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SPIN-CROSSOVER AND THERMOCHROMISM IN COMPLEXES OF IRON(II) IODIDE AND THIOCYANATE WITH 4-AMINO-1,2,4-TRIAZOLE

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Abstract—New complexes of iron(II) iodide and thiocyanate with 4-amino-1,2,4-triazole were synthesized. The complexes were characterized by magnetic measurements, reflection, Mössbauer and IR spectra. The coordination of iron(II) is discussed on the basis of these data. The compounds possess reversible thermochromism (colour change from white to pink) due to the spin transition ${}^5T_2 \rightleftharpoons {}^1A_1$.

Complex compounds with the spin transition (ST) low spin (LS)–high spin (HS) ${}^1A_1 \rightleftharpoons {}^5T_2$ accompanied by thermochromism are promising material which may be used as thermochromic indicators,[1] and also for displays and data recording.[2] Among the thermochromic compounds synthesized, only a fraction possess reversible thermochromism.[1] Besides, many of the complexes changing colour reversibly are unstable or include toxic metals, e.g. mercury. It is therefore desirable to find new thermochromic compounds free of these faults. Iron(II) complexes with 1,2,4-triazole (Htrz) and 4-amino-1,2,4-triazole (NH_2trz)[2] are a promising class of such compounds. For the first time, the reversible change of colour was noticed in the compound $Fe(Htrz)_2(trz)BF_4$.[3] We synthesized and investigated a large group of complex compounds of the composition FeL_3A_2 [L = Htrz, NH_2trz (hereafter L); A = ClO_4^-, Br^-, BF_4^-, NO_3^-].[4–6] The complexes obtained are stable and possess reversible thermochromism (colour changes from white to pink) due to the spin transition ${}^5T_2 \rightleftharpoons {}^1A_1$. The transition temperature (T_c) depends on the nature of the ligand, and particularly on the nature of the anion incorporated into the compound. Therefore, it seemed interesting to enlarge the group of thermochromic iron(II) complexes with 1,2,4-triazoles by incorporating new anions into these compounds.

In the present work, the synthesis and properties of new thermochromic iron(II) iodide and thiocyanate complexes with L are described.

EXPERIMENTAL

Reagents

Metal salts, ascorbic acid and L were obtained commercially. M.p. (L) 82–83°C. Water was deaerated by boiling and aqueous alcohol was deaerated using ascorbic acid.[7]

Synthesis of compounds

FeL_3I_2 (I) $FeSO_4 \cdot 7H_2O$ (1.39 g, 0.005 mol) and $Ba(NO_3)_2$ (1.31 g, 0.005 mol) were dissolved separately in 10 cm^3 of water during heating on a water bath. Ascorbic acid (0.2 g) was added to the solution of $FeSO_4$ as a reducing agent. The solutions were mixed, and the solution with $BaSO_4$ precipitate was left for 2–3 h, then the $BaSO_4$ precipitate was filtered off. To the solution of $Fe(NO_3)_2$ obtained, 0.015 mol (2.49 g) of solid KI

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was added to the point where dissolution was complete, and also a warm solution of L (1.26 g, 0.015 mol) in ethanol. The precipitated white complex was filtered off, washed with ethanol and dried *in vacuo* over $Mg(ClO_4)_2$. All the precipitates obtained were washed and dried following this procedure. Yield of products was 70–80%. Found: C, 12.8; H, 2.1; Fe, 10.3; N, 31.0. Calc. for $C_6H_{12}FeI_2N_{12}$: C, 12.8; H, 2.2; Fe, 9.9; N, 29.9%.

$FeL_{2.5}(NCS)_2 \cdot H_2O$ (**II**). $FeSO_4 \cdot 7H_2O$ (0.70 g, 0.0025 mol) was dissolved in 5 cm^3 of H_2O along with ascorbic acid (0.15 g) and heated on a water bath. $Ba(NO_3)_2$ (0.65 g, 0.0025 mol) was also dissolved in 5–7 cm^3 of water. $BaSO_4$ was precipitated and the mixture left for 2–3 h at room temperature, and then filtered. The solution of $Fe(NO_3)_2$ thus obtained was mixed with a solution of KNCS (1.46 g, 0.0015 mol) in water (3–5 cm^3) and then with a warm solution of L (0.63 g, 0.0075 mol) in 2-propanol (10 cm^3). A white precipitate formed, which after drying became yellow–pink. Found: C, 20.9; H, 2.6; Fe, 13.7; N, 41.9. Calc. for $C_7H_{12}FeN_{12}OS_2$: C, 21.0; H, 3.0; Fe, 14.0; N, 42.0%.

The water content in complex **II** was determined by TGA. On the TG curve in the temperature range 50–90°C, there was a stage corresponding to 5% sample mass loss, and the calculated water content was 4.5%. The presence of water was confirmed by chemical analysis and IR spectroscopy. The iron content was determined by complexonometric analysis after decomposition of the sample in concentrated $HClO_4$ and concentrated H_2SO_4, or by atomic absorption spectroscopy. The compounds were insoluble in ethanol, acetone, DMSO, DMFA, and $CHCl_3$; they decomposed gradually in water.

Methods of study

Magnetic susceptibility of polycrystalline samples was measured using the Faraday method in a pumped out ampoule in the temperature range of 78–400 K. Effective magnetic moment was calculated with the formula $\mu_{eff} = (8\chi' T)^{1/2}$, where χ' is molar magnetic susceptibility corrected for diamagnetism. Mössbauer spectra were measured at 295 and 78 K with an NP-610 spectrometer using ^{57}Co as source. Chemical shifts were determined with respect to α-Fe at 295 K. For precision determination of shifts of complex LS forms, the method described in Ref. 8 was used. Diffuse reflection spectra (DRS) were recorded with a "Unicam-700 A" spectrometer. IR absorption spectra were recorded with a "Specord 75 IR" spectrophotometer in the range 400–3600 cm^{-1} and a "Specord M-80" in the range 200–600 cm^{-1}. The samples were measured using Nujol mulls and potassium bromide discs. X-ray data for the powers of the complexes were obtained with a DRON-UM I diffractometer with filtered copper radiation.

RESULTS AND DISCUSSION

Complexes of iron(II) iodide and thiocyanate with L were obtained from water–alcohol solutions ($C_{Fe} = 0.2$ mol dm^{-3}) using an L : Fe molar ratio of three. The composition of the solid phases obtained varied. Iron(II) iodide solution necessary for the synthesis of complex **I** may also be obtained by the reaction of BaI_2 and $FeSO_4$. Compounds **I** and **II** possess reversible thermochromism; at room temperature compound **I** is white and compound **II** is yellow–pink; when cooling they become pink, and at room temperature the initial colours are recovered.

Study of the dependence of μ_{eff} (T) for complex **I** and dehydration under experimental conditions for complex **II** showed that thermochromism of these compounds was connected with a change of the iron(II) spin state. The character of $\mu_{eff}(T)$ dependence for complexes **I** and **II** appeared to be different (Fig. 1). For compound **I**, a quite sharp spin transition $^5T_2 \rightleftharpoons {}^1A_1$ with hysteresis was observed, which is typical for compounds of iron(II) with Htrz and L containing Cl^-, Br^-, NO_3^-, BF_4^- and ClO_4^- ions synthesized previously.[4–6] Note that the transition characteristics (T_c and value of hysteresis) for complex **I** were somewhat different for the samples obtained using different synthesis procedures. This fact was not unexpected and confirmed the conclusion about the influence of the method of preparation on the spin transition characteristics.[2,4] For complex **I** obtained by different synthesis procedures, the following temperatures of direct (heating) and reverse (cooling) transitions were found (K): $T_c\uparrow = 270$–280, $T_c\downarrow = 260$–278. In contrast to **I**, for the dehydrated

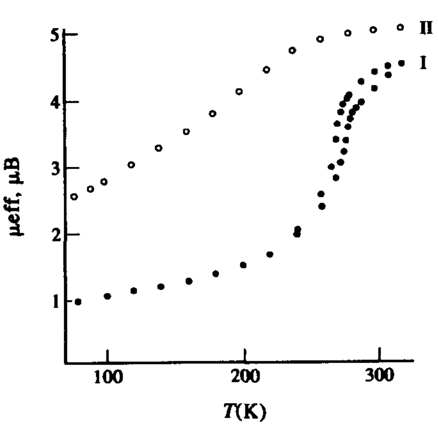

Fig. 1. $\mu_{eff}(T)$ dependence for complexes **I** and **II**.

complex **II**, a smooth dependence of $\mu_{eff}(T)$ was observed, and hysteresis was practically absent (Fig. 1). At the same time, for both compounds at room temperature, predominance of the HS state of iron(II) is characteristic.

DRS of complex **I** contain bands at 570 and 890 nm, and that of complex **II** at 530 and 920 nm. The first band is assigned to the $^1A_1 \rightleftharpoons {}^1T_1$ *d–d* transition in a distorted octahedral ligand field, and it is present in the spectra of all the complexes of composition FeL_3A_2,[4–6] in which the LS form dominates at room temperature. So, the presence of the LS form, on the DRS data, is noticeable in spite of the fact that the HS form dominates in **I** and **II** at room temperature. The second band in the DRS may be related to the $^5T_2 \rightleftharpoons {}^5E$ *d–d* transition. Its position coincides with the position of the corresponding band in the high-spin $Fe(Htrz)_2Cl_2$ spectrum.[4]

Mössbauer spectra of the complexes measured at 295 and 78 K are shown in Fig. 2, and spectral parameters are given in Table 1. The results obtained show that iron(II) ions in complex **I** at 295 K are mainly in the HS state (LS contribution is less than 5%), whereas at 75 K they are only in the LS state. Note that for the samples obtained by other synthesis procedures we observed more intensive lines of the LS form at 295 K. This corresponds to the data from magneto-chemical studies. The Mössbauer spectrum of the HS form of complex **I** at 295 K shows a quadrupole dublet ($I_1/I_2 = 1.12 \pm 0.03$) with lines of practically the same width ($\Gamma_1 = \Gamma_2 = 0.26$ mm s^{-1}) as in the case of $FeL_3(ClO_4)_2$[5] and $Fe_{0.5}Zn_{0.5}L_3(NO_3)_2$.[9] Its parameters, chemical shift and quadrupole splitting practically coincide with the spectral parameters of the present complexes. This shows that the local surroundings of iron(II) ions for the HS form of the compounds in all three cases is equivalent, i.e. there are no major differences in ionicity of the Fe—N bonds or degree of FeN_6 coordinational core distortion. The LS form spectrum of complex **I** at 78 K is similar to the $FeL_3(NO_3)_2$ spectrum chosen as a standard,[4] but a difference exists in enhancement of the δ and ε parameters, which is quite clear. This is evidence of some increase of the ionicity of Fe—N bonds and reduction of local symmetry surrounding the metal atom.

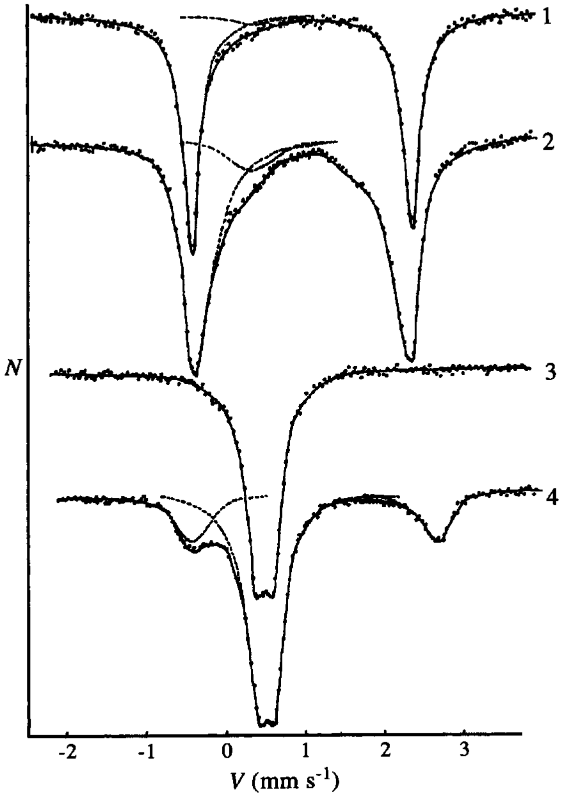

Fig. 2. Mössbauer spectra for complex **I** at 295 K (1) and 78 K (3), and complex **II** at 295 K (2) and 78 K (4).

To determine the nature of the asymmetry of lines observed at 295 K for complex **I**, we measured the Mössbauer spectra of a sample diluted with amorphous SiO_2, and also for an absorber oriented at an angle of 45° to the direction of gamma-quantal radiation. In these measurements, the value of the line asymmetry did not change. This allowed us to relate the asymmetry observed at 295 K to dynamic anisotropy of oscillations of iron atoms in the lattice, i.e. to the Goldansky–Kariagin effect.[10] This effect indicates different values of mean squared displacements of iron atoms along the $\langle z^2 \rangle$ chain and in the perpendicular directions ($\langle x^2 \rangle$, $\langle y^2 \rangle$). The difference $\langle z^2 \rangle - \langle x^2 \rangle$ is determined to be -1.50×10^{-18} cm^2 with the known method.[10] In this case, the electric potential gradient on iron nuclei appears to be lowest in energy in a crystal field of trigonal symmetry, and the FeN_6 octahedron should be distorted along the C_3 axis, i.e. along the chain.[11]

Quadrupole doublet lines of the HS form for complex **II** at 295 K are characterized by a noticeable broadening in comparison with the doublet lines of complex **I** ($\Gamma_1 = \Gamma_2 = 0.43$ mm s^{-1}), and they are also asymmetric; there is a moderate integral asymmetry there, and the inner slopes of the components are more gentle. This indicates that in the complex at 295 K more than one type of iron(II) ion in the HS state is present, and their local surroundings are somewhat different. In this case, for the bulk of iron(II) ions, there is relatively high quadrupole splitting observed, as shown in Table 1, and for other ions this parameter is lower. The chemical shift for the HS form at 295 K is typical for complexes of the class studied.

At 78 K, the spectral parameters of the HS form

Table 1. Mössbauer spectral parameters of complexes **I**, **II** and $FeL_3(NO_3)_2$

Compound	Spin state	$T = 295$ K		$T = 78$ K	
		δ (mm s^{-1})	ε (mm s^{-1})	δ (mm s^{-1})	ε (mm s^{-1})
$FeL_3(NO_3)_2$	LS	0.425 ± 0.001	0.20 ± 0.02	0.485 ± 0.002	0.23 ± 0.02
FeL_3I_2 (**I**)	HS	1.04 ± 0.02	2.79 ± 0.02	—	—
	LS	~ 0.42	~ 0.25	0.499 ± 0.002	0.30 ± 0.02
$FeL_{2.5}(NCS)_2 \cdot H_2O$ (**II**)	HS	1.04 ± 0.02	2.73 ± 0.02	1.16 ± 0.02	3.11 ± 0.02
	LS	~ 0.42	~ 0.25	0.519 ± 0.002	0.30 ± 0.02

for compound **II** are somewhat different: the value of δ at the expense of room temperature shift, and ε as a result of change of Boltzmann's population of $3d$ levels of iron(II) ions. The quadrupole doublet lines in this case remain broad. The LS form for complex **II** shows some chemical shift in comparison with $FeL_3(NO_3)_2$[4] and with complex **I**, and the same quadrupole splitting as in **I**, which indicates the same degree of coordinational core distortion in **I** and **II**.

The presence of non-equivalent types of iron(II) ions in the HS state is a fundamental structural particularity of complex II. This fact, and also the extended temperature dependence of $\mu_{eff}(T)$, set this complex apart from other compounds of the class studied. Presumably, there is a connection between the presence of non-equivalent iron(II) ions in the lattice of a compound and extended ST. It may be suggested that non-equivalent iron(II) ions pass into the LS state at different temperatures. We observed such ions but we do not know what it is connected with. We can only note that such iron(II) ion non-equivalence in the HS state has also been fixed for other systems.[12] Authors assigned them to splitting of the $^5T_2$ term in a crystal field of trigonal symmetry into $^5A_1$ and ^5E states.

In the low frequency IR spectra range of complexes **I** and **II**, there is an intense absorption band with a maximum at about 260 cm^{-1} which relates to ν(FeN) for the HS form of the iron(II) complexes.[4] The absence of bands of the LS form in these spectra is obviously caused by the fact that the recording was performed at a temperature higher than room temperature ($t \sim 37°$C). Under these conditions, complexes chiefly contain the HS form, that has been indicated by the $\mu_{eff}(T)$ dependence (Figs 1 and 2). Some splitting and a shoulder on the high-frequency side of this band are caused by the fact that L has an absorption band in the region of 300 cm^{-1}.

In the region of ring torsion vibrations (600–700 cm^{-1}) in spectra of complexes **I** and **II**, an intensive band at *ca* 620 cm^{-1} and a weak band at 680–700 cm^{-1} have been observed, which are evidence of preservation or only an insignificant distortion of C_{2v} symmetry, and the possibility of L coordination as a bidentate-bridge ligand (with N^1 and N^2 atoms) or/and as a monodentate with one of the ring nitrogen atoms. However, the shift of valence vibration band ν(NN) of the N—N exocyclic bond in the spectra of complexes **I** and **II** into high frequency range in comparison with the spectrum of L confirms bidentate-bridge L coordination.[13] In the L spectrum, there is an intense doublet at 1185–1204 cm^{-1}, and in the spectra of complexes **I** and **II** there is a mean intensity band at 1215 cm^{-1}. At the same time, in the spectrum of **II** the band with maximum 1215 cm^{-1} has a shoulder at 1200 cm^{-1}. In the authors' opinion, this suggests the presence of L coordinated monodentately, because in this case ν(NN) should be shifted into the high frequency range to a small degree.

The character of the ν(CN) and ν(CS) band shifts of the complexes' spectra in comparison with KNCS spectrum indicates the mode of thiocyanate ion coordination.[14,15] In the spectrum of compound **II**, the intense doublet band ν(CN) at 2065–2080 cm^{-1} is shifted to high frequency in comparison with the ν(CN) (2050 cm^{-1}) band for KNCS. At the same time, the weak ν(CS) band at 780 cm^{-1}[16] is shifted to higher frequency in comparison with the ν(CS) band at 745 cm^{-1} for KNCS. Such shifts of the ν(CN) and ν(CS) bands confirms NCS$^-$ ion coordination to iron(II) through the nitrogen atom. In the low frequency range of the spectrum it is difficult to separate the ν(FeN) band from the NCS$^-$ ion because of the superposition of the ν(FeN)(NCS) and ν(FeN)(L) bands, as in the case of complexes with 3,5-dimethylpyrazole.[17]

An analysis of all the data obtained allows us to conclude that there is distorted octahedral iron(II) coordination in complexes **I** and **II** and that the composition of the coordination core is FeN_6. Compound **I**, as with other complexes of FeL_3A_2 composition,[4,5] appears to have a polynuclear structure, analogous to the $CuL_3(ClO_4)_2$ structure.[13] An unlimited linear chain with metal atoms bonded together by three bidentate bridging L molecules is a structural unit in these compounds. The ligand is coordinated by N^1 and N^2 ring atoms. Cooperative effects connected with the presence of a polymeric structure cause a sharp change of μ_{eff}[12,18,19] for complex **I**. For compound **II**, the structure is most likely to be dimeric, the same as in Mn_2(4-methyl-1,2,4-triazole)$_5(NCS)_4$.[20] In this compound, the manganese atom has a distorted octahedral MnN_6 core, which is formed by N^1 and N^2 atoms of three bidentate-bridge molecules of a ligand, nitrogen atoms of two molecules of a ligand coordinated monodentately and two NCS^- groups. Anion coordination, and also the iron(II) atoms' non-equivalence, may lead the $\mu_{eff}(T)$ curves for compound **II** to become more gradual.

Determination of the T_c value for FeL_3I_2 and the data[4,5] allowed us to enlarge the row of temperature (K) change of direct spin transition for the complexes of the FeL_3A_2 composition depending on A: ClO_4^- (210) < I^- (270–280) < Br^- (312) < BF_4^- (335) < NO_3^- (342). It is clear that there is no direct dependence of T_c on the anion's size and nature. Since the NH_2 group tends to form a hydrogen bond with atoms, we have tried to follow, in the IR spectra, the position of valence vibration ν(NH) frequencies in complexes with different anions. The analysis of IR spectra in the 3000–4000 cm^{-1} range indicated that, depending on the anion, the values of ν(NH) in complexes of composition FeL_3A_2 fall in the following order:

$$ClO_4^- > NO_3^- > I^- > Br^- > BF_4^-.$$

It is clear that there is no direct dependence between T_c and anion capacity for hydrogen bonding.

An essential dependence of T_c for FeL_3A_2 complexes on the anion's nature holds much promise for a further search for new thermochromic compounds of composition FeL_3A_2 by varying the anion in order to synthesize substances with a reversible change of colour in a desirable temperature range.

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