ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 8, pp. 1945–1951. © Pleiades Publishing, Ltd., 2015.

Extraction–Spectrophotometric and Theoretical (Hartree–Fock) Investigations of a Ternary Complex of Iron(II) with 4-Nitrocatechol and 2,3,5-Triphenyl-2*H*-tetrazolium[1]

K. B. Gavazov, V. B. Delchev, G. K. Toncheva, and Z. G. Georgieva

Faculty of Chemistry, University of Plovdiv "Paisii Hilendarskii," 24 Tsar Assen Str., 4000 Plovdiv, Bulgaria
e-mail: kgavazov@abv.bg

Received April 13, 2015

Abstract—The complex formation and solvent extraction were studied in a system containing iron(II), 4-nitrocatechol (4NC), 2,3,5-triphenyl-2*H*-tetrazolium chloride (TTC), water, and chloroform. Under the optimum conditions, the extracted complex has a composition of 1 : 1 : 2 (Fe–4NC–TTC) and could be represented with the formula $(TT^+)_2[Fe^{II}(4NC^{2-})(OH)_2]$. Theoretical calculations were performed at the HF/3-21G* level in order to elucidate the geometric structure of the complex and electron distribution according to the crystal field theory. The results showed that the most stable configuration is tetrahedral low-spin structure. Some equilibrium constants (association, distribution, and extraction) and characteristics (absorption maximum, molar absorption coefficient, recovery factor, Beer's law limits, etc.) concerning the application potential of the studied extraction–chromogenic system were determined.

Keywords: iron(II), 4-nitrobenzene-1,2-diol, liquid–liquid extraction, ion association, HF calculations, ground-state optimizations

DOI: 10.1134/S1070363215080241

Iron is a transition metal which is widely spread in earth's crust and invariably present in all natural products. Its typical oxidation states are 3+ and 2+. The complexation behaviour of iron(III) toward 4-nitrobenzene-1,2-diol (4-nitrocatechol, 4NC), a nitroaromatic compound of interest in various scientific areas (biochemistry, environmental chemistry, enzymology, analytical chemistry, pharmacology, etc.) [1, 2], has been well studied in connection with non-heme iron-containing enzymes [3–6], design of chelators for treating iron overload [7, 8], surface chemistry [9], chemistry of marine environment [10], stability assessment [11, 12], and applicability to spectrophotometric analysis [12, 13]. However, the data for systems containing iron(II) and 4NC are relatively scarce. Tyson [5] has reported the absorption maximum and molar absorption coefficient of the 1 : 1 Fe(II)–4NC complex at pH = 8.5. Nepal and Dubey [14] have studied potentiometrically the complex formation between Fe(II) and 4-NC in aqueous solution. They have reported the formation of 1 : 1 and 1 : 2 Fe–4NC complexes and concluded that these complexes exhibit abnormal stability due to very high crystal field stabilization energy (CFSE). Dong and Lai [6] have investigated by quantum mechanical/molecular mechanical calculations the reaction mechanism of the dioxygen activation by a non-heme Fe(II)-containing enzyme with 4NC as a substrate.

We previously reported [13] a liquid–liquid extraction–chromogenic system containing Fe(III), 4NC, and a widely used [15–26] cationic ion-association reagent, 2,3,5-triphenyl-2*H*-tetrazolium chloride (TTC). The next step, study of a similar system containing Fe(II) instead of Fe(III), is accomplished here. Having in mind the obtained results (a simple 1 : 1 : 2 composition of the extracted Fe–4NC–TTC complex), we extended the scope of our investigations by including theoretical calculations at the HF/3-21G* level.

Liquid–liquid extraction–spectrophotometric optimization. Figure 1 shows the electronic absorption spectra in chloroform of the ternary complex extracted at different pH values. They are characterized by two maxima at about λ = 437–438 and 495 nm. The short-wave maximum is more intense. However, due to the high absorbance of the blank solution at λ = 437–438 nm, the maximum at λ = 495 nm is more suitable for spectrophotometric measurements.

---

[1] The text was submitted by the authors in English.

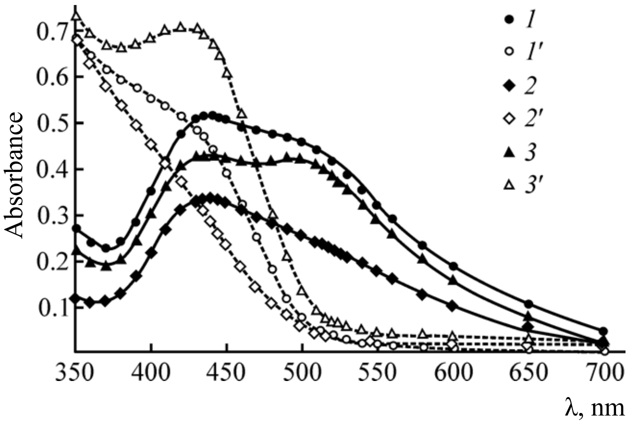

Fig. 1. Electronic absorption spectra of the (*1–3*) chloroform-extracted ternary complex [Fe(II)–4NC–TTC] and (*1′–3′*) blank solutions (4NC–TTC) at pH (*1*, *1′*) 6.0, (*2*, *2′*) 5.5, and (*3*, *3′*) 6.5; $c_{\mathrm{Fe(II)}} = 5.2 \times 10^{-5}$ M, $c_{\mathrm{4NC}} = 3.0 \times 10^{-4}$ M, $c_{\mathrm{TTC}} = 6.0 \times 10^{-4}$ M.

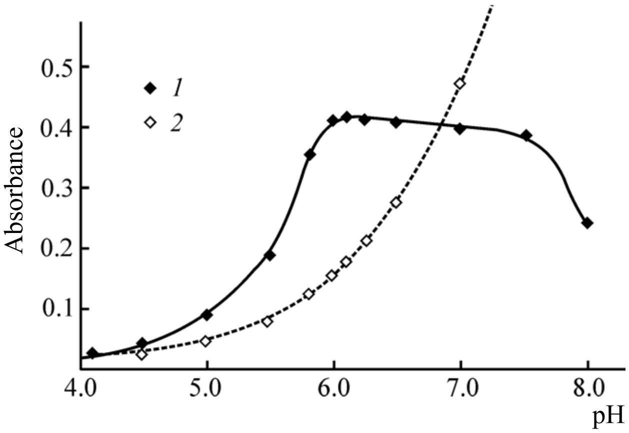

Fig. 2. Effect of pH on the absorbance (λ = 495 nm) of the (*1*) extracted ternary complex and (*2*) blank; $c_{\mathrm{Fe(II)}} = 4.5 \times 10^{-5}$ M, $c_{\mathrm{4NC}} = 4.0 \times 10^{-4}$ M, $c_{\mathrm{TTC}} = 1.2 \times 10^{-4}$ M.

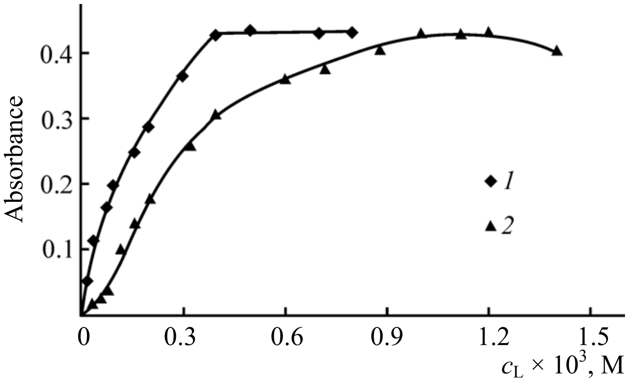

Fig. 3. Effect of the ligand (L) concentration on the absorbance (λ = 495 nm) of the extracted ternary complex: (*1*) L = 4NC, $c_{\mathrm{Fe(II)}} = 4.5 \times 10^{-5}$ M, $c_{\mathrm{TTC}} = 1.2 \times 10^{-4}$ M; (*2*) L = TTC, $c_{\mathrm{Fe(II)}} = 4.5 \times 10^{-5}$ M, $c_{\mathrm{4NC}} = 4.0 \times 10^{-4}$ M.

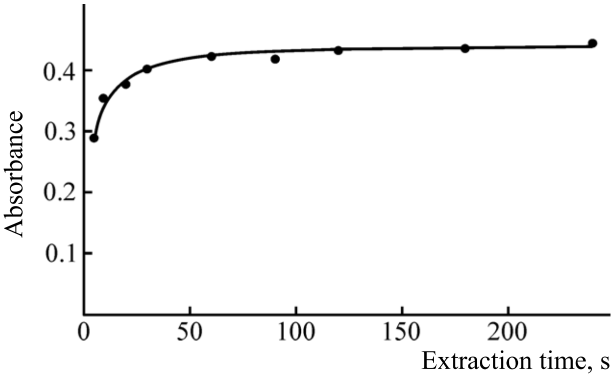

Fig. 4. Effect of the extraction time on the absorbance (λ = 495 nm) of the extracted ternary complex; $c_{\mathrm{Fe(II)}} = 4.5 \times 10^{-5}$ M, $c_{\mathrm{4NC}} = 4.0 \times 10^{-4}$ M, $c_{\mathrm{TTC}} = 1.0 \times 10^{-4}$ M.

The following other parameters were optimized: pH, concentration of the reagents, and shaking time (Figs. 2–4). The optimal conditions are given in Table 1.

Composition and formula. The molar 4NC-to-Fe(II) and TTC-to-Fe(II) ratios were determined by the mobile equilibrium method [27] (Fig. 5) and by the Asmus straight-line method [28]. The experimental data presented in Fig. 3 were used for this purpose. The results showed that the extracted ternary complex has a composition of 1 : 1 : 2 (Fe–4NC–TTC). One can conclude that the Fe(II)–4NC anionic chelate has a double negative charge, since TTC forms monovalent cation (TT^+) [13, 15–26] and the Fe(II)-to-TTC molar ratio is 1 : 2 (Fig. 5, *2*). Considering the 1 : 1 Fe-to-4NC molar ratio (Fig. 5, *1*) and the ability of Fe(II) to hydrolyze and form complexes with a coordination number of 4 [29, 30], we suggest the following formula of the extracted complex: $(TT^+)_2[Fe^{II}(4NC^{2-})(OH)_2]$.

Ground-state equilibrium geometry. In order to clarify the structure of the suggested complex, we performed theoretical calculations at the Hartree–Fock level using 3-21G* basis set. We optimized two structures with different spin multiplicities, quintet (Fig. 6) and triplet (Fig. 7), which correspond to the low- and high-spin complexes.

As seen from Fig. 6, the quintet system shows some close interactions between the 4NC oxygen atoms and TT^+. Most commonly they are of the $O_{4NC}\cdots H_{Ph\text{-}TT+}$ type. The nitro group of 4NC participates in close interactions with hydrogen atoms of the benzene rings of TT^+. With regard to the coordination environment of Fe(II), one can see that the structure of the complex is tetrahedral. The two HO–Fe(II) bonds are about 1.8 Å long which agrees well with the previously reported dioxygen complex of Fe(II) [31]. The Fe–O_{4NC} bonds are slightly longer, and the $O_{4NC}FeO_{4NC}$ angle is quite small (84.7°) as a result of the chelate ring strain. It should be mentioned that the Fe–O_{4NC} bond lengths are close to those formed between Al(III) and the catechol oxygen atoms in the Al(III)–4NC octahedral 1 : 1 and 1 : 2 complexes [32]. They are shorter than the corresponding V–O and W–O bonds in the V(V) and W(VI) complexes with 3,5-dinitrocatechol [33].

On the basis of the crystal field theory, we calculated the energies of the ligand field and isotropic field which were used to determine the CFSE of the low- (electron configuration $e^4t_2^2$) and high-spin (electron configuration $e^3t_2^3$) tetrahedral complexes. The 3*d*-AO is split into two groups of orbitals, $e(3d_{z^2}, 3d_{x^2-y^2})$ and $t_2(3d_{xy}, 3d_{xz}, 3d_{yz})$ with the energies $E_e = -0.6\Delta$ and $E_{t2} = 0.4\Delta$. As the splitting parameter Δ we took the absorption maximum of the complex, $\Delta = \lambda_{\max} = 437.5$ nm = 22 857 cm^{-1}. The data obtained are listed in Table 2. They show that the low-spin complex should be more stable than the high-spin one in the tetrahedral ligand field.

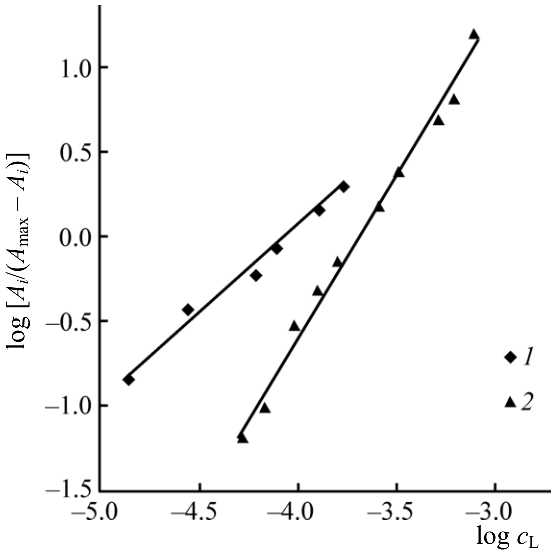

Fig. 5. Determination of the ligand-to-Fe(II) molar ratios by the mobile equilibrium method: (*1*) L = 4NC, $y = 1.01x + 4.08$; (*2*) L = TTC, $y = 1.92x + 7.07$.

The second Fe(II)-4NC-TT complex with a triplet spin multiplicity (two single electrons, corresponding

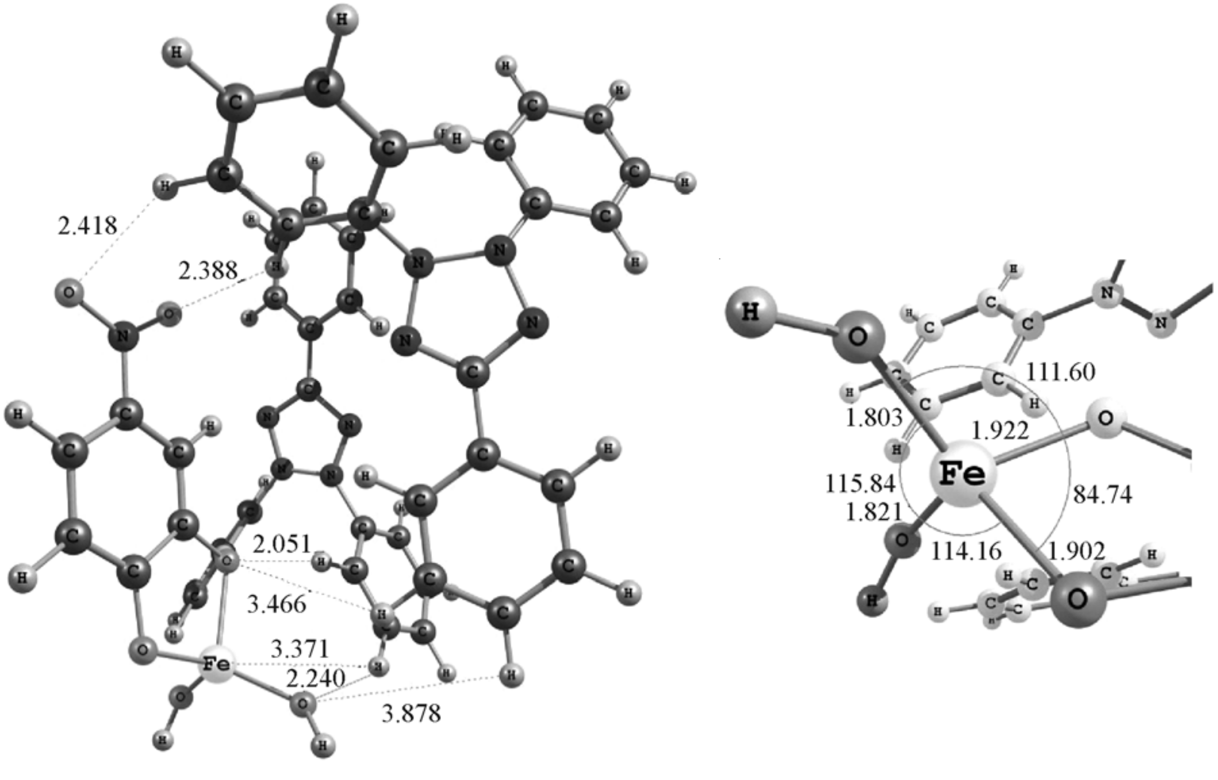

Fig. 6. Optimized ground-state geometry of the Fe(II)–4NC–TT complex with a quintet spin multiplicity.

Table 1. Extraction–spectrophotometric optimization of the system Fe(II)-4NC-TTC-water-chloroform

Parameter	Optimization range	Optimal value/ range	Figure
Wavelength, nm	Visible range	495	Fig. 1
pH of the aqueous phase	4–8	6	Fig. 2
Concentration of 4NC, M	$(0.2–8.0) \times 10^{-4}$	$(4.0–5.0) \times 10^{-4}$	Fig. 3
Concentration of TTC, M	$(0.4–14) \times 10^{-4}$	$(1.0–1.2) \times 10^{-3}$	Fig. 3
Extraction time, s	5–240	120	Fig. 4

to the low-spin complex mentioned above) was optimized starting from the optimized geometry of the tetrahedral complex. The optimization led to a structure with square–planar configuration of Fe(II) and oxygen atoms of the ligands (Fig. 7). This part of the complex forms an irregular square with slightly deformed plane: the dihedral angles $O^1O^2O^3O^4$ and $O^2O^3O^4O^1$ are –29.8° and 28.8°, respectively. The transformation tetrahedral → square–planar is characterized by a heat effect of $\Delta H = 555.3$ kJ/mol.

Extraction equilibrium constants. The following equilibria should be considered for the extraction system.

Table 2. Calculated ligand and isotropic filed energies and CFSEs of the tetrahedral complex

Crystal field parameter	Low-spin $e^4t_2^2$	High spin $e^3t_2^3$
$E_{\mathrm{l.f.}}$, cm^{-1}	1728.6	5437.7
$E_{\mathrm{i.f.}} = P$, cm^{-1}	19150.0	19150.0
CFSE, cm^{-1}	–17421.4	–13714.3

(1) Ion-associate formation in the aqueous phase:

$$2TT^+ + [Fe(OH)_2(L)]^{2-} \overset{\beta}{\rightleftarrows} (TT^+)_2[Fe(OH)_2(L)]^0, \quad (1)$$

$$\beta = [(TT^+)_2[Fe(4NC)(OH)_2]]/[TT^+]^2 \times [Fe(4NC)(OH)_2].$$

(2) Distribution of the complex between the aqueous and chloroform phases:

$$(TT^+)_2[Fe(4NC)(OH)_2]_{aq} \overset{K_D}{\rightleftarrows} (TT^+)_2[Fe(4NC)(OH)_2]_{org}, \quad (2)$$

$$K_D = [(TT^+)_2[Fe(4NC)(OH)_2]]_{org}/[(TT^+)_2[Fe(4NC)(OH)_2]]_{aq}.$$

(3) Extraction from water to chloroform:

$$2TT^+_{aq} + [Fe(4NC)(OH)_2]^{2-}_{aq} \overset{K_{ex}}{\rightleftarrows} (TT^+)_2[Fe(4NC)(OH)_2]_{org}, \quad (3)$$

$$K_{ex} = [(TT^+)_2[Fe(4NC)(OH)_2]]_{org} / [TT^+]^2_{aq}[Fe(4NC)(OH)_2]_{aq}.$$

The calculated values of these constants are shown in Table 3 along with those obtained for the analogous system containing Fe(III) [13]. The association constant β was determined by the mobile equilibrium method [27] (Fig. 5, *2*) and Holme–Langmyhr method

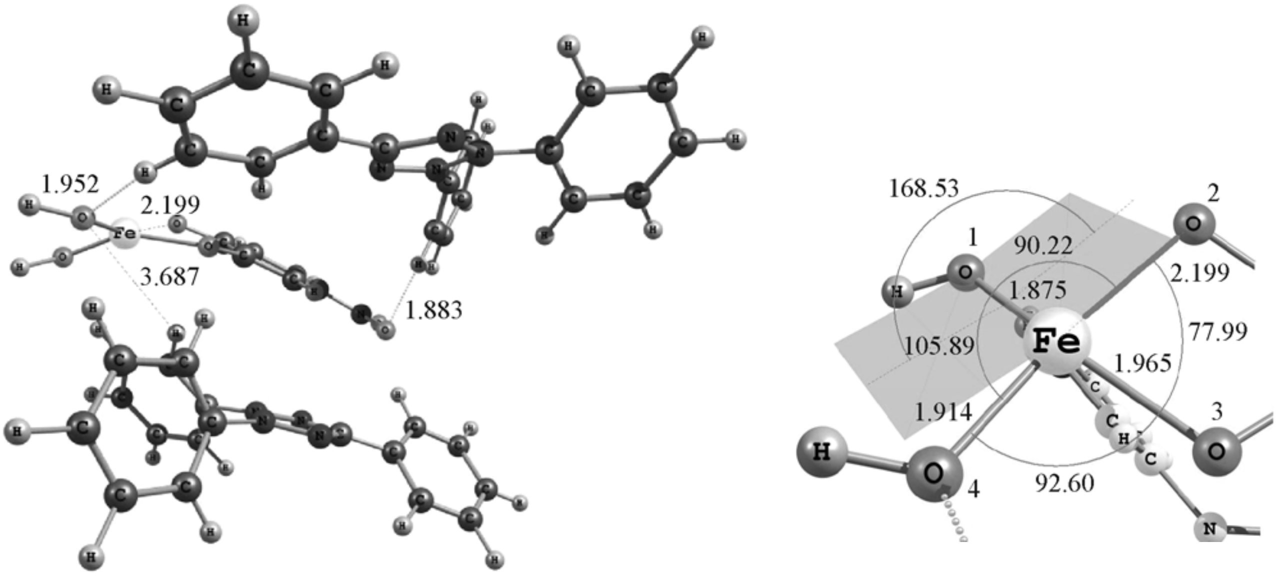

Fig. 7. Optimized ground-state geometry of the Fe(II)–4NC–TT complex with a triplet spin multiplicity.

Table 3. Calculated equilibrium constants (confidence probability 95%) for the extraction systems containing 4NC, TTC, and Fe(II) or Fe(III)

Constant	Extraction system	
	$[Fe^{II}(OH)_2(4NC)]^{2-}$–$TT^+$–water–chloroform	$[Fe^{III}(4NC)_3]^{3-}$–TT^+–water–chloroform [13]
$\log\beta$	7.36 ± 0.05^a ($n = 10$) 7.4 ± 0.2^b ($n = 10$)	11.3 ± 0.1^a ($n = 5$) 11.0 ± 0.2^b ($n = 7$)
$\log K_D$	1.44 ± 0.02^c ($n = 3$)	1.49 ± 0.02^c ($n = 3$)
$\log K_{ex}$	8.80 ± 0.07^d	12.8 ± 0.1^d

[a] Holme–Langmyhr method. [b] Mobile equilibrium method. [c] Calculated by the formula $K_D = A_1/(A_3 - A_1)$. [d] Calculated by the formula $\log K_{ex} = \log K_D + \log\beta$, where β was determined by the Holme–Langmyhr method.

[34]. The distribution constant (K_D) was calculated from the absorbance after single and triple extractions. The extraction constant (K_{ex}) was calculated by the equation $\log K_{ex} = \log\beta + \log K_D$.

Calibration graph characteristics. The relation between the concentration of Fe(II) and absorbance of the extracted complex was studied under the optimum conditions. A good linearity was obtained in the concentration range from 0.5 to 6.0 μg cm^{-3} (r = 0.9991, n = 7). The linear regression equation was $A = 0.170\,c + 0.007$, where A is the absorbance and c is the concentration of Fe(II) (μg cm^{-3}). The standard deviations of the slope and intercept were 0.004 and 0.008, respectively. The detection (DL) and quantitation limits (QL) were calculated as 3 and 10 standard deviations of the intercept divided by the slope [35] and were DL = 0.15 μg cm^{-3} and QL = 0.50 μg cm^{-3}. The molar absorption coefficient (ε) and Sandell's sensitivity (SS) were $\varepsilon_{495} = 9.5 \times 10^3$ L mol^{-1} cm^{-1} and $SS_{495} = 5.9 \times 10^{-3}$ μg cm^{-2}.

Thus, Fe(II) forms an ion-association complex, $(TT^+)_2[Fe(OH)_2(4NC)]$, with 4-nitrobenzene-1,2-diol (4NC) and 2,3,5-triphenyltetrazolium chloride. The anionic part of the complex, $[Fe(OH)_2(4NC)]^{2-}$, contains iron(II) in tetrahedral coordination. Two bulky hydrophobic triphenyltetrazolium cations (TT^+) ensure electroneutrality and complete transfer of the complex into organic phase. The results presented in this work highlight the differences between Fe(II) and Fe(III) regarding their ability to form extractable ternary complexes and enrich the knowledge of the coordination and extraction chemistry of Fe(II).

EXPERIMENTAL

Iron(II) solutions (9×10^{-4} M) were prepared every day by dissolving the required amount of ferrous ammonium sulphate hexahydrate in double-distilled water acidified with dilute sulfuric acid (pH ~ 1) [36, 37]. Aqueous solutions of 4-nitrobenzene-1,2-diol (2×10^{-3} M, Fluka) and 2,3,5-triphenyl-2*H*-tetrazolium chloride (4×10^{-3} M, Loba Feinchemie) were used. The organic solvent (chloroform) was redistilled and used repeatedly. The acidity of the aqueous medium was adjusted by means of a buffer solution prepared by mixing 2 M aqueous solutions of CH_3COOH and NH_4OH. The resulting pH was checked by a Hanna HI 83140 pH meter. A Camspec M508 spectrophotometer (United Kingdom) equipped with 1-cm cells was used for the absorption measurements.

Determination of the optimal extraction conditions. Aliquots of Fe(II), 4NC, and TTC solutions and buffer solution (3 mL) were introduced into separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL, 10 mL of chloroform was added, and the mixtures were shaken for extraction. Portions of the organic extracts were transferred through paper filters into spectrophotometric cells, and the absorbances were measured against the corresponding blank samples.

Determination of the distribution constant. The distribution constant K_D was calculated by the formula $K_D = A_1/(A_3 - A_1)$, where A_1 is the absorbance obtained after a single extraction (under the optimal extraction conditions, Table 1), and A_3 is the absorbance obtained after a triple extraction under the same conditions. The final volume of the solutions in both cases was 25 mL [13].

Theoretical calculations. The ground-state geometries of the complexes were optimized at the Hartree–Fock level of theory using 3-21G* basis functions for each atom. The spin multiplicities of the complexes were set to quintet and triplet, which implied four and two single electrons of Fe(II) distributed among the split 3*d*-AO. The charge of the system is zero. Initially, we optimized separately the anionic complex $[Fe(4NC)(OH)_2]^{2-}$ and the tetrazolium cation TT^+. Subsequently we constructed the whole electroneutral complex in order to find out its electronic and geometric structure.

The stability of the low- and high-spin complexes in the tetrahedral ligand field was estimated by CFSE which was calculated by the equation CFSE = $E_{l.f.} - E_{i.f.}$, where $E_{l.f.}$ and $E_{i.f.}$ are the ligand and isotropic field energies, respectively. For the low- and high-spin tetrahedral complexes of Fe(II), $E_{l.f.} = P$ [P = 19 150 cm^{-1} is the spin splitting energy of Fe(II)], and $E_{l.f.}$ was calculated by the equations:

$$E_{l.f.} = 3E_e + 2\,E_{t2} + 2\,P \text{ (low-spin complex } e^4t_2^2\text{)},$$

$$E_{l.f.} = 3\,E_e + 3\,E_{t2} + P \text{ (high-spin complex } e^3t_2^3\text{)}.$$

The energies of the two sets of 3*d*-AO in the tetrahedral ligand field are E_e = –0.6 D and E_{t2} = 0.4 D, where Δ is the splitting parameter.

ACKNOWLEDGMENTS

The authors are grateful to the Research Fund of the University of Plovdiv "Paissii Hilendarski" (contract no. NI15-HF001) for the financial support.

REFERENCES

1. Gavazov, K.B., *Acta Chim. Slov.*, 2012, vol. 59, no. 1, p. 1.
2. Salahifar, E., Nematollahi, D., Mahyari, A., and Nosratzadegan, K., *J. Electrochem. Soc.*, 2015, vol. 162, no. 6, p. G19. DOI: 10.1149/2.0791506jes.
3. Skrzypczak-Jankun, E., Borbulevych, O.Y., and Jankun, J., *Acta Crystallogr., Sect. D*, 2004, vol. 60, no. 3, p. 613. DOI: 10.1107/S0907444904000861.
4. Spaapen, L.J.M.,Verhagen, J., Veldink, G.A., and Vliegenthart, J.F.G., *BBA: Lipids Lipid Metab.*, 1980, vol. 617, no. 1, p. 132. DOI: 10.1016/0005-2760(80) 90230-1.
5. Tyson, C.A., *J. Biol. Chem.*, 1975, vol. 250, no. 5, p. 1765.
6. Dong, G. and Lai, W., *J. Phys. Chem. B*, 2014, vol. 118, no. 7, p. 1791. DOI: 10.1021/jp411812m.
7. Crisponi, G. and Remelli, M., *Coord. Chem. Rev.*, 2008, vol. 252, nos. 10–11, p. 1225. DOI: 10.1016/j.ccr.2007.12.014.
8. Nurchi, V.M., Pivetta, T., Lachowicz, J.I., and Crisponi, G., *J. Inorg. Biochem.*, 2009, vol. 103, no. 2, p. 227. DOI: 10.1016/j.jinorgbio.2008.10.011.
9. Vasudevan, D. and Stone, A.T., *J. Colloid Interface Sci.*, 1998, vol. 202, no. 1, p. 1. DOI: 10.1006/jcis.1998.5422.
10. Luther, G.W. III, Rozan, T.F., Witter, A., and Lewis, B., *Geochem. Trans.*, 2001, vol. 2, no. 9, p. 65. DOI: 10.1039/b105736g.
11. Hakkinen, P., *Finn. Chem. Lett.*, 1984, vol. 3, p. 59.
12. Toncheva, G.K., Stefanova, T.S., and Gavazov, K.B., *Orient. J. Chem.*, 2015, vol. 31, no. 1, p. 327. DOI: 10.13005/ojc/310137.
13. Gavazov, K., Stefanova T., and Toncheva, G., *J. Chem. Technol. Metall.*, 2013, vol. 48, no. 6, p. 642.
14. Nepal, J.K. and Dubey, S.N., *Indian J. Chem., Sect. A*, 1986, vol. 25, no. 5, p. 485.
15. Zhang, S.-F., Yang, X.-G, Liu, Z., Li, W-H, and Hou, B.-R., *Acta Crystallogr., Sect. E*, 2007, vol. 63, no. 6, p. m1583. DOI: 10.1107/S160053680702034X.
16. Moreno-Villoslada, I., González, F., Rivera, L., Hess, S., Rivas, B.L., Shibue, T., and Nishide, H., *J. Phys. Chem. B*, 2007, vol. 111, no. 22, p. 6146. DOI: 10.1021/jp071782m.
17. Xie, T., Brockner, W., and Gjikaj, M., *Z. Naturforsch., Teil B*, 2009, vol. 64, no. 9, p. 989.
18. Nakashima, K., Kawame, N., Kawamura, Y., Tamada, O., and Yamauchi, J., *Acta Crystallogr., Sect. E*, 2009, vol. 65, no. 11, p. m1406. DOI: 10.1107/S1600536809041464.
19. Gjikaj, M., Xie, T., and Brockner, W., *Z. Anorg. Allg. Chem.*, 2009, vol. 635, nos. 6–7, p. 1036. DOI: 10.1002/zaac.200801392.
20. Gjikaj, M., Xie, T., and Brockner, W., *Z. Anorg. Allg. Chem.*, 2009, vol. 635, nos. 13–14, p. 2273. DOI: 10.1002/zaac.200900174.
21. Fun, H-K, Chia, T.S., Mostafa, G.A.E., Hefnawy, M.M., and Abdel-Aziz, H.A., *Acta Crystallogr., Sect. E*, 2012, vol. 68, no. 8, p. o2567. DOI: 10.1107/S1600536812032941.
22. Buttrus, N.H., Alyass, J.M., and Mohammad, A.F., *J. Chem. Chem. Eng.*, 2013, vol. 7, p. 613.
23. Creanga, D. and Nadejde, C., *Chem. Pap.*, 2014, vol. 68, no. 2, p. 260. DOI: 10.2478/s11696-013-0429-2.
24. Gavazov, K., Lekova, V., Boyanov, B., and Dimitrov, A., *J. Therm. Anal. Calorim.*, 2009, vol. 96, no. 1, p. 249. DOI: 10.1007/s10973-008-9421-4.
25. Toncheva, G., Gavazov, K., Lekova, V., Stojnova, K., and Dimitrov, A., *Cent. Eur. J. Chem.*, 2011, vol. 9, no. 6, p. 1143. DOI: 10.2478/s11532-011-0101-z.
26. Stefanova, T.S., Simitchiev, K.K., and Gavazov, K.B., *Chem. Pap.*, 2015, vol. 69, no. 4, p. 495. DOI: 10.1515/chempap-2015-0048.
27. Zhiming, Z., Dongsten, M., and Cunxiao, Y., *J. Rare Earths*, 1997, vol. 15, no. 3, p. 216.

28. Asmus, E., *Fresenius. J. Anal. Chem.*, 1960, vol. 178, no. 2, p. 104. DOI: 10.1007/bf00467200 .
29. Hawrelak, E.J., Bernskoetter, W.H., Lobkovsky, E., Yee, G.T., Bill, E., and Chirik, P.J., *Inorg. Chem.*, 2005, vol. 44, no. 9, p. 3103. DOI: 10.1021/ic048202+.
30. Walker, I.M. and Drago, R.S., *J. Am. Chem. Soc.*, 1968, vol. 90, no. 25, p. 6951. DOI: 10.1021/ja01027a010.
31. Collman, J.P., Gagne, R.R., Reed, C.A., Robinson, W.T., and Rodley, G.A., *Proc. Natl. Acad. Sci. USA*, 1974, vol. 71, no. 4, p. 1326.
32. Cornard, J.-P., Lapouge, C., and Merlin, J.-C., *Chem. Phys.*, 2007, vol. 340, nos. 1–3, p. 273. DOI: 10.1016/j.chemphys.2007.09.010.
33. Delchev, V.B., Gavazov, K.B., and Shterev, I.G., *J. Mol. Model.*, 2014, vol. 20, no. 12, p. 1. DOI: 10.1007/s00894-014-2549-1.
34. Holme, A. and Langmyhr, F.J., *Anal. Chim. Acta*, 1966, vol. 36, p. 383. DOI: 10.1016/0003-2670(66)80066-1.
35. Shrivastava, A. and Gupta, V.B., *Chron. Young Sci.*, 2011, vol. 2, no. 1, p. 21. DOI: 10.4103/2229-5186.79345.
36. Mehra, M.C. and Katyal, M., *Bull. Environ. Contam. Toxicol.*, 1983, vol. 30, no. 1, p. 337. DOI: 10.1007/bf01610142.
37. Akl, M.A., Mori, Y., and Sawada, K., *Anal. Sci.*, 2006, vol. 22, no. 9, p. 1169. DOI: 10.2116/analsci.22.1169.