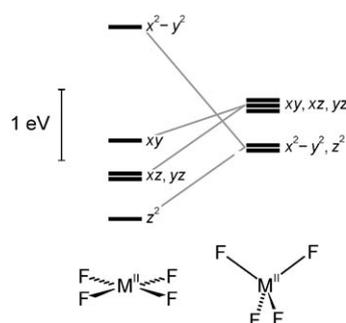


# A Stable Molecular Entity Derived from Rare Iron(II) Minerals: The Square-Planar High-Spin- $d^6$ $\text{Fe}^{\text{II}}\text{O}_4$ Chromophore\*\*

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Even under such disparate conditions as in a metalloenzyme active site or in the solid framework of a magnetic material, there are only a few parameters that determine the properties of a given metal center: the type of ligands and the metal oxidation state, coordination number, and spin state. For low-coordinate metals, the latter two parameters are highly interdependent and, in contrast to octahedral centers that exhibit both high- and low-spin states, tetracoordinate metals are almost invariably either high-spin tetrahedral or lower-spin non-tetrahedral. Exceptions to the rule are found in the rigid frameworks of solids that seem to force the metal atom into an environment considered unstable in a molecular analogue. Thus the rare mineral gillespite and the oxide ceramic  $\text{SrFeO}_2$  contain square-planar high-spin  $\text{Fe}^{\text{II}}\text{O}_4$  centers, which to date had never been found in a molecular entity. We have now synthesized the first coordination compounds of this type by employing a bis(bidentate) diolato environment. The origin of the planarization of the complexes is an unusually strong Jahn–Teller-initiated destabilization of the expected tetrahedral structure, which results in a high structural flexibility of the chromophore that is strongly correlated with its color.

Square-planar ( $SP-4$ ) coordination of central metal atoms is the domain of low-spin electronic configurations. The stereochemical origin of  $SP-4$  coordination is an optimal spatial separation of the ligand valence electrons and the metal d electrons. In the most common case, low-spin  $d^8$ , a particularly pronounced spatial d-electron anisotropy results, which makes these centers important for biological and technical catalysis.<sup>[1]</sup>  $SP-4$  coordination is less frequent for other  $d^n$  configurations.<sup>[2]</sup> For the important  $d^6$  iron(II) centers, an  $SP-4$  environment is found at times for the  $S=1$  spin state, which is the lowest possible spin for square-planar  $d^6$  complexes.<sup>[3]</sup> Figure 1 summarizes the stereochemical origin of these findings. Square-planar coordination is thus expected in a ligand field that is strong enough to efficiently separate the antibonding  $d_{x^2-y^2}$  orbital from the remaining group of four. As a result, the  $d_{x^2-y^2}$  orbital is left empty while



**Figure 1.** The splitting of the metal d orbitals in a square-planar (left) and a tetrahedral field (right) of four fluorido ligands in an  $[\text{M}^{\text{II}}\text{F}_4]^{2-}$  dianion. The ordinate is scaled using the energetic separation of the  $\alpha$ -spin frontier MOs from a uB3LYP/tzvp calculation on high-spin  $d^5$   $[\text{Mn}^{\text{II}}\text{F}_4]^{2-}$  ( $S=5/2$ ; closely grouped orbitals are degenerate). The z axis is chosen as in Figure 5; the single  $\beta$ -spin electron of a high-spin  $d^6$  configuration occupies the  $d_{z^2}$  orbital in non- $T_d$  structures.

the other four orbitals show little separation and thus are filled according to Hund's rule ( $S=0$  for  $d^8$ ,  $S=1$  for  $d^6$ ).<sup>[4]</sup> High-spin complexes seem to be largely excluded from these developments since their weak-field state seems to contradict an efficient separation of ligand valence electrons and metal d electrons. Hence, for the very few examples of high-spin  $d^8$   $SP-4$  compounds, a peculiar concurrence of electronic and steric contributions is discussed.<sup>[5]</sup>

In agreement with these points, tetracoordinate high-spin ( $S=2$ )  $\text{Fe}^{\text{II}}$  complexes are generally found with structures close to tetrahedra instead of squares for stereochemical reasons.<sup>[4b]</sup> Accordingly, the planar structure has been found to be unstable in DFT approaches regarding methyl and chlorido ligands.<sup>[6]</sup> In fact, no specific example of a square-planar high-spin  $d^6$  center, instead of the usual intermediate-spin state ( $S=1$ ), has ever been reported from the field of coordination chemistry.<sup>[7]</sup> A few remarkable examples for square-planar high-spin,  $S=2$ ,  $d^6$ -ferrous species, however, do exist, but all from solid-state science:

- 1) The rare mineral gillespite,  $\text{BaFe}^{\text{II}}\text{Si}_4\text{O}_{10}$ , contains the isolated square-planar high-spin  $\text{Fe}^{\text{II}}\text{O}_4$  chromophore in its red normal-pressure form, with the oxygen atoms being terminal  $\text{O}^-$  functions of cyclotetrasilicate anions.
- 2) The sheet silicate eudialyte (Figure 2) provides a similarly coordinated, isolated site for ferrous centers.
- 3) The oxide ceramics  $\text{CaFe}^{\text{II}}\text{O}_2$  and  $\text{SrFe}^{\text{II}}\text{O}_2$  contain puckered (Ca) or strictly planar (Sr)  $\text{Fe}^{\text{II}}\text{O}_4$  sheets of vertex-linked  $\text{Fe}^{\text{II}}\text{O}_4$  groups, the same sheets being part of the more complex structures of the related solids  $\text{Sr}_3\text{Fe}_2\text{O}_5$  and  $\text{Sr}_3\text{Fe}_2\text{O}_4\text{Cl}_2$ .<sup>[8]</sup>

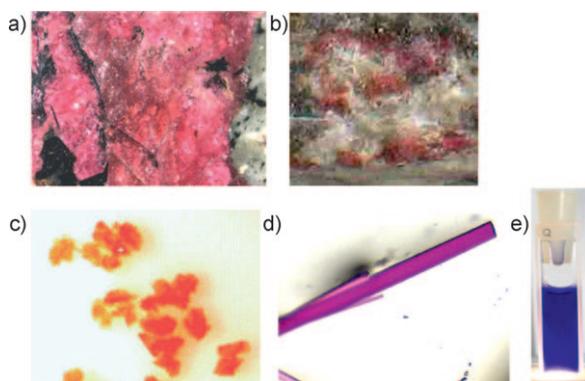
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As molecular entities with a planar high-spin  $\text{Fe}^{\text{II}}\text{O}_4$  core have never been described, these solids are believed to force the ferrous centers into an unstable bonding state that is not accessible outside the rigid framework of a crystal.<sup>[8d]</sup> In the same context, a recent contribution from protein science is noteworthy: High-spin ferrous sites with low coordination number and coordinated to oxygen only, including tetracoordination in an irregular geometry, is proposed for the ferrous B site of the dinuclear ferroxidase centers of ferritins.<sup>[9]</sup>

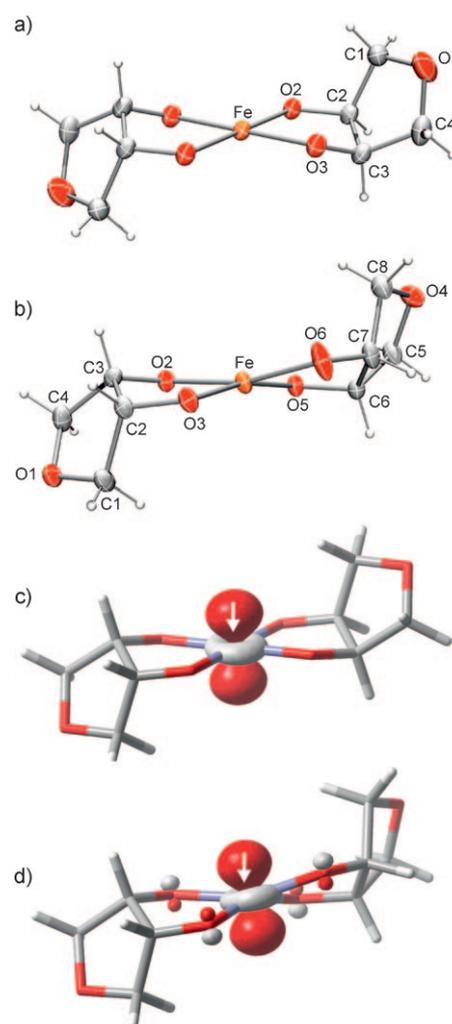
Considering the present state of knowledge, the result that we obtained experimentally during studies on carbohydrate-metal complexes was unexpected. A strongly alkaline (LiOH or NaOH) aqueous solution of the furanose mimic anhydroerythritol (*meso*-oxolane-3,4-diol) and ferrous chloride gave a reddish-blue solution, from which, depending on the conditions, orange-red crystals of the tetrahydrates  $\text{Li}_2[\text{FeL}_2]\cdot 4\text{H}_2\text{O}$  (**1**) or  $\text{Na}_2[\text{FeL}_2]\cdot 4\text{H}_2\text{O}$  (**2**), or violet crystals of the nonahydrate  $\text{Na}_2[\text{FeL}_2]\cdot 9\text{H}_2\text{O}$  (**3**) were grown, L being the *meso*-oxolane-3,4-diolate dianion (Figure 2).<sup>[10]</sup> The struc-



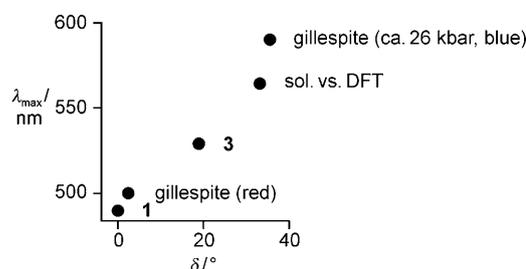
**Figure 2.** The  $\text{Fe}^{\text{II}}\text{O}_4$  chromophore in a) eudialyte (from Chibine Tundra, Kola Peninsula, Russia), b) gillespite (on sanbornite, from the vicinity of the Yosemite Valley, California, USA), c) crystals of **1**, d) crystals of **3**, and e) the mother liquor of **1**. The distortion of the planar chromophores in (a), (b), and (c) increases through (d) to (e) (Table 1, Figure 4), and the wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) increases in the same direction (Table 1).

tures of the ferrate anions in **1** and **3** are shown in Figure 3 a,b. In **1** and **2**, isolated  $\text{FeO}_4$  cores, which are planar owing to their crystallographic  $C_i$  symmetry, show about the same atomic distances found in the above-mentioned silicates and oxides (Table 1). In agreement with the typical Fe–O distances, the high-spin state in **1** was confirmed by SQUID magnetometer measurements. In **3**, the planar  $\text{FeO}_4$  chromophore is slightly distorted towards a tetrahedron. The extent of the distortion of violet **3** is roughly intermediate between the red normal-pressure and the blue high-pressure form of gillespite (Table 1, Figure 4), the latter resulting from a phase transition above approximately 20 kbar.<sup>[8a,11]</sup>

The bidentate oxolanediolate ligand is a simple and unspectacular chelator which is expected to be far less structure-directing than, for example, the silicate network of a crystal. What, then, enables this ligand to stabilize the rare



**Figure 3.** X-ray structures and DFT results. a) The centrosymmetric ferrate(II) anion in crystals of **1** (ellipsoids set at 60% probability; almost the same anion was found in **2**). b) The distorted ferrate(II) anion in crystals of **3** (ellipsoids set at 50% probability). c) The 3d  $\beta$ -spin-bearing molecular orbital (drawn at an isovalue of 0.08) from uB3LYP calculations of the free dianion in the square-planar structure ( $C_i$  symmetry imposed), 2.2 kJ mol<sup>-1</sup> above the minimum-energy structure. d) The minimum-energy structure ( $\delta = 33.3^\circ$ , see also 19.1° for **3**).



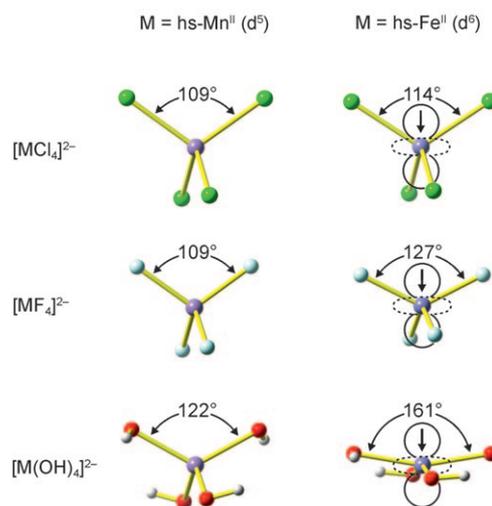
**Figure 4.** The gradual red-to-blue transition of  $\text{Fe}^{\text{II}}\text{O}_4$  chromophores on increasing distortion from planarity in terms of  $\lambda_{\text{max}}$  over  $\delta$ . At the “solution versus DFT” point, the distortion of the DFT minimum structure is assigned to the color of the solution (see also Table 1).

**Table 1:** Mean Fe–O distances in high-spin FeO<sub>4</sub> cores and the color of substances with an isolated FeO<sub>4</sub> chromophore (the 2D-FeO<sub>4/2</sub>-sheet oxides are black).<sup>[a]</sup>

	Fe–O <sub>mean</sub> [Å]	δ [°]	Color	λ <sub>max</sub> [nm]
<b>1</b>	1.997	0	red	490
<b>2</b>	1.998	0	red	
gillespite I	1.984 <sup>[11]</sup>	0	red	500 <sup>[15]</sup>
SrFeO <sub>2</sub>	1.996 <sup>[16]</sup>	0		
<b>3</b>	1.989	19.1	violet	529
CaFeO <sub>2</sub>	1.979 <sup>[8d]</sup>	25.8		
gillespite II (21 kbar)	1.992 <sup>[11]</sup>	33.6	blue	580 <sup>[15]</sup>

[a] The distortion of the O<sub>4</sub> square is given as the dihedral angle δ of two FeO<sub>2</sub> triangles (0°: square planar, 90°: tetrahedral). Owing to the large standard deviations of the Fe–O distances in the partly occupied iron positions in the giant unit cell of eudialyte, no values for this mineral are listed. The λ<sub>max</sub> value of solid samples of **1** and **3** were taken as the maximum of the Kubelka–Munk function applied to reflectance spectra. The λ<sub>max</sub> value of the mother liquor of **1** was 564 nm.

high-spin ferrous *SP*-4 coordination? As a key to answer this question, three related mononuclear high-spin [Fe<sup>II</sup>X<sub>4</sub>]<sup>2-</sup> species and their high-spin [Mn<sup>II</sup>X<sub>4</sub>]<sup>2-</sup> analogues were analyzed in a DFT approach using the unrestricted-B3LYP/tzvp level of theory: the experimentally known and theoretically well-understood [Fe<sup>II</sup>Cl<sub>4</sub>]<sup>2-</sup> ion, its unknown [Fe<sup>II</sup>F<sub>4</sub>]<sup>2-</sup> homologue, and, most closely related to the title compounds, a hydrogen-bonded conformer of the structurally still uncharacterized [Fe<sup>II</sup>(OH)<sub>4</sub>]<sup>2-</sup> ion, which has been described as a blue solution species.<sup>[12]</sup> Owing to the overall high-spin configuration, the difference between the d<sup>6</sup>-iron(II) and the d<sup>5</sup>-manganese(II) species is the presence of a single β-spin d electron in the former, which introduces an anisotropy in the almost isotropic electron density of the five α-spin electrons. The result is shown in Figure 5: The top-left structure shows the expected regular tetrahedral structure of the tetrachloridomanganate (left). Its distortion to the unstable square-planar conformer expends 100 kJ mol<sup>-1</sup>.<sup>[4b]</sup> The minimum structure of the iron analogue is close to that of the manganate structure. A Jahn–Teller (JT) distortion, which stabilizes the only β-spin orbital, is rather small in terms of structural parameters (Figure 5, top right). However, the path towards the unstable *SP*-4 isomer (69 kJ mol<sup>-1</sup>) is considerably flattened in terms of energy. Both the structural and the energetic influence of the JT contribution are enhanced in the fluorido analogues, which approach the diolato case in terms of parameters such as the metal–ligand distance and the π-donor ability. Figure 5 (center) shows that the Mn<sup>II</sup> complex maintains its regular tetrahedral structure, and that the energy cost of planarization (95 kJ mol<sup>-1</sup>) is almost the same as for the chlorido homologue. The ferrous analogue, however, is markedly distorted. More importantly, an energetic expense of only 32 kJ mol<sup>-1</sup> was computed for the transformation of the minimum structure to the square-planar conformer, which is only a third of the value for the Mn<sup>II</sup> analogue. We interpret the flattened minimum-to-planar path by a pronounced repulsive interaction of the ligand valence electrons on one hand and the metal β-spin d electron on the other. Therefore, a rationale to achieve a planar high-spin-Fe<sup>II</sup> center becomes tangible. Preserving the weak-field

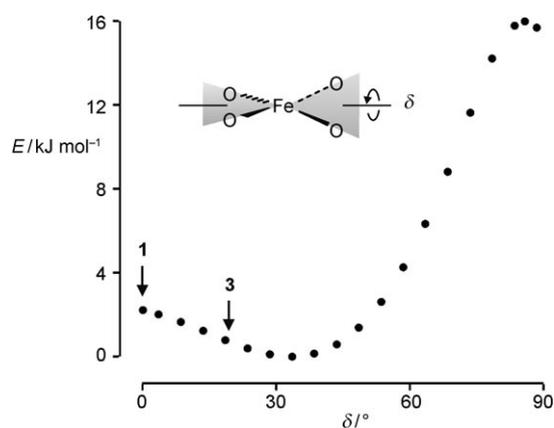


**Figure 5.** Jahn–Teller flattening of tetrahedral structures. The results of uB3LYP/tzvp calculations on high-spin [M<sup>II</sup>X<sub>4</sub>]<sup>2-</sup> ions. Left: High-spin d<sup>5</sup> [Mn<sup>II</sup>X<sub>4</sub>]<sup>2-</sup> ions as reference states that lack 3d β-spin density. Right: The stereoelectronic influence of the single β-spin electron (contours drawn at an isovalue of roughly 0.1) embedded in the almost spherical α-spin density of the half-filled 3d subshell of the high-spin [Fe<sup>II</sup>X<sub>4</sub>]<sup>2-</sup> anions.

character of a ligand to ensure the high-spin case, a short contact of the metal and a preferably highly charged, π-basic ligand should result in a high JT destabilization of the tetrahedral structure. At the same time, an increasing inter-ligand repulsion, which goes along with the increasing charge, has to be counteracted.

Figure 5 (bottom) shows an attempt to illustrate this hypothesis by means of the hydrogen-bridged conformers of the tetrahydroxidometallates. The ferrate ion is calculated to be almost planar owing to a well-balanced sum of influences. Since a hydroxido oxygen atom bears a higher negative charge than a fluorido ligand, the tetrahedron's JT destabilization reaches a high value. At the same time, the in-plane repulsion between the oxygen atoms is minimized by allowing the protons to bridge them by intramolecular hydrogen bonds. This latter effect is also active in the manganate and flattens the reference complex to some extent.

All of the real-world compounds mentioned above that contain (almost) square-planar species exhibit a similar balance of contributions. Thus all compounds use the high, non-delocalized, negative charges of relatively small O<sup>-</sup>/O<sup>2-</sup>-type ligands, and all of the compounds have some kind of substitute for the bridging protons of the [Fe<sup>II</sup>(OH)<sub>4</sub>]<sup>2-</sup> ion: alkylene and hydrogen-bond bridges in our compounds, a silicate network in the minerals, and, neighboring cations in the network of the oxide ceramics. The balancing of influences along the transformation paths causes a peculiarity that is demonstrated for the title anion in Figure 6: the transformation path, which has its minimum very roughly midway between square planar and tetrahedral, is flat in terms of energy. Thus the blue solution species shows a marked distortion from both planar and tetrahedral, a conformation that is mostly conserved in the “soft” crystalline environment of the water-rich nonhydrate **3**, but is planar-



**Figure 6.** A minimum potential energy scan at the uB3LYP/tzv/6-31G(d,p) level of theory for the free  $[\text{Fe}^{\text{II}}\text{L}_2]^{2-}$  dianion ( $S=2$ );  $\text{L} = \text{meso-oxolane-3,4-diolate}(2-)$ , showing the flattened transformation path. The independent variable is the dihedral angle  $\delta$  between the two  $\text{FeO}_2$  triangles of the two chelate rings ( $\delta=0^\circ$ : square planar,  $\delta=90^\circ$ : tetrahedral). The positions of the anions in **1** and **3** are marked.

ized in the more rigid tetrahydrate structures **1** and **2**: all within an energetic range of a few kilojoules per mole. The flat transformation path, which spans less than  $20 \text{ kJ mol}^{-1}$  from the minimum structure to the almost tetrahedral transition state, and ascends less than  $3 \text{ kJ mol}^{-1}$  from the minimum to the square planar structure, is thus the origin of the color variability in the individual chromophore, allowing orange-red crystals to grow from blue mother liquors.

A closer look at compounds formally containing simple  $[\text{Fe}^{\text{II}}\text{X}_4]^{2-}$  anions shows a significant restriction that allows us to understand the fact that square-planar high-spin complexes are by no means widespread. The requirement for strong JT flattening of a coordination tetrahedron in the area of weak-field ligands lays the focus on oxygen donor ligands. On one hand, delocalized charge, as in carboxylate or related donors, is detrimental to tetracoordination, as the usual coordination number (CN) of six will be electrostatically favorable in the absence of the typical accumulation of charge that favors a lower CN. On the other hand, hydroxido or alkoxido and also the related fluoro ligands are able to disperse their charge by another mechanism: they tend to bridge two or more central metals. Compounds such as  $\text{BaFeF}_4$  have thus been found with bridging fluoride ions in a CN6-type structure.<sup>[13]</sup> In light of this experience, the oxolane backbone of the diolato ligand of this work serves as a sterically active bridging blocker. Recent results on a subgroup of tetracoordinate  $\text{Fe}^{\text{II}}\text{N}_4$  compounds should be noted at this point: Structures of high-spin ferrous bis(imine) complexes that meet the requirement of decreased bridging ability of the ligand, but lack the high charge on the donor atoms typical for the title compounds of this work, are intermediate between tetrahedral and square planar ( $\delta$  values of  $49$  and  $57^\circ$ ).<sup>[14]</sup>

In conclusion, we have succeeded in extending the rules of coordination chemistry to include the Jahn–Teller flattening of seemingly steep transformation paths of electrostatically burdened centers. Enhanced JT flattening thus can stabilize square planar high-spin  $d^6$  centers despite their “wrong” spin state by a marked separation of the negative charge on the

ligand atoms and the thus stereochemically active d electrons (Figure 3c,d). This result reveals square-planar high-spin centers to be building blocks of reasonable stability. The designers of oxide ceramics that are based on planar high-spin centers may thus be encouraged by the discovery that they use an intrinsically stable building unit instead of a rare structural oddity. Current work by our group is directed towards the chemical properties of high-spin  $d^6$  centers. Planarization of these centers stabilizes the only  $\beta$ -spin, which is the electron removed upon oxidation of the ferrous center. Adjustment of the structure of the center, a process that is possible in the active site of a protein, where a low coordination number may be forced by the characteristics of the site, should thus be a means of adjusting its redox potential.

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- [10] Crystal data for  $\text{Li}_2[\text{FeL}_2]\cdot 4\text{H}_2\text{O}$  (**1**). Orange-red platelets ( $0.21 \times 0.12 \times 0.04 \text{ mm}$ ),  $a = 10.388(2)$ ,  $b = 4.857(1)$ ,  $c = 14.453(3) \text{ \AA}$ ,  $\beta = 110.64(3)^\circ$ ,  $V = 682.4(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho = 1.684 \text{ g cm}^{-3}$ ,  $\mu = 1.150 \text{ mm}^{-1}$ . 5044 reflections, 1565 unique,  $R_{\text{int}} = 0.0562$ ,  $R_1 = 0.032$ ,  $wR_2 = 0.084$ ,  $S = 1.067$ , max/min difference densities:  $0.682$  and  $-0.574 \text{ e \AA}^{-3}$ . Crystal data for  $\text{Na}_2[\text{FeL}_2]\cdot 4\text{H}_2\text{O}$  (**2**). Orange-red needles ( $0.27 \times 0.12 \times 0.05 \text{ mm}$ ).  $P\bar{1}$ ,  $a = 5.2313(2)$ ,  $b = 8.3937(2)$ ,  $c = 9.1104(3) \text{ \AA}$ ,  $\alpha = 108.964(2)$ ,  $\beta = 97.829(2)$ ,  $\gamma = 106.947(2)^\circ$ ,  $V = 349.90(2) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho = 1.794 \text{ g cm}^{-3}$ ,  $\mu = 1.186 \text{ mm}^{-1}$ . 3863 reflections, 2038 independent,  $R_{\text{int}} = 0.0289$ ,  $R_1 = 0.0274$ ,  $wR_2 = 0.0705$ ,  $S = 1.084$ , max/min difference densities:  $0.789$  and  $-0.533 \text{ e \AA}^{-3}$ . Crystal data for  $\text{Na}_2[\text{FeL}_2]\cdot 9\text{H}_2\text{O}$

- (3). Violet needles (0.25 × 0.11 × 0.08 mm). *P*21/*n*, *a* = 5.5697(1), *b* = 12.2906(2), *c* = 28.5083(3) Å,  $\beta$  = 91.419(1)°, *V* = 1950.94(5) Å<sup>3</sup>, *Z* = 4,  $\rho$  = 1.594 g cm<sup>-3</sup>,  $\mu$  = 0.886 mm<sup>-1</sup>. 15455 reflections, 4451 independent,  $R_{\text{int}}$  = 0.0207, *R*1 = 0.0232, *wR*2 = 0.0630, *S* = 1.047, max/min difference densities: 0.374 and -0.246 e Å<sup>-3</sup>. CCDC 799104 (1), 799103 (2), and 799105 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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