The First Example of a True “Turnbull’s Blue” Family Compound with Trapped Iron Oxidation States

Vitaly V. Pavlishchuk,*[a] Iryna A. Koval,[a] Eugeny Goreshnik,[b] Anthony W. Addison,*[c]
Gerard A. van Albada,[d] and Jan Reedijk[d]

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The first compound of a true Turnbull's Blue family [i.e. an iron(II) hexacyanoferrate(III)] complex with valence-trapped states of iron – $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (Ukrainian Red, UR) was synthesized. It crystallizes in the trigonal space group P3, a = 12.038(8) Å, b = 12.038(8) Å, c = 14.342(7) Å, α = 90.00°, β = 90.00°, γ = 120.00°. The unit cell of UR consists of separate $[Fe([9]ane\text{-}S_3)_2]^{2+}$ cations, $[Fe(CN)_6]^{3-}$ anions and 5.3 molecules of water. Encapsulation of the Fe^{II} in the homoleptic thioether environment plays the dual role of stabilizing Fe^{II} and protecting the central metal ion from direct bridging with hexacyanoferrate(III) anions. The absence of such interactions and trapping of iron oxidation states in the cations and anions was demonstrated by X-ray diffraction and magnetic susceptometry. Magnetic measurements are consistent with diamagnetic Fe^{II} inside the macrocyclic moieties and S = 1/2 for Fe^{III} in the hexacyanoferrate(III) anions.

Introduction

Until the 1960’s Turnbull’s Blue was believed to be iron(II) hexacyanoferrate(III), $Fe_3[Fe(CN)_6]_2$. This saga began 300 years ago when Berlin and Diesbach prepared Prussian Blue, also called Berlin Blue. The Prussian Blue synthesis heralded not only the discovery of a new family of cyanides, but initiated a whole field of coordination chemistry. Prussian Blue was ascribed as being the iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$, in contrast to the similarly intense blue pigment Turnbull’s Blue. Recently[1−3] all these various iron cyanides have been consolidated into a single family of Prussian Blues (PB’s). In this paper we use this name solely in reference to iron-containing cyanoferrates. Only since the 1960s have the identities of Prussian ($Fe_4[Fe(CN)_6]_3$) and Turnbull’s Blues (“$Fe_3[Fe(CN)_6]_2$”) been elucidated by magnetochemistry and Mössbauer spectroscopy.[2,4−10] These methods, as well as subsequent X-ray examination[11] revealed that Prussian Blue and Turnbull’s Blue are both iron(III) hexacyanoferrates(II), containing high spin Fe^{3+} cations and $[Fe(CN)_6]^{4-}$ with low-spin Fe^{II}, linked by cyanide bridges. Thus, a real “Turnbull’s Blue” simultaneously containing Fe^{II} and $[Fe(CN)_6]^{3-}$ has never been reported. Detailed examination of PB’s molecular and electronic structures suggest a significant exchange interaction between ions, and valence delocalization[1,10,12,13] along the Fe−C≡N−Fe bonds. All PB′s have been assigned as Robin and Day Class II mixed-valence systems.[14] In such systems partial valence delocalization occurs, and two oxidation states are still distinguishable by physical methods. Until now, only polymeric PB’s with magnetic interaction or valence delocalization between iron atoms have been described in the literature.[1,10,12,13,16−18] The detection of high-temperature ferromagnetic ordering in a number of PB-family complexes containing different metal ions connected by CN^- bridges has stimulated the design and study of new magnetic materials based on these compounds.[1,15−21] The recent discovery of photoinduced magnetization in a cobalt-containing PB analog may be of practical interest for the development of photochemically tunable molecular magnets.[22] From this point of view, the synthesis of true Turnbull’s Blue complexes with trapped oxidation states is still a challenge and is of significant fundamental interest. Blocking of such iron-iron interactions may be achieved by shielding the iron cations with homoleptic macrocyclic ligands, generating around them a coordinatively saturated environment which precludes any bridging by anions. Comparison of the magnetic and electronic properties of complexes containing cyano bridges with those that do not can reveal the details of the roles of such bridging groups in superexchange interactions between the metal centers. In this paper we report the synthesis and properties of the first

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[a] L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine,
252039, Kiev, prosp. Nauki, 31, The Ukraine
Fax:(internat.) +380 44 265 6216
E-mail: pavlisvv@phyche.freenet.kiev.ua
[b] Department of Chemistry, I. Franko Lviv State University,
290005, Lviv, The Ukraine
[c] Department of Chemistry, Drexel University,
Philadelphia, PA 19104, USA
Fax: (internat.) +1-215/895-1265
E-mail: addisona@drexel.edu
[d] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: (internat.) +31 71 527 4451
E-mail: reedijk@chem.leidenuniv.nl

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example of a true Turnbull′s Blue (i.e. iron(II) hexacyanoferrate(III)) complex with valence-trapped states of iron − $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$, which we refer to as Ukrainian Red (UR).

Results and Discussion

Synthesis

The reaction of $[Fe([9]ane\text{-}S_3)_2](ClO_4)_2$ with $K_3[Fe(CN)_6]$ in aqueous solution in molar ratio 3:2 results in precipitation of shiny ruby colored crystals of product, while the color of the solution changes to dull yellow. If the reaction mixture is allowed to stand for several days an additional amount of product forms, along with a minor amount of classic PB colloid. The analytical data agree with the formula $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$ for the bulk product, while an X-ray diffraction study proves the constitution of a single crystal to be $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2{\cdot}5.3H_2O$ (vide infra). Ukrainian Red shows no sign of redox exchange between its cations and anions during crystallization, so in contrast to classical PB's, the Fe^{III} ions in UR remain as hexacyanoferrate(III) anions, and the Fe^{II} ions are muffled by two trithiamacrocyclic ligands. Its composition thus matches formally the *virtual* classic Turnbull's Blue composition $(Fe_3[Fe(CN)_6]_2)$, but with iron(II) in macrocyclic moieties. The hexathiamacrocyclic environment around Fe lends significant relative stabilization to the Fe^{2+} oxidation state[23] and because of the consequently high $E_{1/2}$ value[23] for the $[Fe([9]ane\text{-}S_3)_2]^{3+/2+}$ couple, the hexacyanoferrate(III) ions cannot oxidize $[Fe([9]ane\text{-}S_3)_2]^{2+}$ to $[Fe([9]ane\text{-}S_3)_2]^{3+}$. In addition, the macrocyclic shielding in UR prevents the formation of cyanide bridges between Fe^{II} and Fe^{III} and thus is also crucial for preventing electron delocalization between these two iron atoms in different oxidation states. $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$ is insoluble in most common solvents. In order to confirm the integrity of the iron centers during the reaction and the absence of interactions between them in the complex salt, we investigated the crystal and molecular structure of UR as well as its IR and optical spectra and magnetochemical behavior.

Table 1. Crystal data for Ukrainian Red

Empirical formula	$C_{48}H_{76}Fe_5N_{12}O_2S_{18}$
Formula mass	1709.6
Crystal System	trigonal
Space group	*P*3
Dimensions	0.22 × 0.12 × 0.10
a (Å)[a]	12.038(8)
b (Å)	12.038(8)
c (Å)	14.342(7)
α	90.00
β	90.00
γ	120.00
V (Å^3)	1800(3)
Z	1
$\rho_{calcd.}$ (g cm^{-3})	1.632(3)
μ(Mo-K_α, cm^{-1})	15.61
R_{int}	0.039
$wR(F^2)$	0.037

[a] The standard deviations are reported in parentheses.

Molecular Structure and Physical Properties of Ukrainian Red

Crystallographic parameters for $[Fe([9]ane\text{-}S_3)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$ are given in Table 1. Selected bond lengths and angles are summarized in Table 2. A perspective view appears in Figure 1.

Table 2. Selected bond lengths (Å) and bond angles (°) in Ukrainian Red

Bond lengths			
Fe(1)−S(1)	2.23(1)	Fe(1)−S(1a)	2.23(1)
Fe(1)−S(1b)	2.23(1)	Fe(1)−S(6)	2.27(1)
Fe(1)−S(6a)	2.27(1)	Fe(1)−S(6b)	2.27(1)
Fe(2)−S(2)	2.24(1)	Fe(2)−S(2a)	2.24(1)
Fe(2)−S(2b)	2.24(1)	Fe(2)−S(5)	2.27(1)
Fe(2)−S(5a)	2.28(1)	Fe(2)−S(5b)	2.27(11)
Fe(3)−S(3)	2.23(1)	Fe(3)−S(3a)	2.23(1)
Fe(3)−S(3b)	2.23(1)	Fe(3)−S(4)	2.25(1)
Fe(3)−S(4a)	2.25(1)	Fe(3)−S(4b)	2.25(1)
Fe(4)−C(10)	1.91(2)	Fe(4)−C(10a)	1.91(2)
Fe(4)−C(10b)	1.91(2)	Fe(4)−C(15)	1.95(1)
Fe(4)−C(15a)	1.95(2)	Fe(4)−C(15b)	1.95(1)
Fe(5)−C(1)	1.95(2)	Fe(5)−C(1a)	1.95(2)
Fe(5)−C(1b)	1.95(2)	Fe(5)−C(11)	1.94(2)
Fe(5)−C(11a)	1.94(2)	Fe(5)−C(11b)	1.94(2)
C(1)−N(3)	1.16(2)	C(10)−N(2)	1.14(2)
C(15)−N(1)	1.15(2)	C(11)−N(4)	1.12(3)
Angles[a]			
S(1)−Fe(1)−S(6)	90.8(4)	S(1)−Fe(1)−S(6a)	179.6(5)
S(1)−Fe(1)−S(6b)	90.3(4)	S(1a)−Fe(1)−S(1b)	89.6(4)
S(1a)−Fe(1)−S(6)	90.3(4)	S(1a)−Fe(1)−S(6a)	90.8(4)
S(1a)−Fe(1)−S(6b)	179.6(5)	S(1b)−Fe(1)−S(6)	179.6(5)
S(1b)−Fe(1)−S(6a)	90.3(4)	S(1b)−Fe(1)−S(6b)	90.8(4)
S(1)−Fe(1)−S(1a)	89.6(4)	S(1)−Fe(1)−S(1b)	89.6(4)
S(6)−Fe(1)−S(6a)	89.3(4)	S(6)−Fe(1)−S(6b)	89.3(4)
S(6a)−Fe(1)−S(6b)	89.3(4)	S(2)−Fe(2)−S(2a)	90.7(3)
S(2)−Fe(2)−S(2b)	90.7(3)	S(2)−Fe(2)−S(5)	93.8(3)
S(2)−Fe(2)−S(5a)	175.1(4)	S(2)−Fe(2)−S(5b)	87.4(3)
S(2a)−Fe(2)−S(2b)	90.7(3)	S(2a)−Fe(2)−S(5)	87.4(3)
S(2a)−Fe(2)−S(5a)	93.8(3)	S(2a)−Fe(2)−S(5b)	175.1(4)
S(2b)−Fe(2)−S(5)	175.1(4)	S(2b)−Fe(2)−S(5a)	87.4(3)
C(10)−Fe(4)−C(10a)	94.7(8)	C(10)−Fe(4)−C(10b)	94.7(8)
C(10)−Fe(4)−C(15)	94.3(7)	C(10)−Fe(4)−C(15a)	81.9(7)
C(10)−Fe(4)−C(15b)	170.6(8)	C(10a)−Fe(4)−C(10b)	94.7(8)
C(10a)−Fe(4)−C(15)	170.6(8)	C(10a)−Fe(4)−C(15a)	94.3(7)
C(10a)−Fe(4)−C(15b)	81.9(7)	C(10b)−Fe(4)−C(15)	81.9(7)
C(10b)−Fe(4)−C(15a)	170.6(8)	C(10b)−Fe(4)−C(15b)	94.3(7)
C(15)−Fe(4)−C(15a)	89.6(6)	C(15)−Fe(4)−C(15b)	89.6(6)
C(15a)−Fe(4)−C(15b)	89.6(6)	C(1)−Fe(5)−C(1a)	92.7(8)
C(1)−Fe(5)−C(1b)	92.7(8)	C(1)−Fe(5)−C(11)	91.2(8)
C(1)−Fe(5)−C(11a)	89.0(8)	C(1)−Fe(5)−C(11b)	175.6(9)
C(1a)−Fe(5)−C(11a)	91.2(8)	C(1b)−Fe(5)−C(11a)	175.6(9)
C(1b)−Fe(5)−C(11b)	91.2(8)	C(11)−Fe(5)−C(11b)	87.0(9)
C(11)−Fe(5)−C(11b)	87.0(8)	C(1a)−Fe(5)−C(11b)	87.0(9)

[a] Standard deviations in parentheses.

The unit cell of UR consists of separate $[Fe([9]ane\text{-}S_3)_2]^{2+}$cations, $[Fe(CN)_6]^{3-}$ anions and 5.3 molecules of water (Figure 2). The macrocyclic cations are arranged in UR in such a way that the macrocyclic ligands form an unusual linear tube, along whose central axis the iron(II) ions are situated (Figure 3). Two nonequivalent $[Fe(CN)_6]^{3-}$ anions balance the positive charge of the cations, while water molecules occur in the unit cell in two

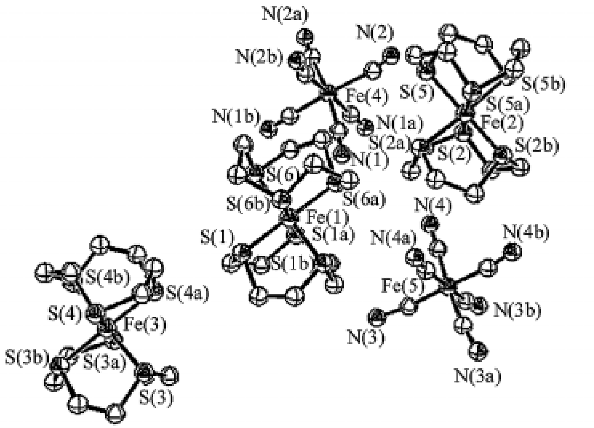

Figure 1. Molecular structure of Ukrainian Red. For clarity of presentation, water molecules and hydrogen atoms are not shown

independent positions with occupancies 1 and 0.77 (the multiplicity of each position is 3, thus 3+3 × 0.77 gives 5.3 water molecules in unit cell). The cations and anions are not connected by CN^- bridges, as is evident from Figure 1. There is no evidence for the existence of hydrogen bonding inside the unit cell.

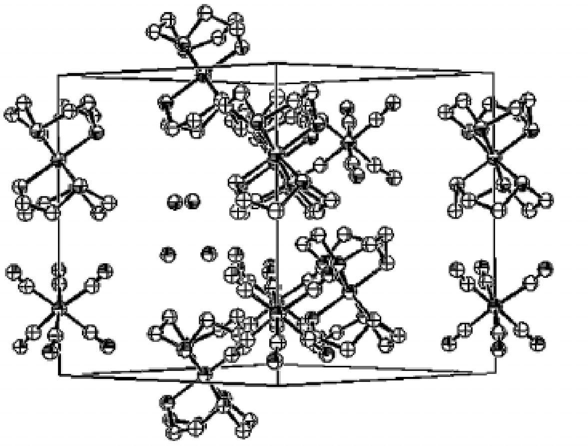

Figure 2. Unit cell content of Ukrainian Red

Similarities between the lattice building blocks in UR and in the starting reagents might be anticipated. Indeed, comparison of the Fe−C bond lengths in UR with those in $K_3[Fe(CN)_6]$[25] shows no significant differences. In the potassium salt, all the Fe−C distances are approximately equal (1.93−1.95 Å), whereas in UR these values vary within slightly larger limits (1.91 and 1.95 Å). These differences between the Fe−C distances are not significant relative to their standard deviations (Table 2) and thus may reveal that the equivalence of the Fe−C bonds is inherited by UR. In the potassium salt, the cyanide ligand $C{\equiv}N^-$ bond lengths are practically constant (1.14−1.16 Å).[24] In UR, they are also within these limits and the mean $[Fe(CN)_6]^{3-}$ radius (the distance between Fe and N) in UR is close to that in $K_3[Fe(CN)_6]$.[25] Previously, a dynamic Jahn−Teller effect in $K_3[Fe(CN)_6]$ was detected by magnetic circular dichroism[26] and Mössbauer spectroscopy,[27] while a static Jahn−Teller distortion was demonstrated for $[Fe([9]ane\text{-}S_3)_2](PF_6)_3$ by Mössbauer spectroscopy.[28] The bond lengths in UR offer no clear evidence in favor of a Jahn−Teller distortion in $[Fe(CN)_6]^{3-}$. Nonetheless, deviations of the C−Fe−C angles from 90° (Table 2) along with nonlinearity of the $Fe{-}C{\equiv}N$ units in UR (Figure 1, Table 2) leave room for speculation about the existence of a Jahn−Teller distortion in this compound.

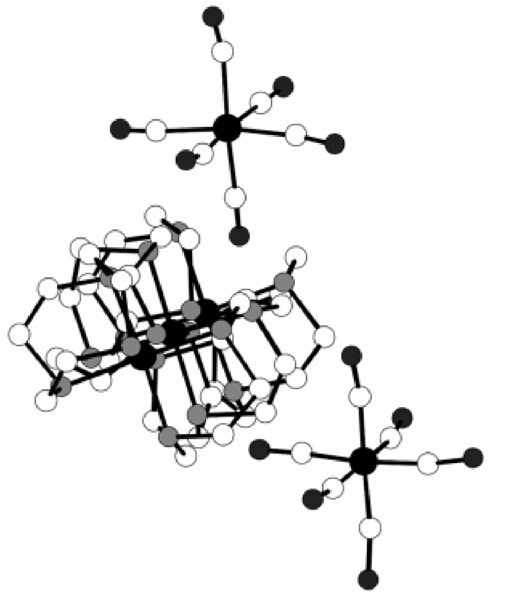

Figure 3. A perspective view of UR

The structural parameters for two of the three $[Fe([9]ane\text{-}S_3)_2]^{2+}$ cations in the UR unit cell (Table 2) also differ slightly from those described earlier in the literature.[23] The angles around Fe(1) of the central macrocycle (Table 2) coincide with those found in $[Fe([9]ane\text{-}S_3)_2](ClO_4)_2$. However, the corresponding angles in the two terminal macrocyclic cations are different (Table 2).[23] The Fe−S distances in UR vary between 2.23 and 2.27 Å, while in the parent $[Fe([9]ane\text{-}S_3)_2](ClO_4)_2$ these values are within 0.01 Å of 2.25 Å.[23] The terminal $[Fe([9]ane\text{-}S_3)_2]^{2+}$ in UR show slightly distorted octahedra as shown by some bond angle deviations from 90° (Table 2). These minor distortions in the cation structure in UR can be attributed to the influence of lattice packing in this compound.

The IR spectrum of UR contains a sharp band at 2100 cm^{-1} with a weaker satellite at 2113 cm^{-1} and a broad shoulder at lower frequency. These absorptions are attributed to the $\nu_{C\equiv N}$ mode of the nonbridging cyanide groups. The splitting of this mode and its broadening at lower frequencies may be attributed to the presence of the different types of cyanide anions in UR.

The reflectance spectrum of UR (Figure 4) shows two strong absorptions at 23,641 and 18,587 cm^{-1}, which originate from the individual ions. The band at 18,587 cm^{-1} is attributed to the $A_{1g} \rightarrow T_{1g}$ d-d transition in the octahedral low-spin d^6 $[Fe([9]ane\text{-}S_3)_2]^{2+}$ cations, as observed in $[Fe([9]ane\text{-}S_3)_2](ClO_4)_2$.[23] The second $A_{1g} \rightarrow T_{2g}$ d-d transition normally observed in $[Fe([9]ane\text{-}S_3)_2]^{2+}$ at 25,316 cm^{-1} is obscured in UR by the broad charge transfer band, π t_{2u} (CN^-) → t_{2g} (Fe^{III}). The band at 23,641 cm^{-1} in UR also arises from hexacyanoferrate(III) and is attributed to σ t_{1u} (CN^-) → t_{2g} (Fe^{III}) charge transfer.[29] In contrast to PB, and as expected for this structure, there is no sign of an intervalence charge transfer band in UR in the region 6,600−30,300 cm^{-1}. Unfortunately, the insolubility of UR in common solvents prevents measurements of its optical spectrum in solution.

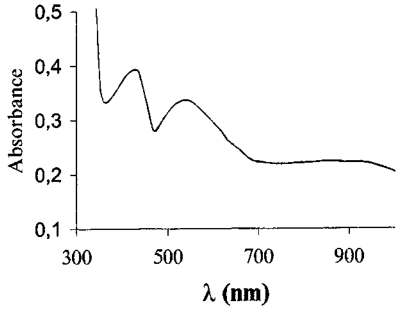

Figure 4. Electronic spectrum of UR in $BaSO_4$ matrices

The magnetochemical results for UR are consistent with the structural and spectral data. The temperature dependence of χT for UR was fitted in agreement with a $^2T_{2g}$ $[Fe(CN)_6]^{3-}$ ground state split under the influence of spin-orbit coupling in the magnetic field model[30,31] (Figure 5):

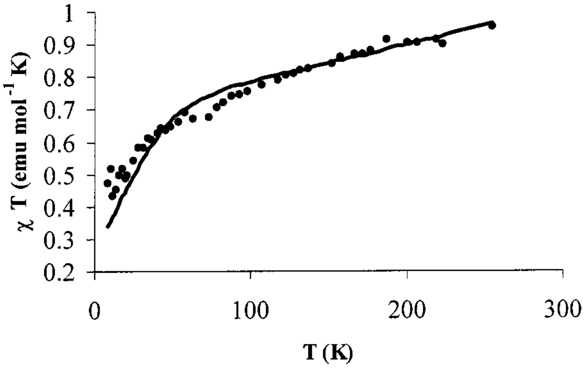

Figure 5. Variable-temperature magnetic data for UR. The solid line was calculated from Equation 1 with $\lambda = -72 \pm 6$ cm^{-1}, $\kappa = 0.75 \pm 0.03$, $TIP = 0.0015 \pm 0.0001$ emu; experimental data. ($R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2_{obs}]^{1/2}$) = 0.029

$$\chi_M = \frac{N\beta^2}{3kT}\left[\frac{3x(1+k)^2 - 8(2+k)^2 + \{30x(1-k)^2 + 8(2+k)^2\}e^{3x/2}}{9x\{1+2e^{3x/2}\}}\right] + TIP$$

κ is the orbital reduction factor, and $x = \kappa\lambda/3$ while the other symbols have their usual meanings. The additional term for temperature independent paramagnetism was introduced in order to reflect coupling between the singlet ground state and nonthermally populated excited states for the low-spin Fe^{2+} cations in the macrocyclic moieties.[31]

The susceptibility data for UR fit well to the above model under the assumption that significant magnetic exchange interactions between ions in the salt are absent. κ-Values for $[Fe(CN)_6]^{3-}$ in previous work[32−37] were also derived without consideration of magnetic exchange at even very low temperatures in $K_3[Fe(CN)_6]$.[38] The calculated κ = 0.75 for the $[Fe(CN)_6]^{3-}$ ion in UR reflects considerable covalency in this anion. The literature values for κ vary between 0.56 and 0.90; however, our value is close to that reported by Figgis.[37] The substantial reduction of λ (ref. between −250[37] and −400[35] cm^{-1}) also might be considered as evidence for the existence of a Jahn−Teller effect[34,35] in the hexacyanoferrate ions in UR. The separation of the $[Fe(CN)_6]^{3-}$ anions from each other is too great (9.5 Å) for significant magnetic exchange between iron(III) atoms.

Conclusion

Summarizing the results of this study, we would like to emphasize that almost three centuries have passed before a compound having a composition consistent with the original Turnbull's Blue formulation was synthesized. Success was achieved mainly due to the chosen synthetic strategy of encapsulating the Fe^{II} inside the homoleptic thioether environment. Such coordination plays the dual role of stabilizing Fe^{II} and protecting the central metal ion from direct bridging with hexacyanoferrate(III) anions. The absence of such interactions and trapping of iron oxidation states in the cations and anions was demonstrated by X-ray diffraction and magnetic susceptibility. In contrast to the classical PB's, assigned as Class II mixed valence systems,[14] UR is a Robin and Day Class I compound which shows no sign of valence delocalization in its spectroscopic and magnetic properties. This study also confirms the significant role of CN^- bridges in the magnetic interactions normally found in PB complexes. Shielding by the macrocyclic ligands prevents magnetic interactions between metal centers, so that UR shows no magnetic exchange between iron atoms. Further work is underway, involving coordinatively unsaturated $[M[9]ane\text{-}S_3]^{n+}$ building blocks and hexacyanoferrate/chromate(III) as potential sources of ferromagnetic materials.

Experimental Section

General Remarks: All reactants and solvents were of reagent grade and used as purchased; $[Fe([9]aneS_3)_2](ClO_4)_2$ was prepared according to the procedure reported by Wieghardt and co-workers.[23]

Physical Measurements: Infrared spectra were measured on a Carl Zeiss-Jena Specord M 75IR spectrometer using KBr pellets. Electronic spectra were recorded by the diffuse reflectance technique using $BaSO_4$ matrices on a Carl Zeiss-Jena Specord M-40 spectrophotometer. The magnetochemical behavior of the complex in the 5−278 K temperature range was studied using a fully automated Manics DSM-8 susceptometer. Data were corrected for diamagnetic contributions, estimated from the Pascal constants.[30]

$[Fe([9]aneS_3)_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ (Ukrainian Red): An aqueous solution of $K_3[Fe(CN)_6]$ (0.088 g, 0.27 mmol) was slowly added to an aqueous solution of $[Fe([9]ane\text{-}S_3)_2](ClO_4)_2$ (0.246 g, 0.40 mmol).

After half an hour, dark ruby colored prisms formed, which were filtered off, washed with water and ethanol and dried in air. Yield: 0.20 g, 63%. Elemental analysis; calcd. for $C_{48}H_{76}Fe_5N_{12}O_2S_{18}$: calcd. C 33.7, H, 4.48, N, 9.83, S, 33.8, Fe, 16.3; found calcd. C 33.6, H, 4.41, N, 9.89, S, 33.6, Fe, 16.0%. IR (cm^{-1}, KBr disc): 3386 (ν_{O-H}), 2113, 2101 ($\nu_{C\equiv N}$). Optical spectrum (solid state) : $\tilde{\nu}_{max}$, cm^{-1}: 23,641, 18,587.

X-ray Crystallographic Study: For X-ray diffraction, the selected crystal was mounted in a glass capillary, set on the goniometer head and carefully centered. X-ray intensity data were measured on an automated four-circle Dartch diffractometer with graphite-monochromated Mo-K_{α} radiation in the θ-2θ scan mode. Rotation and Weissenberg photographs gave preliminary parameters for the trigonal unit cell and Laue class 3 was defined. Any systematic absences were found and space group $P3$ was assigned to the unit cell. The cell parameters were least-squares refined using 24 reflections in the range: $25° \leq 2\theta \leq 30°$. The structure was solved using the CSD program package[20]. Iron and sulfur atoms were found by direct methods, the positions of other non-hydrogen atoms being derived from Fourier synthesis. All H atoms were found by difference Fourier synthesis, and their positional and overall thermal parameters were refined isotropically. Crystallographic data for Ukrainian Red are presented in Table 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138604. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

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