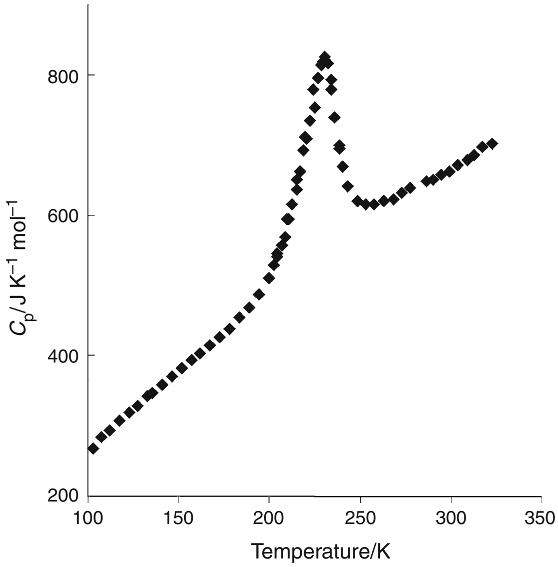

Fig. 1 $C_p(T)$ for complex $Fe(NH_2trz)_3ReO_4$ [40]

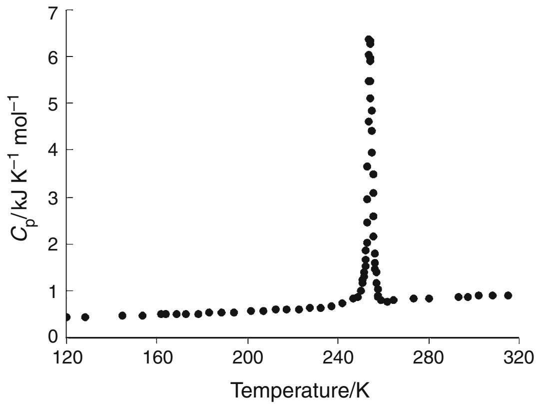

Fig. 2 $C_p(T)$ for complex $Fe(prtrz)_3Br_2{\cdot}4H_2O$ [44]

Heat capacity of $Fe(prtrz)_3(CF_3SO_3)_2{\cdot}5H_2O$ was studied from 88 to 312 K [44]. The behavior of heat capacity in the region of anomaly indicates an intermediate character of the transition between abrupt and smooth SCO. Temperature hysteresis obtained from μ_{eff}(T) measurement is 5° (between 202 and 207 K) [45]. Besides, a small anomaly on $C_p(T)$ dependence curve is observed at 250–280 K which is presumably associated with presence of water traces. The deviation at the maximum of anomaly is less than 5% of regular C_p contribution.

Trinuclear iron (II) complexes

The main difference between the structures of trinuclear and polynuclear complexes of iron (II) with 1,2,4-triazoles is that it is only the central Fe(II) ion in trinuclear compounds which is in the octahedral environment of nitrogen atoms. Coordination cores of both terminal iron ions (depending on the structure of a complex) are supplemented with nitrogen atoms of monodentate coordinated 4R-1,2,4-triazole and oxygens of water molecules to form an octahedral configuration. As a result, only the central iron (II) ion is subject to spin multiplicity change and SCO becomes gradual. According to a magnetochemical study of trimuclear $[Fe_3(pytrz)_8(H_2O)_4](NO_3)_6$ complex carried out at 80–350 K, magnetic moment increases gradually with a slight anomaly at ~215 K. The results of $C_p(T)$ measurement from 8 to 340 K are in accordance with magnetochemical data [46].

A smooth anomaly of heat capacity is observed at 170–250 K, maximum heat capacity ~6% exceeding regular $C_p(T)$ curve in the vicinity of 207 K (Fig. 3). Approximately at this temperature, the substance changes

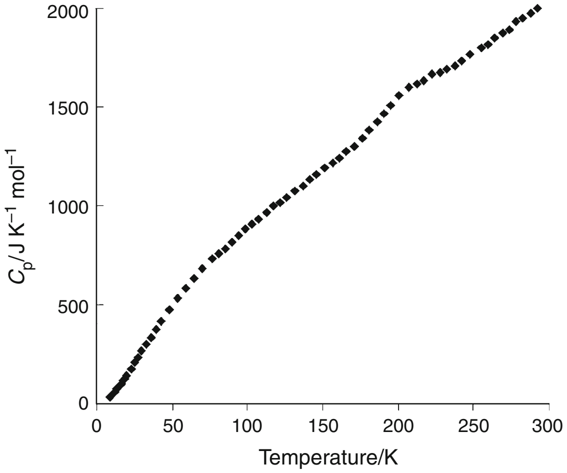

Fig. 3 $C_p(T)$ for complex $[Fe_3(pytrz)_8(H_2O)_4](NO_3)_6$ [46]

its color from pink to white. Meanwhile, entropy $\Delta_{trs}S \approx 15\ \mathrm{J\ K^{-1}\ mol^{-1}}$ which is close to $R\ln5$. This means that the phonon system undergoes only slight changes upon SCO in this case. There is one more very smooth anomaly on $C_p(T)$ curve at 290–340 K. The entropy of the excess contribution of the C_p anomaly is $\sim 6\ \mathrm{J\ K^{-1}\ mol^{-1}}$, the nature of this anomaly is unknown.

A similar behavior of heat capacity within spin transition region takes place in another trinuclear complex $[Fe_3(prtrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$. There is a very smooth anomaly on the $C_p(T)$ curve between 150 and 250 K. The anomaly maximum is observed at $\sim$190 K, being in a good agreement with magnetochemical data. Near this temperature, the substance also changes its color. It should be noted that the transition entropy $\Delta_{trs}S$ is equal (within the experimental error) to the entropy associated with the change of spin state in the complex. Therefore, changes in the phonon system at SCO in this trinuclear complex, just like in the previous one, are minor [43].

Heterometallic complexes

A number of studies consider the impact of partial substitution of Fe(II) ions by other metal ions on SCO character. As mentioned above, abrupt spin transitions with $\mu_{eff}(T)$ hystereses are observed for compounds with strong cooperative interactions in solid-state phase. One of the ways to influence the degree of cooperativity is to introduce into the solid, beside iron ions, ions of another metal (with the same oxidation number) not subject to spin transition. This results in substantial weakening of cooperative interactions between iron ions of and, consequently, to the change of SCO parameters.

The initial iron (II) complex and heterometallic phases $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ ($x = 0.66$, 0.85, 0.93, and 1.00) were studied in references [24, 27]. The initial compound ($x = 1.00$) has been already considered above. The introduction of zinc ions into the complex results in the decrease of T_c and transition entropy. Interestingly, both T_c, and $\Delta_{trs}S$ depend on zinc concentration linearly. At $x \le 0.85$, the anomaly bifurcation disappeared. Heat capacity was measured by means of AVC technique.

Several works dealt with thermal properties of heterometallic complexes using DSC technique. Solid phases such as $[Fe_xM_{1-x}(btr)_2(NCS)_2]\cdot H_2O$ (M = Ni^{2+} and Co^{2+}) were studied. For the series containing Ni^{2+}, the values of x varied as $1.00 \ge x \ge 0.26$ [30], for the series containing Co^{2+}, x value varied as $1.00 \ge x \ge 0.23$ [31]. As mentioned above, the initial $[Fe(btr)_2(NCS)_2]\cdot H_2O$ complex ($x = 1.00$) has a quasi-two-dimensional structure; $\mu_{eff}(T)$ curves demonstrate an abrupt spin transition with broad hysteresis ($\Delta T = 24$ K). In both cases, the transition becomes more gradual and the hysteresis loop narrower as x decreases. Hysteresis disappears completely for $x = 0.45$ upon Ni introduction and for $x = 0.37$ upon Co introduction. Yet there is a difference between behaviors of these two series. In Ni containing complexes, the transition is complete for all x values, whereas in cobalt containing complexes there is residual high-spin Fe^{2+} state that appears and increases at low temperatures, i.e. the transition becomes incomplete.

Transition entropy and enthalpy for the initial complex are 10.0 and 76 $\mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. In phases $Fe_xNi_{1-x}(btr)_2(NCS)_2]\cdot H_2O$, the enthalpy and entropy decrease together with x down to 3.6 and 27.5 $\mathrm{J\ K^{-1}\ mol^{-1}}$ ($x = 0.26$), respectively. For $Fe_xCo_{1-x}(btr)_2(NCS)_2]\cdot H_2O$ the values $\Delta_{trs}H = 2.0\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{trs}S = 17\ \mathrm{J\ K^{-1}\ mol^{-1}}$ at $x = 0.23$. For $0.7 \ge x \ge 0.26$ (Ni) and $1.0 \ge x \ge 0.23$ (CO), the decrease of $\Delta_{trs}H$ and $\Delta_{trs}S$ is linear.

Heterometallic complexes $[Fe_xNi_{1-x}(NH_2trz)_3](NO_3)_2$ ($0.9 \ge x \ge 0.1$) and polynuclear chain structure were synthesized, their magnetic and thermodynamic properties were studied [47]. It was shown that the transition becomes more gradual and shifts to low-temperature region and hysteresis loop ΔT_c becomes narrower when Ni(II) percentage increases (x decreasing). Besides, magnetic moment increases at low temperatures when x decreases to testify incompleteness of transition. The obtained data were explained by comparison of ionic radii of iron (II) ions in HS and LS states and nickel (II) ion. DSC technique was used to obtain experimental values of transition enthalpy. Within the framework of the domain model, theoretical $\Delta_{trs}H$ values were calculated and the domain size (the number n of Fe(II) ions in the domain unit) was estimated.

Similar studies on the metal dilution were made by Jacobi et al. [48, 49] for partially deuterated complexes $[Fe_xZn_{1-x}(2\text{-pic-ND}_2)_3]Cl_2\cdot C_2H_5OD$ on the basis of DSC

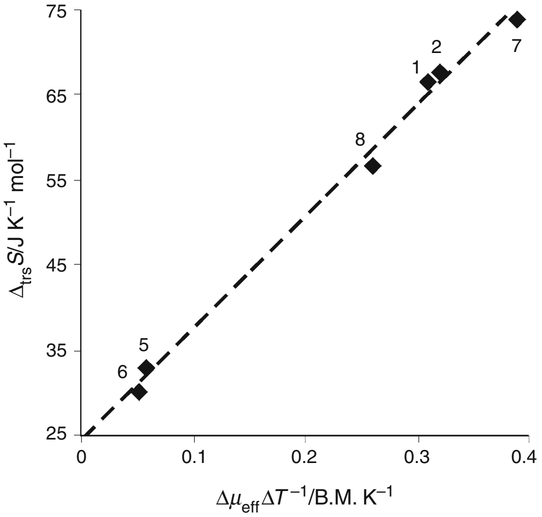

Fig. 4 $\Delta_{trs}S$ values for complexes 6, 5, 8, 1, 2, 7 (Table 3). Plotted on the abscissa axis are the $\Delta\mu_{eff}/\Delta T$ values (B.M./K) for the complexes in the spin transition region [44]

measurements and for $[Fe_{0.73}Zn_{0.27}(2\text{-pic})_3]Cl_2{\cdot}C_2H_5OH$ based on a relaxation microcalorimeter [50].

It was noted that the character of transition as well as the position of maximum on $C_p(T)$ curves distinctly depend on x the way that the peak becomes flatter and displaces to the region of lower temperature as x decreases. Gibbs free energy was determined as a function of temperature. From magnetochemical data, the $\chi(T)$ dependence curve was obtained for HS-state fraction of iron (II) over the temperature range from 4.2 to 300 K. The obtained data were used to give a semiquantitative explanation of peak position on $C_p(T)$ curve without introducing any additional parameters.

Conclusions

When studied polynuclear complexes with (NH_2trz) ligand are ranged according to decrease of SCO temperature (see Table 3), the following conclusions are made. Transition enthalpy and entropy decrease and traits of first-order phase transition gradually disappear when T_{trs} decreases. $Fe(NH_2trz)_3SiF_6{\cdot}H_2O$ is the only exception, presumably due to presence of the water molecule. According to thermodynamic data, SCO is referred to as an abrupt one in some complexes and as a gradual one in others, and in some cases the transition is intermediate between these two.

It is important to note that for all the complexes (except trinuclear ones), $\Delta_{trs}S$ at spin transition is several times higher than $\Delta_{el}S$ associated with multiplicity change.

Both the magnetochemical and thermodynamic data demonstrate a strong dependence between SCO parameters and the structure of the compound, first of all, the outer-sphere anion. The effect is due to the nature and the size of the anion.

Most Fe(II) complexes with 1,2,4-triazoles demonstrate nonzero μ_{eff} for low-spin forms at low temperatures which is expectable for diamagnetic phases. This can be an indication of some incompleteness of transition. Therefore, $\Delta_{trs}S$ obtained from the thermodynamic data could be understated. It was noted [44] that correlations not only between transition temperature and compound structure but also between magnetic and thermodynamic properties can be useful to understand the nature of spin crossover. Having this in mind, a dependence between $\Delta_{trs}S$ and SCO abruptness was obtained in [44]. The abruptness of transition is evaluated according to $\mu_{eff}(T)$ slope in the transition region. The dependence is clearly linear (Fig. 4) for a number of Fe(II) complexes with 1,2,4-triazoles (Table 3). Thus, incompleteness of transition has little effect on the accuracy of $\Delta_{trs}S$ measurement.

One can await that some progress in the thermodynamics of spin crossover in general will be connected also with complexes of other *d*-elements [51] or even magnetic complexes of non-magnetic elements like copper [52].

References

1. Kolle V. Energetic and constitutional hysteresis in bistable molecules. Angew Chem Int Ed. 1991;30:956–8.
2. Kahn O, Krober J, Jay C. Spin transition molecular materials for displays and data recording. Adv Mater. 1992;4:718–28.
3. Konig E, Ritter G, Kulshreshtha SK. The nature of spin-state transitions in solid complexes of iron(II) and the interpretation of some associated phenomena. Chem Rev. 1985;85:219–34.
4. Zelentsov VV, Gabdrakhmanov MN, Sobolev SS. Particle size and crystal properties influence on spin transition of coordination compounds. Chem Phys (Russ). 1986;5:1216–24.
5. Zelentsov VV. Role of the cooperativity in coordination compounds of the 3d-metalls. Russ J Coord Chem. 1992;18:787–95.
6. Gutlich P, Hauser A, Spiering H. Thermal and optical switching of iron(II) complexes. Angew Chem Int Ed Engl. 1994;33:2024–54.
7. Kahn O, Codjovi E. Iron(II)- 1,2,4-triazole spin transition molecular materials. Phil Trans R Soc Lond A. 1996;354:359–79.
8. Lavrenova LG. Larionov SV.Spin transition in the complex compounds of iron(II) with 1,2,4-triazoles and tetrazoles. Russ J Coord Chem. 1998;24:379–96.
9. Boca R, Linert W. Is there a need for new models of the spin crossover? Mon Chem. 2003;134:199–216.
10. Hauser A. Ligand field theoretical considerations. Adv Polym Sci. 2004;233:49–50.
11. Larionov SV. Spin transition in iron(III) and iron(II) complexes. Russ J Coord Chem. 2008;34:237–50.
12. Gütlich P, Coodwin HA, editors. Spin crossover in transition metal compounds. Berlin: Springer-Verlag; 2004.
13. Zelentsov VV, Gerbelev NV, Lapushkin GI. Influence of crystal water on spin transition in $[Fe(5Cl\text{-}Thsa)_2]$. Russ J Coord Chem. 1991;17:59–60.
14. Lavrenova LG, Kirillova EV, Ikorskii VN. Iron(II) complexes with 4-R-1,2,4-triazoles (R = ethyl, propyl) exhibiting $^1A_1 \Leftrightarrow {}^5T_2$ spin transition. Russ J Coord Chem. 2001;27:46–50.
15. Sone K, Fukuda Y. Inorganic thermochromism. Berlin: Springer; 1987.
16. Decurting S, Gütlich P, Kohler CP, Spiering H. Light-induced excited spin state trapping in a transition-metal complex: the hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system. Chem Phys Lett. 1984;105:1–4.
17. Decurting S, Gütlich P, Spiering H. New examples of light-induced excited spin state trapping (LIESST) in iron(II) spin-crossover systems. J Chem Soc Chem Com. 1985:430–2.
18. Erenburg SB, Bausk NV, Lavrenova LG, Mazalov LN. Thermally and optically induced spin transition effect on the structure of iron(II) polymeric complexes. J Synchrotron Rad. 1999;6:576–8.
19. Garsia Y, Ksenofontov V, Gütlich P. Spin transition molecular materials: new sensors. Hyperfine Interact. 2002;139:543–51.
20. Gütlich P, van Koningsbruggen PJ, Renz F. Recent advances of spin crossover research. Struct Bond. 2004;107:27–75.
21. Sorai M, Seki S. Phonon coupled cooperative low-spin ⇔ high spin transition in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ cristals. J Phys Chem Solids. 1974;35:555–70.

22. Sorai M, Seki S. Magnetic heat capacity due to cooperative low-spin ⇔ high-spin transition in $Fe(phen)_2(NCS)_2$ crystal. J Phys Soc Jpn. 1972;33:575.
23. Shipilov VI, Zelentsov VV, Zhdanov VM, Turdakin VA. Phase transition in paramagnetic complexes of thiosemicarbazones of Fe(III). JETP Lett. 1974;19:294–5.
24. Sorai M. Calorimetric investigations of phase transitions occurring in molecule-based materials in which electrons are directly involved. Bull Chem Soc Jpn. 2001;74:2223–53.
25. Nakamoto T, Tan Zhi-Cheng, Sorai M. Heat capacity of the crossover complex $[Fe(2\text{-}pic)_3]Cl_2 \cdot MeOH$: a spin crossover phenomenon with weak cooperativity in solid state. Inorg Chem. 2001;40:3805–9.
26. Nakamoto T, Bhattacharjee A, Sorai M. Cause for unusually large thermal hysteresis of spin crossover in $[Fe(2\text{-}pic)_3]Cl_2 \cdot H_2O$. Bull Chem Soc Jpn. 2004;77:921–32.
27. Sorai M. Heat capacity studies of spin crossover systems. Top Curr Chem. 2004;235:153–70. doi:10.1007/s001090000086.
28. Kulshreshtha SK, Sasikala R. Calorimetric investigations of the low-spin ⇔ high-spin transition in solid ditiocyanatobis(2,2'-bi-2-thiazoline)iron(II). Chem Phys Lett. 1986;123:215–7.
29. Kulshreshtha SK. Nature of spin state transition in Fe(II) thiazoline complexes: specific heat measurements. Proc Indian Acad Sci (Chem Sci). 1990;102:457–60.
30. Martin J-P, Zarembowitch J, Dworkin A, et al. Solid-state effects in spin transitions: role of iron(II) dilution in the magnetic and calorimetric properties of the series $[FexNi_{1-x}(4,4'\text{-bis}(1,2,4\text{-triazole}))_2(NCS)_2] \cdot H_2O$. 1994;33:2617–23.
31. Martin J-P, Zarembowitch J, Bousseksou A, et al. Solid-state effects on spin transitions: magnetic, calorimetric, and Mossbauer-effect properties of $[Fe_xCo_{1-x}(4,4'\text{-bis}(1,2,4\text{-triazole}))_2(NCS)_2] \cdot H_2O$. Inorg Chem. 1994;33:6325–33.
32. Kulshreshtha SK, Iyer RM, Konig E, Ritter G. The nature of spin-state transitions in Fe(II) complexes. Chem Phys Lett. 1984;110: 201–4.
33. Kulshreshtha SK, Iyer RM. Nature of the high-spin ⇔ low-spin transition in $[Fe(bipy)_2(NCS)_2]$. Chem Phys Lett. 1984;108: 501–4.
34. Claude R, Real J-A, Zarembowitch J, et al. Spin transition in $Fe(py)_2L(NCS)_2$ complexes, where py = pyridine and L = 2,2'-bipyrimidine (bpym) and 1,10-phenanthroline (phen): magnetic, calorimetric, and Mossbauer-effect investigation. Crystal structure of $[Fe(py)_2bpym(NCS)_2] \cdot 0.25py$. Inorg Chem. 1990;29: 4442–8.
35. Conti AJ, Kaji K, Nagano Y, et al. Dynamics and phase in spin-crossover complexes: detailed nature of phase transitions in the solvate series bis(3-ethoxysalicylideneaziridinoprorylaminato)iron perchlorate solvate. Inorg Chem. 1993;32:2681–93.
36. Bessergenev VG, Berezovski GA, Lavrenova LG, Larionov SV. Thermodynamic studies of thermochromic phase transition in coordination compound of iron with triazole. In: SPIE Proceedings, San Diego, California, USA, vol 2531. 1995. p. 82–90.
37. Bessergenev VG, Berezovskii GA, Lavrenova LG, Larionov SV. Thermodynamic properties of iron(II) and copper(II) nitrate complexes with 4-amino-1,2,4-triazole. Russ J Phys Chem. 1997; 71:714–9.
38. Berezovskii GA, Bessergenev VG, Lavrenova LG, Ikorskii VN. The thermodynamic properties of iron(II) bromide and perchlorate complexes with 4-amino-1,2,4-triazole. Russ J Phys Chem. 2002;76:1246–50.
39. Berezovskii GA, Pishchur DP, Shakirova OG, Lavrenova LG. The thermodynamic properties of Fe(II) complexes $Fe(NH_2trz)3I_2$ and $Fe(Htrz)_{0.3}(NH_2trz)_{2.7}SiF_6 \cdot H_2O$. Russ J Phys Chem. 2009;83: 1827–31.
40. Berezovskii GA, Shakirova OG, YuG Shvedenkov, Lavrenova LG. Phase transition in iron(II) hexafluorosilicate and perrhenate complexes whith 4-amino-1,2,4-triazole. Russ J Phys Chem. 2003;77:1054–8.
41. Weir RD, Halstead KE, Staveley LAK. Calorimetric study of transitions in hexahydrated fluorosilicates $MsiF_6 \cdot 6H_2O$. Farad Disc Chem Soc. 1980;N69:202–9.
42. Sukharevskii BYa, Boiko FA, Bykov AM, et al. Instability of $CuSiF_6 \cdot 6H_2O$ structure near of the first-order phase transition. Dokl AN SSSR (Russ) 1981;256:1390–3.
43. Berezovskii GA, Bushuev MB, Pishchur DP, Lavrenova LG. Heat capacity of polynuclear $Fe(Htrz)_3(B10H10) \cdot H_2O$ and trinuclear $[Fe_3(prtrz)_6(ReO_4)_4(H_2O)_2](ReO_4)_2$ complexes (Htrz = 1,2,4-triazole, prtrz = 4-propyl-1,2,4-triazole) manifesting $^1A_1$ ⇔ $^5T_2$ spin transition. J Therm Anal Calorim. 2008;93:999–1002.
44. Berezovskii GA, Bushuev MB, Lavrenova LG. The thermodynamic properties of the $Fe(prtrz)_3Br_2 \cdot 4H_2O$ and $Fe(prtrz)_3(CF3\text{-}SO3)_2 \cdot 5H_2O$ complexes (prtrz = 4-propyl-1,2,4-triazole). Russ J Phys Chem. 2004;78:1708–11.
45. Bushuev MB, Lavrenova LG, Ikorskii VN, et al. Iron(II) complexes with 4-R-1,2,4-triazoles (R = ethyl, propyl, isopropyl): syntheses and properties. Russ J Coord Chem. 2004;30:284–90.
46. Shakirova OG, Lavrenova LG, Shvedenkov YuG et al. Synthesis and physicochemical study of iron(II), cobalt(II), nickel(II), and copper(II) complexes with 4-(2-pyridyl)-1,2,4-triazole. Russ J Coord Chem. 2004;30:473–9.
47. Shvedenkov YuG, Ikorskii VN, Lavrenova LG, et al. $^1A_1$ ⇔ $^5T_2$ spin transition in the solid phases of $FexNi_{1-x}(Atr)_3(NO_3)_2$ (Atr = 4-amino-1,2,4-triazole). J Struct Chem. 1997;38:578–84.
48. Jacobi R, Spiering H, Wiehl L, Gmelin E, Gutlich P. Thermoanalitic investigations on mixed crystals of spin-crossover system $[Fe_xZn_{1-x}(2\text{-pic-}ND_2)_3]Cl_2 \cdot EtOD$. Inorg Chem. 1988;27: 1823–7.
49. Jacobi R, Spiering H, Gutlich P. Thermodynamics of the spin transition in $[FexZn_{1-x}(2\text{-pic})_3]Cl_2$ EtOH. J Phys Chem Solids. 1992;53:267–75.
50. Jacobi R, Romstedt H, Spiering H, Gutlich P. Microcalorimetry of the spin-transition systems $[Fe(bts)_2(NCS)_2]$ and $[Fe(2\text{-}pic)_3]Cl_2 \cdot$ EtOH in the range 15 K < T < 300 K. Angew Chem Int Ed Engl. 1992;31:178–80.
51. Dziewulska-Kułaczkowska A. Manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 4-oxo-4H-1-benzopyran-3-carboxaldehyde: thermal, spectroscopic and magnetic characterization. J Therm Anal Calorim. 2010;101:1019–26.
52. Tokoro N, Yamashita S, Igashira-Kamiyama A, Fujioka J, Konno T, Nakazawa Y. Low-temperature heat capacity of heptacopper(II) complex $[Cu_7(\mu3\text{-}Cl)_2(\mu3\text{-}OH)_6\text{-}(d\text{-pen-disulfide})_3]$. J Therm Anal Calorim. 2010;99:149–52.