Crystal Structure and Magnetic Characteristics of a New 3-Methylisoquinolinium Tetrachloridoferrate(III)

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Abstract. The crystal structure of a new 3-methylisoquinolinium [3-Me(IsoQH)] salt, [3-Me(IsoQH)][FeCl$_4$], was determined. The iron cation is tetracoordinated by chlorine anions, and it adopts a slightly distorted tetrahedral coordination. In the crystal structure, there are π···π stacking interactions between the 3-methylisoquinolinium cations in an ABAB infinite arrangement, N−H···Cl hydrogen bonds, and C−H···Cl intermolecular interactions. Magnetic measurements of a powdered sample were carried out. A negative Weiss constant as well as the intermolecular exchange parameter for [3-Me(IsoQH)][FeCl$_4$] indicate the occurrence of antiferromagnetic interactions transmitted in the crystal lattice.

Introduction

Tetrahalogenidoferrates(III) have been studied by many research teams. Because of the presence of a high-spin d^5 Fe^{III} atom in these systems and their tetrahedral coordination geometry, tetrahalogenidoferrates(III) may be useful as simple models for the determination of physicochemical properties of the Fe−S proteins [1−3]. Recent literature data show also that compounds with paramagnetic tetrahalogenidoferrate(III) ions can be considered as novel, potentially attractive magnetic materials [4−6].

Tetrahalogenidoferrates(III) have been known to form binary compounds [7−9] with cations of quaternary *n*-alkyl-ammonium salts, irrespective of the molar ratio of the used reactants. With the pyridinium and quinolinium cations, both composition and structure of the resulting salts depend on the nature and location of a substituent in the aromatic ring. In the majority of cases, heteroanionic salts of general formula of either (AH)$_3$[FeCl$_4$]$_2$Cl are formed with AH denoting a pyridinium cation [10], 4-chloro-, 4-bromopyridinium [11] or (BH)$_2$[FeCl$_4$]Cl with BH standing for 2- and 8-methylquinolinium cations [12, 13] and an 8-hydroxyquinolinium [14] one. A markedly smaller family of the compounds is represented by salts of nitrogen-containing aromatic bases and tetrachloridoferrates(III) with a cation/anion ratio of 1:1, as for instance [QH][FeCl$_4$] [15] and [4-NH$_2$-2-Me(QH)][FeCl$_4$] [16].

Unexpectedly, during the synthesis of the compound with 3-methylisoquinoline, we obtained [3-Me(IsoQH)][FeCl$_4$] which, in contrast to the recently presented 2-methylquinolinium [2-Me(QH)] heteroanionic salt of stoichiometry [2-Me(QH)]$_2$[FeCl$_4$]Cl [12], turned out to be a binary salt. In this article, the synthesis, crystal structure as well as magnetic properties of [3-Me(IsoQH)][FeCl$_4$] are presented.

Results and Discussion

Structural Description

The [3-Me(IsoQH)][FeCl$_4$] is a first example of an isoquinoline derivative complex containing the [FeCl$_4$]$^−$ ion. The asymmetric unit of 3-methylisoquinolinium tetrachloridoferrate(III) consists of two 3-methylisoquinolinium cations (denoted A and B for those containing atoms N1 and N21, respectively) and two tetrachloridoferrate(III) anions (Figure 1). Both 3-methylisoquinolinium cations lie on a mirror plane, as well as the Fe1, Cl2, Cl3, Fe11, Cl12 and Cl13 atoms making up the [FeCl$_4$]$^−$ anions. As a consequence of special positions of the constraints for all the atoms of the cations, both [3-Me(IsoQH)]$^+$ ions are planar and all the torsion angles of the cations are equal either to 0 or 180°. In addition, one of the tetrachloridoferrate(III) anions contains a disordered Cl atom; the occupancy ratio of the two sites was refined and converged to 0.86(2):0.14(2) for Cl1A and Cl1B atoms, respectively.

In the crystal structure, the ions are linked through C−H···Cl intermolecular interactions (Figure 1 and Table 1), which can be regarded as a weak hydrogen bond [17] forming layers. The layers are linked through N−H···Cl in-

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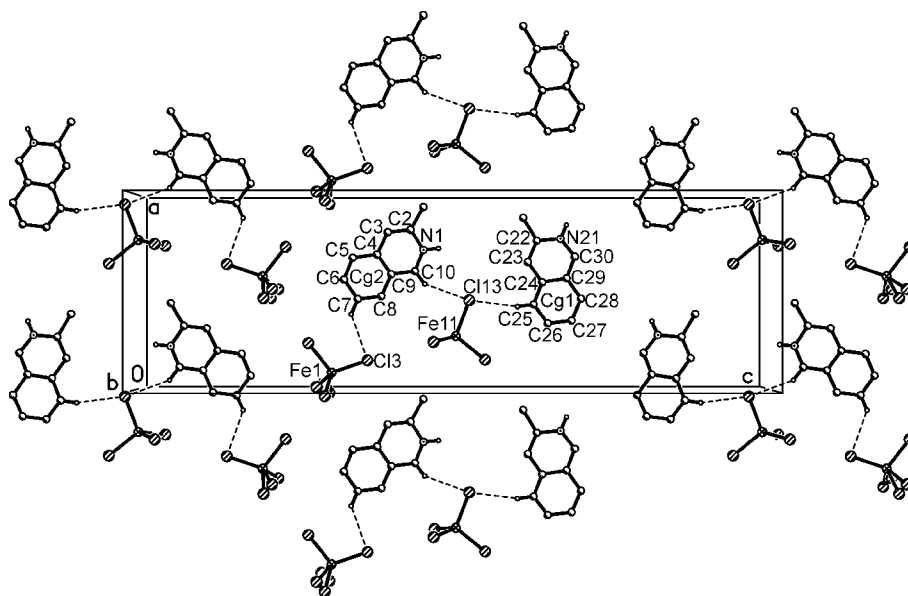 University of Wrocław
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Figure 1. Arrangement of the ions of [3-Me(IsoQH)][FeCl₄] in the unit cell viewed along the *b* axis. The C−H···Cl interactions are represented by dashed lines. H atoms not involved in the interactions have been omitted. Cg represents the centre of gravity of the rings, as follows: Cg1 ring C24−C29 and Cg2 ring C4−C9.

termolecular interactions (Table 1) and $\pi \cdots \pi$ stacking interactions (Table 2) between the cations in an ABAB infinite arrangement (Figure 2).

Table 1. Hydrogen bond lenghts for [3-Me(IsoQH)][FeCl₄]. Distances are in Å and angles in °.

D−H	A	d(D−H)	d(H···A)	< D−H···A	d(D···A)
N1−C1	Cl11#1	0.86	2.69	3.369(6)	137
N21−C21	Cl1A#1	0.86	2.80	3.507(6)	140
C7−H7	Cl3	0.93	2.80	3.536(11)	137
C10−H10	Cl13	0.93	2.73	3.553(8)	148
C25−H25	Cl13	0.93	2.79	3.696(11)	165

Symmetry code: (#1) −x +1, y + 1/2, −z + 1

Table 2. $\pi \cdots \pi$ stacking interactions in [3-Me(IsoQH)][FeCl₄] (distances are in Å and angles in °). Cg represents the centre of gravity of the rings as follows: Cg1 in ring C4−C9 and Cg2 in ring C24−C29. Cg···Cg is the distance between ring centroids. The dihedral angle is that between the planes of the CgI and CgJ rings. The interplanar distance is a perpendicular distance of CgI from ring J. The offset is the perpendicular distance of ring I from ring J.

CgI	CgJ	Cg···Cg	Dihedral angle	Interplanar distance	Offset
Cg1	Cg2#1	3.765(2)	0.0(2)	3.594(2)	1.093(2)
Cg2	Cg1#1	3.756(2)	0.0(2)	3.594(2)	1.093(2)

Symmetry code: (#1) −x +1, y + 1/2, −z + 1

Magnetic Properties

The magnetic properties of the [3-Me(IsoQH)][FeCl₄] complex were determined over the temperature range 1.8−300 K. The $\chi_M T$ value for [3-Me(IsoQH)][FeCl₄] at 300 K is 4.25 cm³·mol⁻¹ K (5.84 B.M.). The $\chi_M T$ product decreases with temperature to 0.229 cm³·mol⁻¹ K
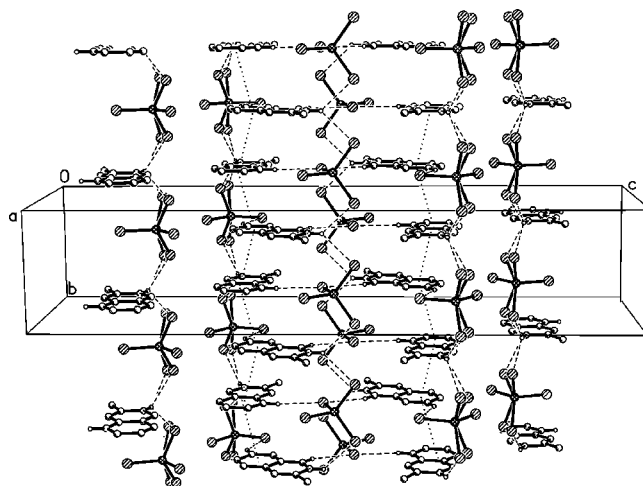

Figure 2. A part of the packing of [3-Me(IsoQH)][FeCl₄] showing the arrangement of cations and anions in the crystal, viewed along the *a* axis. The N−H···Cl and C−H···Cl interactions are represented by dashed lines, and $\pi \cdots \pi$ interactions by dotted lines. H atoms not involved in the interactions have been omitted.

(1.36 B.M.) at 1.8 K. The decrease in the $\chi_M T$ values over the whole temperature range is due to antiferromagnetic interactions between the Fe^III ions transmitted in the crystal lattice.

The susceptibility curve for the complex exhibits a sharp maximum indicating the presence the antiferromagnetic ordering with a Neel temperature (T_N) of approximately 7.5 K.

In this situation the magnetic data were fitted by using a susceptibility equation for S = ⁵/₂, [Equation (1)] To elucidate the significance of exchange between the iron(III) ions

Table 3. Magnetic data and the nearest Fe···Fe distance for [QH][FeCl$_4$], [4-NH$_2$-2-Me(QH)][FeCl$_4$] and [3-Me(IsoQH)][FeCl$_4$].

Compound	g	zJ' /cm^{-1}	R	Curie constant /cm$^3 \cdot$ mol^{-1}	Weiss constant /K	Nearest Fe···Fe distance /Å
[QH][FeCl$_4$]	1.98	−0.40	2.58×10^{-4}	4.28	−2.95	6.331 [15, 16]
[4-NH$_2$-2-Me(QH)][FeCl$_4$]	2.01	−1.32	2.33×10^{-4}	4.37	−9.76	5.260 [16]
[3-Me(IsoQH)][FeCl$_4$]	2.03	−2.28	5.62×10^{-5}	4.52	−18.4	6.189 [this work]

in the crystal lattice, a molecular field correction term was also included, Equation (2) [18],

$$\chi_M = \frac{N\beta^2 g^2}{3kT} S(S+1) \tag{1}$$

$$\chi_M^{corr} = \frac{\chi_M}{1 - \frac{2zJ'}{N\beta^2 g^2 \chi_M}} \tag{2}$$

where N is the Avogadro's number, g the spectroscopic splitting factor, β the Bohr magneton, k the Boltzmann constant, zJ' the intermolecular exchange parameter and z is the number of the nearest neighbour Fe^{III} atoms.

The best fit parameters, g, zJ', the agreement factor R $(R = \overset{n}{\underset{i}{\Sigma}} \frac{1}{(\chi_i^{exp})} (\chi_i^{exp} - \chi_i^{calc})^2 \overset{n}{\underset{i}{\Sigma}} \frac{1}{(\chi_i^{exp})}$ as well as the Curie and Weiss constants determined from the relation $1/\chi_M T = f(T)$ over the temperature range $50-300$ K for the [3-Me-(IsoQH)][FeCl$_4$] complex are collected in Table 3. The variation of magnetization M vs. magnetic field H for the [3-Me(IsoQH)][FeCl$_4$] complex at 2 K is linear over the whole field range and indicates the magnetization of 1.41 B.M. at 5 T. The negative Weiss constants and intermolecular exchange parameter obtained from the calculation confirm the occurrence of antiferromagnetic interactions between the iron atoms in the crystal lattice.

In a previous article [16], we reported on two tetrachloridoferrates(III) with quinolinium cations. The intermolecular exchange parameter for [4-NH$_2$-2-Me(QH)][FeCl$_4$] is ca. 3.3 times larger than for [QH][FeCl$_4$], which is due to a distinctly smaller distance between neighbouring iron(III) ions in the crystal lattice of the former. On the other hand, in the [3-Me(IsoQH)][FeCl$_4$] complex the strength of the antiferromagnetic interactions is ca. 5.7 times stronger than in [QH][FeCl$_4$]. It is worth noting that in spite of the shorter Fe···Fe distance in the crystal lattice of [4-NH$_2$-2-Me(QH)][FeCl$_4$] the intermolecular exchange parameter is ca. 1.7 times larger than that for its 3-methylisoquinoline counterpart (Table 3). This finding provides a further proof in favour of the hypothesis that the strength of antiferromagnetic interactions depends not only on the distance between the magnetic Fe^{III} ions, but also on the arrangement of the Fe$-$X···X$-$Fe entities within the crystal lattice [19]. Both the literature survey [10, 20] and our previous studies [21$-$23] have shown that the exchange of the chlorido by a bromido ligand results in enhanced strength of antiferromagnetic interactions. On this basis, an increased strength of interactions between the electrons of Fe^{III} in the crystal lattice of the bromido counterpart, [3-Me(IsoQH)][FeBr$_4$], can be envisaged.

The EPR spectra of [3-Me(IsoQH)][FeCl$_4$] recorded at room temperature, 77 K, and 4.5 K indicate a single isotropic line characteristic only of an unresolved $^6S_1$ state and the $+^1/_2 \leftrightarrow -^1/_2$ transition (Table 4). The EPR spectrum of the Fe^{III} ion in the tetrahedral crystal field strongly depends on the character of the tetrahedral distortion and the composition of the coordination sphere (kind of the ligands) [22, 23]. For a sample containing symmetric anionic form of [FeCl$_4$]$^-$ good quality, intensive signals of the EPR spectra are seen (Figure 3).

Table 4. EPR data for [3-Me(IsoQH)][FeCl$_4$].

Compound	293 K		77 K		4.5 K	
	g_{iso}	δ_{Hpp} [a] (Gs)	g_{iso}	δ_{Hpp} [a] (Gs)	g_{iso}	δ_{Hpp} [a] (Gs)
[3-Me(IsoQH)][FeCl$_4$]	2.01$_1$	175	1.93$_8$	290	2.04$_2$	320

[a] Peak to peak linewidth.
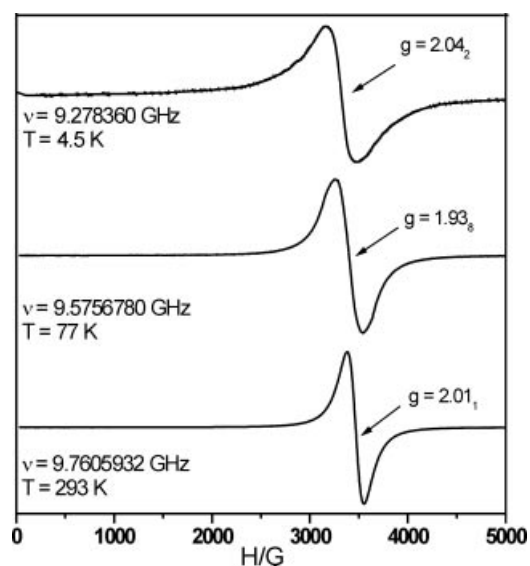
Figure 3. EPR (X-band) spectrum of powdered [3-Me(IsoQH)]-[FeCl$_4$] at room temperature, 77 and 4.5 K.

Experimental Section

Synthesis

The synthesis of 3-methylisoquinolinium tetrachloridoferrate(III) was carried out by using a procedure similar to the one reported for the preparation of bis(2-methylquinolinium) tetrachloridoferrate(III) chloride [21, 24]. Thus, an ethanol solution of anhydrous ferric chloride was first prepared by dissolving FeCl$_3$ (ca. 0.03 mol) in ethanol (15 mL, 96 %). Afterwards, a stoichiometric quantity of a 12 M HCl solution was added to this solution followed by an ethanol solution (15 mL) of 3-methylisoquinoline (ca. 0.03 mol). The mixture was left for crystallization in a refrigerator. Within a fortnight, a yellow-orange amorphous precipitate of [3-Me-

Table 5. Selected geometric parameters for [3-Me(IsoQH)][FeCl$_4$].

Anion

Bond lengths /Å		Angles /°			
Fe1−Cl1A	2.202(6)	Cl1B−Fe1−Cl1B#	117.0(13)	Cl3−Fe1−Cl1A#	107.1(2)
Fe1−Cl1A#	2.202(6)	Cl1B−Fe1−Cl3	117.8(7)	Cl1A−Fe1−Cl1A#	109.1(2)
Fe1−Cl1B	1.96(2)	Cl1B#-Fe1−Cl3	117.8(7)	Cl12−Fe11−Cl11	107.98(12)
Fe1−Cl1B#	1.96(2)	Cl2−Fe1−Cl3	108.98(12)	Cl12−Fe11−Cl11	111.45(8)
Fe1−Cl2	2.142(3)	Cl1B#-Fe1−Cl1A	116.1(8)	Cl13−Fe11−Cl11	109.26(7)
Fe1−Cl3	2.177(3)	Cl2−Fe1−Cl1A	112.2(3)	Cl13−Fe11−Cl11#	109.26(7)
Fe11−Cl11	2.178(2)	Cl3−Fe1−Cl1A	107.1(2)	Cl13−Fe11−Cl11#	107.42(10)
Fe11−Cl11#	2.178(2)	Cl1B−Fe1−Cl1A#	116.1(8)		
Fe11−Cl12	2.163(3)	Cl2−Fe1−Cl1A#	112.2(3)		
Fe11−Cl13	2.175(3)				

Cation

Bond lenghts/Å	Molecule A	B	Angles /°	Molecule A	B
N1−C10	1.316(11)	1.315(14)	C10−N1−C2	123.8(7)	123.9(10)
N1−C2	1.381(12)	1.366(12)	C3−C2−N1	117.3(8)	118.0(10)
C2−C3	1.313(12)	1.321(13)	C3−C2−C11	126.5(9)	126.0(9)
C2−C11	1.498(12)	1.532(14)	N1−C2−C11	116.2(8)	116.1(10)
			C2−C3−C4	122.0(8)	121.4(8)

symmetry code: (#) x, −y + 1/2, z

(IsoQH)][FeCl$_4$] formed, which was removed by filtration. To the filtrate, ethanol (ca. 5 mL, 96 %) was added and the solution was left for further crystallization in the refrigerator.

After a month, yellow-orange crystals appeared. The compound was dried with P$_4$O$_{10}$ in a vacuum desiccator. The composition of the compound was confirmed by elemental analysis (C, H, N) and potentiometric titration of the chloride with a standardized 0.1 M AgNO$_3$ solution: C$_{10}$H$_{10}$Cl$_4$FeN (341.9): Calcd: C, 35.12; H, 2.93; Cl, 41.5; N, 4.1; found: C, 35.28; H, 2.93; Cl, 41.8; N, 4.2 %.

Structure Determination

Crystal data and structure refinement of 3-methylisoquinolinium tetrachloridoferrate(III): empirical formula: C$_{10}$H$_{10}$Cl$_4$FeN; formula weight: 341.65; diffractometer: KUMA KM-4 [25]; wavelength: λ(Mo-K_α) = 0.71073 Å; measurement temperature: 295.0(2) K; scan mode: 2°/ω; crystal system: space group: orthorhombic, *Pnma*; unit cell dimensions: a = 10.992(2) Å, b = 7.1888(1) Å, c = 35.805(7) Å, volume: 2829.0(9) Å^3; Z = 8, calculated density: 1.605 Mg·m^{-3}; absorption coefficient: 1.794 mm^{-1}; F(000): 1368; crystal size / shape / colour: 0.4 × 0.3 × 0.2 mm / rectangular prism / yellow-orange; θ range for data collection: 2.17 to 25.04°; index ranges: $-13 \leq h \leq 0$, $-8 \leq k \leq 2$, $-42 \leq l \leq 0$; reflections collected / unique: 3522 / 2690 [R_{int} = 0.0688]; completeness to 2θ = 50.04°: 98.5 %; refinement method: full-matrix least-squares on F^2 (using the program SHELXL-97 [26] based on 194 parameters); data / restraints / parameters: 2690/0/194; goodness-of-fit on F^2: 0.877; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0455, $wR2$ = 0.0870; R indices (all data): $R1$ = 0.1264, $wR2$ = 0.2007; largest diff. peak and hole: 0.406 and -0.536 eÅ^{-3}.

The initial phase angle determination was performed with SHELXS [27]. All H atoms were placed geometrically and refined using a riding model with N−H = 0.86 Å, C−H = 0.93 Å and U$_{iso}$(H) = 1.2U$_{eq}$(C) [C−H = 0.96 Å and U$_{iso}$(H) = 1.5U$_{eq}$(C) for the methyl H atoms]. The structure of the compound (showing the conformation and atom numbering system) is shown in Figure 1 [28]. Molecular packing in the crystal, as shown in Figure 2, was prepared with PLUTO-78 [29]. The computational material for

publication was prepared using the PLATON program [30]. Interatomic bond lengths and angles are listed in Table 5 and intermolecular contacts are summarised in Table 1 and Table 2. Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates, and equivalent isotropic displacement parameters for non-hydrogen atoms, hydrogen-atom coordinates, and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. 695079.

Magnetic Measurements and EPR Spectra

All details for the measuring devices and the experimental setup are described in [22].

References

[1] J. P. McNamara, M. Sundararajan, I. H. Hillier, *J. Mol. Graph. Model.* **2005**, *24*, 128.

[2] M. C. Smith, Y. Ciao, H. Wang, S. J. George, D. Coucouvanis, M. Koutmos, W. Sturhahn, E. A. Alp, J. Zhao, S. P. Kramer, *Inorg. Chem.* **2005**, *44*, 5562.

[3] V. V. Vrajmasu, E. Münck, E. L. Bominaar, *Inorg. Chem.* **2004**, *43*, 4867.

[4] N. Toyota, T. Suzuki, *C. R. Chim.* **2007**, *10*, 37.

[5] E. Coronado, P. Day, *Chem. Rev.* **2004**, *104*, 5419.

[6] S. Noguchi, A. Kuribayashi, M. Wang, H. Fujiwara, T. Sugimoto, T. Ishida, *J. Magn. Magn. Mater.* **2007**, *310*, 1087.

[7] C. A. Clausen, M. L. Good, *Inorg. Chem.* **1970**, *9*, 220.

[8] D. J. Evans, A. Hill, D. L. Hughes, G. J. Leigh, *Acta Crystallogr., Sect. C* **1990**, *46*, 1818.

[9] M. T. Hay, S. J. Geib, *Acta Crystallogr., Sect. E* **2005**, *61*, m190.

[10] R. Shaviv, C. B. Lowe, J. A. Zora, C. B. Aakeröy, P. B. Hitchcock, K. R. Seddon, R. L. Carlin, *Inorg. Chim. Acta* **1992**, *198*, 613.

[11] J. A. Zora, K. R. Seddon, P. B. Hitchcock, C. B. Lowe, D. P. Shum, R. L. Carlin, *Inorg. Chem.* **1990**, *29*, 3302.

[12] D. Wyrzykowski, A. Sikorski, T. Lis, A. Konitz, Z. Warnke, *Acta Crystallogr., Sect. E* **2006**, *E62*, m1737.

[13] R. Kruszyński, D. Wyrzykowski, E. Styczeń, L. Chmurzyński, *Acta Crystallogr., Sect. E* **2007**, *63*, m2279.

[14] G. A. Bottomley, A. M. Carter, L. M. Engelhardt, F. J. Lincoln, J. M. Patrick, A. H. White, *Aust. J. Chem.* **1984**, *37*, 871.

[15] D. Wyrzykowski, A. Sikorski, A. Konitz, Z. Warnke, *Acta Crystallogr., Sect. E* **2006**, *62*, m3562.

[16] D. Wyrzykowski, Z. Warnke, R. Kruszyński, J. Kłak, J. Mroziński, *Transition Met. Chem.* **2006**, *31*, 765.

[17] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford **1999**.

[18] J. S. Smart, *Effective Field Theories of Magnetism*, W. B. Saunders Comp., Philadelphia and London **1966**.

[19] C. B. Lowe, R. L. Carlin, A. J. Schultz, C.-K. Loong, *Inorg. Chem.* **1990**, *29*, 3308.

[20] C. B. Lowe, A. J. Schultz, R. Shaviv, R. L. Carlin, *Inorg. Chem.* **1994**, *33*, 3051.

[21] Z. Warnke, R. Kruszyński, J. Kłak, A. Tomkiewicz, D. Wyrzykowski, *Inorg. Chim. Acta* **2006**, *359*, 1582.

[22] D. Wyrzykowski, R. Kruszyński, J. Kłak, J. Mroziński, Z. Warnke, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2071.

[23] D. Wyrzykowski, R. Kruszyński, J. Kłak, J. Mroziński, Z. Warnke, *Inorg. Chim. Acta* **2008**, *361*, 262.

[24] R. Kruszyński, D. Wyrzykowski, L. Chmurzyński, *Acta Crystallogr., Sect. E* **2007**, *63*, m1727.

[25] *Kuma KM−4 Software User's Guide Version 3.1.* Oxford Diffraction, Wrocław, **1989**.

[26] G. M. Sheldrick, *SHELXL97*, Program for Crystal Structure Refinement, University of Göttingen, **1997**.

[27] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[28] C. K. Johnson, *ORTEP II*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN **1976**.

[29] S. Mortherwell, S. Clegg, *PLUTO-78*, Program for Drawing and Molecular Structure, University of Cambridge **1978**.

[30] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.