Inorganica Chimica Acta 363 (2010) 4059–4064

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# High-temperature spin-crossover in coordination compounds of iron(II) with tris(pyrazol-1-yl)methane

O.G. Shakirova [a], L.G. Lavrenova [a,c], V.A. Daletsky [a], E.A. Shusharina [a,c], T.P. Griaznova [b], S.A. Katsyuba [b,*], V.V. Syakaev [b], V.V. Skripacheva [b], A.R. Mustafina [b], S.E. Solovieva [b]

[a] A.V. Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk 630090, Russia
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russia
[c] Novosibirsk State University, Pirogov Str. 2, Novosibirsk 630090, Russia

## ARTICLE INFO

*Article history:*
Received 21 May 2010
Received in revised form 29 July 2010
Accepted 7 August 2010
Available online 12 August 2010

*Keywords:*
Inclusion
p-Sulfonatothiacalix[4]arene
Crystal structure
IR
NMR

## ABSTRACT

Novel mononuclear Fe(II) complexes of tris(pyrazol-1-yl)methane $[Fe\{HC(pz)_3\}_2]^{2+}$ with $SiF_6^{2-}$ and p-sulfonatothiacalix[4]arene ($TCAS^{4-}$) as counterions were obtained. The compounds were characterized by magnetic susceptibility method, IR and UV–Vis spectroscopy. The structure of $[Fe\{HC(pz)_3\}_2]SiF_6$ has been analyzed by single-crystal X-ray diffraction. The $^1H$ NMR spectroscopy measurements of $[Fe\{HC(pz)_3\}_2]_2(TCAS)$ in aqueous solution reveal the outer sphere inclusion of $[Fe\{HC(pz)_3\}_2]^{2+}$ into the cyclophanic cavity of $TCAS^{4-}$. The temperature induced spin-crossover $^1A_1 \Leftrightarrow {}^5T_2$, accompanied by thermochromism, has been revealed from the temperature dependence of $\mu_{eff}$ and IR spectra for both complexes. The comparative analysis of magnetochemical and spectroscopy data elucidates the effect of the cyclophanic counterion on the physico-chemical properties of Fe(II) complex.

## 1. Introduction

Coordination compounds with $d^4$–$d^7$ electronic configuration in octahedral ligand environment have gained much attention due to their spin-crossover (SCO) behavior [1–8]. The reversible transfer from the low spin (LS) to high spin (HS) states can be induced by external input, such as temperature, pressure or light irradiation. Complexes with rather long lifetimes of LS and HS states are of great interest, both from a fundamental perspective and for potential application in molecular devices [8,9]. The complexes, which are changing their colour under SCO, gain the enhanced attention due to their particular importance for practical application. Complexes of Fe(II) with some polynitrogen-containing ligands, such as 1,2,4-triazole, tetrazole and their derivatives exemplify the thermochromic SCO complexes [5]. The SCO behavior, including abruptness, temperature and completeness of SCO transition, is greatly dependent on ligands' structure (a nature of substituents is of particular importance), counterion and solvent effects [2,10–14]. The large series of thermochromic complexes of Fe(II) with 1,2,4-triazoles of formula $Fe(4\text{-}Rtrz)_3A_n{\cdot}mH_2O$ (R = H, $NH_2$; $n = 1, 2$; $m = 0, 1$) was obtained by the Novosibirsk group [5,10–12]. These complexes are of polynuclear chain structure with ferrous ion being in the octahedral environment, where the coordination core is $FeN_6$. Most of the complexes demonstrate an abrupt SCO $^1A_1 \Leftrightarrow {}^5T_2$ with hysteresis on the temperature curves of the effective magnetic moment ($\mu_{eff}$) and thermochromism [5,10–12]. The temperature of SCO depends on the composition of the compounds and varies from 200 to 400 K.

The series of Fe(II) complexes with tris(pyrazol-1-yl)methane ($HC(pz)_3$, Scheme 1) $[Fe\{HC(pz)_3\}_2]A_2{\cdot}nH_2O$, $A = Cl^-$, $Br^-$, $I^-$, $1/2SO_4^{2-}$, $n = 0$–7 also demonstrate SCO and thermochromism, SCO temperatures ($T_c$) being within the range of 400–445 K [15].

The references [16–21] represent the synthesis of Fe(II) complexes of $HC(pz)_3$ with various counterions, but some of these reports lack the magnetical measurements. The significant counter-ion and solvent effects on the SCO behavior ($T_c$ in particular) were revealed for the series of $[Fe\{HC(pz)_3\}_2]A_2{\cdot}nH_2O$, $A = Cl^-$, $Br^-$, $I^-$, $1/2SO_4^{2-}$, $n = 0$–7 [15]. Though the effect of the counter ion is well known, it is not entirely predictable. Macrocyclic anions represent rather interesting alternative as counterions for SCO complexes, while at the moment these data are very rare, if any. The sulfonated derivatives of calix[$n$]arenes represent the series of highly charged polyanions, which can serve as counterions for $[Fe\{HC(pz)_3\}_2]^{2+}$. p-Sulfonatothiacalix[4]arene ($TCAS^{4-}$) is one of the promising outer-sphere counterions for positively charged

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* Corresponding author. Tel.: +7 843 27 318 92; fax: +7 843 27 322 53.
*E-mail addresses:* shakirova_olga@mail.ru (O.G. Shakirova), ludm@niic.nsc.ru (L.G. Lavrenova), dalvas@niic.nsc.ru (V.A. Daletsky), knilav@ngs.ru (E.A. Shusharina), gryaznovat@iopc.ru (T.P. Griaznova), skatsyuba@yahoo.com, katsyuba@iopc.ru (S.A. Katsyuba), vsyakaev@iopc.ru (V.V. Syakaev), viktoriya@iopc.ru (V.V. Skripacheva), asiya@iopc.ru (A.R. Mustafina), svsol@iopc.ru (S.E. Solovieva).

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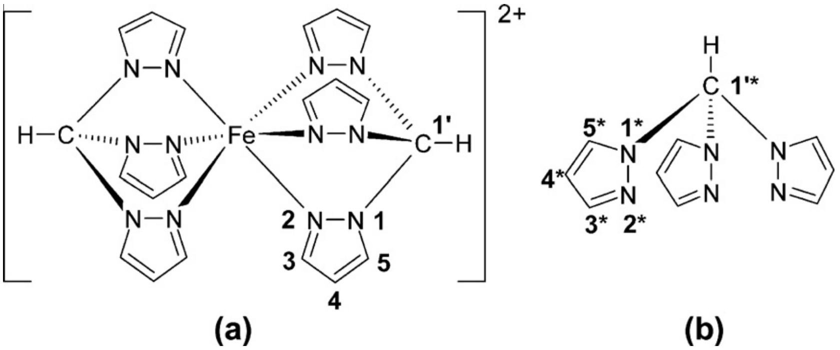
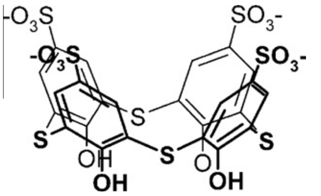
doi:10.1016/j.ica.2010.08.013



**Scheme 1.** Schematic representation of $[Fe\{HC(pz)_3\}_2]^{2+}$ (a) and ligand $HC(pz)_3$ (b).



**Scheme 2.** Tetraanion of p-sulfonatothiacalix[4]arene ($TCAS^{4-}$).

complexes (Scheme 2) [22,27]. Therefore the present work extends the range of the outer sphere anions of $[Fe\{HC(pz)_3\}_2]^{2+}$ by adding p-sulfonatothiacalix[4]arene ($TCAS^{4-}$) and $SiF_6^{2-}$. The latter anion is chosen because of its previously revealed dramatic effect on SCO behavior of Fe(II) complexes, which was rather different for various ligands [11]. The most important peculiar feature of $TCAS^{4-}$ as the outer-sphere counterion is the presence of the hydrophobic cavity decorated with four $-SO_3Na$ groups, which easily dissociate in aqueous solutions, providing tetra-anion with high affinity towards positively charged metal complexes (Scheme 2). Thus the present work introduces the synthesis of $[Fe\{HC(pz)_3\}_2]^{2+}$ complexes with $TCAS^{4-}$ and $SiF_6^{2-}$ as counterions and the comparative analysis of their magnetic and spectral properties.

## 2. Experimental

$FeSO_4 \cdot 7H_2O$ from Sigma was purified by recrystallization from acidified aqueous solution. Ascorbic acid from ICN Biomedical, $Ba(NO_3)_2$, $(NH_4)_2SiF_6$, acetone from Aldrich were used as purchased. Tris(pyrizol-1-yl)methane was synthesized in accordance with the improved procedure [30]. $Na_4[TCAS]$ was synthesized according to procedure [31].

All aqueous solutions were prepared with bidistilled water.

### *2.1. Synthesis of $[Fe\{HC(pz)_3\}_2]SiF_6$ (I)*

A 1 mmol (0.28 g) of $FeSO_4 \cdot 7H_2O$ was dissolved in 3 ml of distilled water, acidified by 0.1 g of ascorbic acid. A solution of $Ba(NO_3)_2$ (1 mmol, 0.26 g) in 7 ml of water was slowly added to the solution obtained. The precipitate of the barium sulfate was removed from solution. A solution of tris(pyrazol-1-yl)methane (0.43 g, 2 mmol) in acetone (5 ml) was added to the resulting aqueous solution of iron(II) nitrate and then an aqueous solution (7 ml) of $(NH_4)_2SiF_6$ (2 mmol, 0.36 g) was rapidly added. Immediately after mixing of the initial solutions, a purple precipitate was formed, which was magnetically stirred for 1 h. The precipitate was transferred onto a filter, washed with water and ethanol, dried in air and in a dessicator over anhydrone. Yield ~88%. IR (nujol/perfluorinated nujol, $cm^{-1}$): 3129, 3053 $cm^{-1}$ ($\nu_{CH}$); 1573–1533, 1516, 1446 $cm^{-1}$ (ring stretchings), 715 $cm^{-1}$ ($\nu_{SiF}$), 478 $cm^{-1}$ ($\delta_{SiF}$). *Anal.* Calc. for $C_{20}H_{20}F_6FeN_{12}Si$ (626.38): C, 38.4; H, 3.2; N, 26.8; Fe, 8.9. Found: C, 38.2; H, 3.4; N, 26.6; Fe, 8.5%.

The single crystals suitable for X-ray diffraction were selected from the bulk of the precipitate and according to powder X-ray diffraction data they corresponded to a composition of polycrystalline sample.

### *2.2. Synthesis of $[Fe\{HC(pz)_3\}_2]_2(TCAS)$ (II)*

A weighed portion of $[Fe\{HC(pz)_3\}_2]SiF_6$ (0.025 g, 0.04 mmol) was dissolved in distilled water (10 ml) under heating. A solution of $Na_4[TCAS]$ (0.0362 g, 0.04 mmol) in water (10 ml) was added to the solution of $[Fe\{HC(pz)_3\}_2]SiF_6$. Both solutions were deoxygenated through bubbling of argon. Immediately after mixing of the initial solutions, a purple precipitate was formed, which was magnetically stirred for 1 h. The precipitate was transferred onto a filter, washed with water, dried in air and in a dessicator over anhydrone. Yield ~70%. IR (nujol/perfluorinated nujol, $cm^{-1}$): 3374 $cm^{-1}$ ($\nu_{OH}$); 3125, 2984 $cm^{-1}$ ($\nu_{CH}$); 1562, 1516, 1446 $cm^{-1}$ (ring stretchings), 1280–1248 $cm^{-1}$ ($\nu_{SO}$). *Anal.* Calc. for $C_{64}H_{52}O_{16}Fe_2N_{24}S_8$ (1781.44): C, 43.2; H, 2.9; N, 18.9; Fe, 6.3. Found: C, 43.3; H, 2.6; N, 18.3; Fe, 6.2%.

### *2.3. Methods*

The elemental (C, H, N) analysis was performed on EURO EA 3000 (EuroVector). The analysis of metal content was performed by EDTA titration after thermal decomposition of complexes in a mixture of concentrated $H_2SO_4$ and $HClO_4$ (1:2).

X-ray diffraction study of complex I was carried out by a standard procedure on an automated four circle Bruker Nonius X8Apex diffractometer equipped with a two-dimensional CCD-detector at 150(2) K (Mo Kα-radiation, $\lambda = 0.71073$ Å, graphite monochromator). The single crystal dimensions were 0.37 × 0.08 × 0.07 mm. The reflection intensities were measured by $\varphi$ scanning of narrow (0.5°) frames. The absorption corrections were applied empirically by the SADABS program. The structure was solved by the direct method and refined by full matrix least-squares in the anisotropic approximation for nonhydrogen atoms using SHELXTL software [32]. All hydrogen atoms were located geometrically. The X-ray experiment details and crystallographic characteristics for complex I are presented in Table 1. Table 2 contains interatomic distances for $FeC_{20}N_{12}H_{20}SiF_6$. The static magnetic susceptibility of polycrystalline samples was measured by a Faraday method in the temperature range of 275–500 K at an external magnetic field strength of up to 5 kOe. The effective magnetic moments were calculated as $\mu_{eff} = (8\chi'_M T)^{1/2}$, where $\chi'_M$ is the molar magnetic susceptibility, corrected for diamagnetism. The heating (cooling) rate in the field of SCO was 0.5 K/min.