

Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties of a Dinuclear Iron(III) Complex Asymmetrically Bridged by a Phenoxo and a Methoxo Group

C. T. Zeyrek^a, A. Elmali^b, and Y. Elerman^b

^a Turkish Atomic Energy Authority, 06690 Lodumlu-Ankara, Turkey

^b Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Besevler-Ankara, Turkey

Reprint requests to Prof. Dr. A. Elmali. E-mail: elmali@eng.ankara.edu.tr

Z. Naturforsch. **60b**, 940–944 (2005); received May 17, 2005

A new dinuclear iron(III) derivative $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ ($\text{L} = 1,3\text{-bis}[\text{N}-(5\text{-chloro-2-hydroxybenzylidene})\text{-2-aminoethyl}]\text{-2-(5-chloro-2-hydroxyphenyl)imidazolidine}$) has been synthesized, its crystal structure determined and magnetically characterized. The two iron(III) ions are asymmetrically bridged by a phenoxo and a methoxo group and separated by $3.150(2)\text{Å}$. The magnetic susceptibility of the complex was measured over the range $5\text{--}349.3\text{ K}$ and the observed data were successfully simulated by the equation based on the spin-Hamiltonian operator $H = -J\vec{S}_1 \cdot \vec{S}_2$, indicating very weak antiferromagnetic coupling between the iron ions with $J = -11.3\text{ cm}^{-1}$. The magnetic and structural parameters of the compound and the nature of the magnetic super-exchange interaction are discussed and compared with data of similar dinuclear iron(III) complexes.

Key words: Dinuclear Iron(III) Complex, Super-Exchange Interactions, Antiferromagnetic Coupling, Schiff Base, Imidazolidine

Introduction

The electronic and magnetic properties of dinuclear iron(III) complexes have been extensively studied in recent years [1–3]. They provide structural models for dinuclear sites in several proteins involved in oxygen storage by hemerytherin and oxygen activation by methanemonooxygenase [4–7]. In addition, these systems were treated as model systems for the understanding of the size and magnitude of exchange coupling interactions by theoretical considerations.

Gorun and Lippard suggested a quantitative magnetostructural relationship for dinuclear iron(III) centers, doubly bridged by oxygen atoms [8]. The influence of the geometrical parameters in Fe_2O_2 bridging systems, the Fe–O bond distances and the Fe–O–Fe bond angles, on the super-exchange integral, however, is not yet understood in detail due to lack of structural data [9–11]. Studies of some iron complexes have shown that the oxo-bridge is responsible for the strong antiferromagnetic coupling (usually $-50 > J > -200\text{ cm}^{-1}$) [12–15] and that complexes with alkoxo, phenoxo, or hydroxo bridges are weakly coupled (usually $0 > J > -30\text{ cm}^{-1}$) [15, 16–19].

We reported previously the structures and magnetic properties of several dinuclear iron(III) complexes [16, 20–24]. In an attempt to accumulate more data for further discussion of magneto-structural correlations for this type of complexes, we present here the synthesis, X-ray structural and magnetic characterization of a derivative of the closely related ligand L, $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ containing a cyclic Fe-OMe-Fe-OPh unit (Fig. 1).

Experimental Section

Preparation of $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$

The dinuclear Fe(III) complex was prepared in two steps (Fig. 1). A solution of triethylenetetramine (2.2 g, 15 mmol) in methanol (20 ml) was added dropwise to a methanolic solution (40 ml) of 5-chlorosalicylaldehyde (6.32 g, 45 mmol) with stirring at room temperature. The Schiff base ligand was obtained in the form of yellow crystals. For the preparation of the Fe(III) complex, a 15 ml quantity of a 0.1 M solution of CH_3ONa in methanol was added to a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the same solvent (0.54 g, 2 mmol, in 20 ml). To the resulting solution was added with stirring a solution of L in methanol (0.58 g, 1 mmol). The dark blue solution was allowed to evaporate at room temperature for one

Table 1. Crystallographic data for the investigated complex.

Formula	C ₂₈ H ₂₇ Cl ₅ Fe ₂ N ₄ O ₄
Formula weight (g·mol ⁻¹)	772.49
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> [Å]	12.790(1)
<i>b</i> [Å]	18.779(1)
<i>c</i> [Å]	24.950(2)
Vol [Å ³]	5992.6(7)
<i>Z</i>	8
<i>D</i> _{calc} [g·cm ⁻³]	1.712
<i>μ</i> [cm ⁻¹]	1.457
<i>F</i> (000)	3136
<i>θ</i> Range for data collection	2.53° < <i>θ</i> < 30.17°
Index ranges	0 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 26 0 ≤ <i>l</i> ≤ 34
Reflections collected	8398
Independent reflections	8390
Data / parameters	8390 / 383
Goodness-of-fit on <i>F</i> ²	1.192
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0306, <i>wR</i> = 0.0828
Final <i>R</i> indices (all data)	<i>R</i> = 0.0396, <i>wR</i> = 0.0974
Largest diff. peak and hole [eÅ ⁻³]	0.310 and -0.904

Table 2. Selected bond lengths (Å) and bond angles (°) characterizing the inner coordination sphere of the iron(III) centers (see Fig. 2 for labeling scheme adopted).

Fe1...Fe2	3.150(2)		
Fe1-N1	2.108(1)	Fe2-N3	2.280(1)
Fe1-N2	2.315(1)	Fe2-N4	2.088(1)
Fe1-O1	1.893(1)	Fe2-O2	2.096(1)
Fe1-O2	2.073(1)	Fe2-O3	1.956(1)
Fe1-O3	1.967(1)	Fe2-O4	1.897(1)
Fe1-C11	2.310(1)	Fe2-C12	2.316(1)
O1-Fe1-O2	92.1(1)	O2-Fe2-O3	76.6(1)
O1-Fe1-O3	103.4(1)	O2-Fe2-O4	90.6(1)
O2-Fe1-O3	76.0(1)	O3-Fe2-O4	102.5(1)
O1-Fe1-N1	88.3(1)	O2-Fe2-N3	82.9(1)
O2-Fe1-N1	89.8(1)	O2-Fe2-N4	87.9(1)
O3-Fe1-N1	162.3(1)	O3-Fe2-N4	160.5(1)
O1-Fe1-N2	164.4(1)	O3-Fe2-N3	89.7(1)
O2-Fe1-N2	82.6(1)	O4-Fe2-N3	164.5(1)
O3-Fe1-N2	89.7(1)	O4-Fe2-N4	89.2(1)
N1-Fe1-N2	77.0(1)	N3-Fe2-N4	76.6(1)
N2-Fe1-C11	90.6(1)	O2-Fe2-C12	171.4(1)
O1-Fe1-C11	96.3(1)	O3-Fe2-C12	97.5(1)
O2-Fe1-C11	170.3(1)	O4-Fe2-C12	96.8(1)
O3-Fe1-C11	96.3(1)	N3-Fe2-C12	90.9(1)
N1-Fe1-C11	95.5(1)	N4-Fe2-C12	96.5(1)
Fe1-O2-Fe2	98.2(1)	Fe1-O3-Fe2	106.8(1)

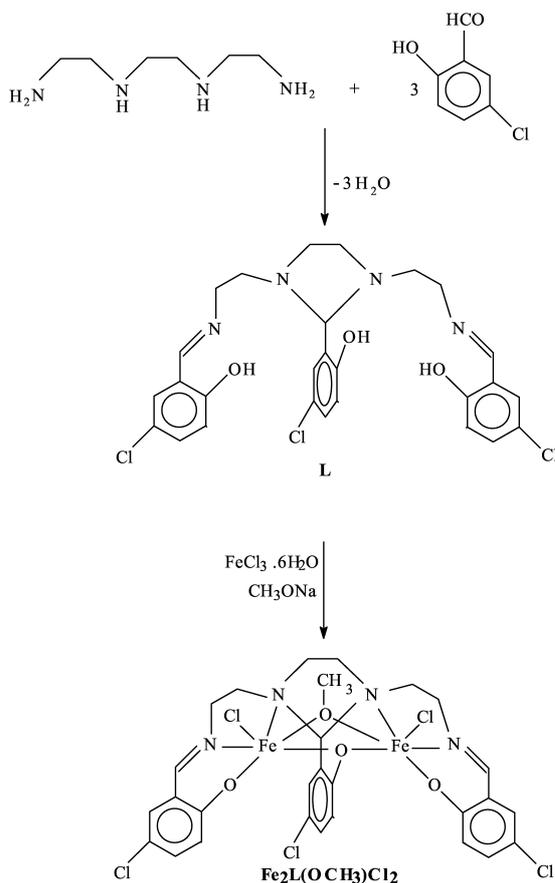


Fig. 1. Preparation of the dinuclear iron(III) complex.

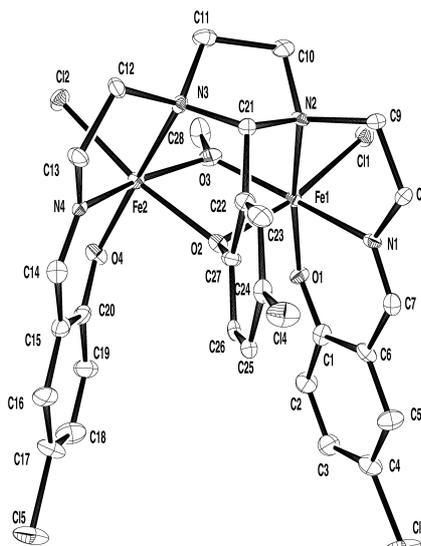


Fig. 2. View of the molecule. Displacement ellipsoids are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity.

day to give prismatic dark blue crystals, which were collected, washed with cold absolute ethanol and finally dried in air. Yield 0.76 g (67.9%), C₂₈H₂₇Cl₅Fe₂N₄O₄ (772.49): calcd. C 43.61, H 3.45, N 7.34, Fe 14.50; found C 43.54, H 3.52, N 7.25, Fe 14.46. Infrared spectrum (cm⁻¹, KBr disk): $\tilde{\nu}$ (phenolic C–O) 1539 cm⁻¹; $\tilde{\nu}$ (azomethinic C–N) 1622 cm⁻¹.

X-ray structure determination

Crystals of $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ were mounted on an Enraf-Nonius CAD-4 diffractometer (graphite monochromatized Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) [25]. Experimental conditions are summarized in Table 1. The structure was solved by SHELXS-97 and refined with SHELXL-97 [26, 27]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 \AA) and refined using a riding model. H atom displacement parameters were restricted to be $1.2U_{\text{eq}}$ of the parent atom. Selected bond distances and bond angles are listed in Table 2. An ORTEP view of the molecular structure is given in Fig. 2 [28]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-271906 [29].

Susceptibility measurements

Variable-temperature magnetic susceptibility measurements of a powdered sample were performed with a QUANTUM Design SQUID magnetometer in the temperature range 5–349.3 K. The applied field was 2 T. Diamagnetic corrections of the molar magnetic susceptibility were applied using Pascal's constant [30]. The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$, where χ is the magnetic susceptibility per Fe(III) ion.

Results and Discussion*X-ray crystal structures*

The crystal structure of $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ is built of discrete dinuclear molecules. In the dinuclear unit, the Fe(III) ions are asymmetrically bridged by phenoxy and methoxy oxygen atoms. The geometry around the iron(III) ions is distorted octahedral, as shown in Fig. 2. One oxygen and two nitrogen atoms (*cis*) of the Schiff base ligand (L) occupy three coordination sites; the remaining three sites are occupied by the two bridging oxygen atoms of the phenoxy and methoxy groups and a terminal chlorine atom. The whole molecule has a nearly perfect C_s symmetry with the mirror plane perpendicular to the iron-oxygen ring. In the compound, the bridging oxygen atoms O2 and O3, and the carbon atoms of C21–C27, and C28 lie approximately on this mirror plane. Deviations of these atoms from the least-squares pseudomirror plane are given in Table 3. The dihedral angle between the Fe1O2O3 and Fe2O2O3 planes is $11.9(1)^\circ$. The iron(III) ions are displaced from the coordination plane by $0.082(1) \text{ \AA}$ for Fe1 and Fe2. The $\text{Fe}\cdots\text{Fe}$ and $\text{O2}\cdots\text{O3}$ separations are $3.150(2)$ and $2.514(2) \text{ \AA}$, re-

Table 3. Least-squares pseudomirror plane within the $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ molecule, $0.362(2)x + 18.745(2)y + 1.332(2)z = 2.845(3)$.

Atom	Dev (\AA)	Atom	Dev (\AA)
O2	0.050 (1)	O3	−0.024 (1)
C21	−0.016 (1)	C22	0.030 (1)
C23	0.026 (1)	C24	−0.021 (1)
C25	−0.029 (1)	C26	−0.009 (1)
C27	0.036 (1)	C28	−0.024 (1)
Cl4	−0.020 (1)		

spectively. The bridging angle at the phenoxy oxygen atom, $98.2(3)^\circ$, is smaller than that at the methoxy oxygen atom, $106.8(4)^\circ$. The average bridging phenolic oxygen-iron bond length is $2.085(1) \text{ \AA}$, the average $\text{Fe}-\text{OCH}_3$ distance is $1.962(2) \text{ \AA}$. The $\text{Fe}-\text{N}(\text{imine})$ bond lengths of $2.108(1)$ and $2.088(1) \text{ \AA}$ are significantly shorter than the $\text{Fe}-\text{N}(\text{amine})$ bond lengths of $2.315(1)$ and $2.280(1) \text{ \AA}$. The overall geometrical distortion is as expected for an octahedral low-spin d^5 iron(III) ion with hexadentate chelation. The geometry is similar to that of related binuclear iron complexes [15, 16–19]. The ipso-phenoxy and methoxy carbon atoms are displaced on opposite sides of the bridging plane by $0.216(1) \text{ \AA}$ for C27 and $0.148(1) \text{ \AA}$ for C28, respectively.

The complexation reaction is different from the selective imidazolidine ring opening reaction observed earlier in a different ligand system [31]. Imidazolidine ring-cleavage with removal of one aldehyde molecule was observed for reactions of the L ligand with ferrous perchlorate hexahydrate in 1:2 mole ratio in aqueous methanol in air [32]. However, the title complex was prepared by reacting the ligand with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1:2 mole ratio in air, and the imidazolidine ring is not cleaved regenerating the diamine.

Spectroscopic properties

The most significant effects of coordination on the vibrational spectrum of free salicylaldimine Schiff ligands have previously been observed between ~ 1500 and $\sim 1650 \text{ cm}^{-1}$ [33–35], attributed to the azomethinic $\nu(\text{C}-\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ stretching modes, respectively. In this spectral region the free Schiff base ligand L exhibits two strong bands, azomethinic $\nu(\text{C}-\text{N})$ at 1640 cm^{-1} and phenolic $\nu(\text{C}-\text{O})$ at 1503 cm^{-1} [32]. On complex formation, the $\nu(\text{C}-\text{N})$ decreases, and $\nu(\text{C}-\text{O})$ increases: to 1621 and 1539 cm^{-1} for $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$, respectively.

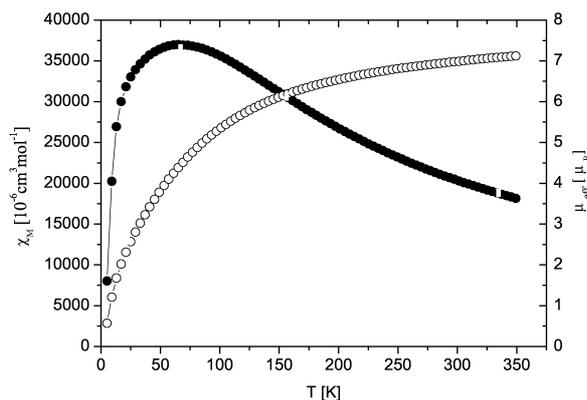


Fig. 3. The molar magnetic susceptibilities (●) and magnetic moment (○) χ per iron(III) vs. temperature T curves.

Magnetic properties

The magnetic susceptibility and the magnetic moment of the complex are shown as a function of temperature in Fig. 3. The magnetic data was fitted using the expression for molar susceptibility vs. T derived from the spin exchange Hamiltonian, $H = -J \vec{S}_1 \cdot \vec{S}_2$, where J is the interaction parameter between two spin carriers with $S_1 = S_2 = 5/2$ as given in eq. (1).

$$\chi = (1 - x_p)\chi'' + 2x_p\chi' + TIP \quad (1)$$

$$\chi'' = \frac{C}{T} \left[2\exp(2x) + 10\exp(6x) + 28\exp(12x) + 60\exp(20x) + 110\exp(30x) \right] \cdot \left[1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x) \right]^{-1}$$

$$\chi' = \frac{C}{3T}, \quad x = \frac{J}{kT}, \quad C = \frac{N_L g^2 \mu_B^2}{k}$$

For a satisfactory fit it was necessary to include a Curie-Weiss term in order to correct for a paramagnetic impurity; x_p is the molar amount of this mononuclear impurity. The temperature-independent paramagnetism (TIP = $400 \cdot 10^{-6} \text{ cm}^3/\text{mol}$ for each iron atom) was also taken into account. The best-fit parameters obtained with eq. (1) by using a standard least-squares program were $J = -11.3 \text{ cm}^{-1}$ and $x_p = 0.04\%$. An isotropic g value of 2.0 was assumed. The effective magnetic moment per iron(III) at 349.3 K is $7.12 \mu_B$, but $0.57 \mu_B$ at 5 K, and decreases rapidly as the temperature is lowered to liquid helium temperature.

Table 4. Structural and magnetic data for a series of asymmetrically bridged Fe(III)–Fe(III) complexes.

Compound	Fe··Fe (Å)	(Fe–O) (Å) ^e	P (Å) ^f	α (°) ^g	J (cm ⁻¹)	J_{calc} (cm ⁻¹) ⁱ
Present work	3.150	2.024	1.956	102.5	-11.3	-15.3
a	3.133	2.024	1.965	101.7	-10.8	-13.7
b	3.139	2.013	1.975	102.5	-8.0	-12.1
c	3.162	2.018	1.965	103.5	-7.4	-13.7
d	3.662	2.023	1.986	125.4	-7.7	-10.5

^a [Fe₂(L)(OCH₃)Cl]₂ (L = 1,3-bis[N-(3,5-dichloro-2-hydroxybenzylidene)-2-aminoethyl]-2-(3,5-dichloro-2-hydroxyphenyl)imidazolidine) [24]; ^b [Fe₂(sal₃trien)(OMe)] (sal₃trien = trisalicylidene-triethylene-tetraamine) [10]; ^c [Fe₂(sal₃trien)(OH)] [37]; ^d [Fe₂(bbap)-(OEt)(O₂PPh₂)(H₂O)] (bbap = 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol) [38]; ^e (Fe–O) is the average distance between the iron and the bridging oxygen atoms of hydroxo-, alkoxo- or phenoxo- groups; ^f describing the shortest superexchange pathway between the two metal centers; ^g α (°) average bridging angle, which includes the hydroxo-, alkoxo- or phenoxo-oxygen atom; ⁱ the calculated spin exchange coupling constant according to Gorun *et al.* [8];

The selected structural and magnetic data of the title compound and similar complexes are listed in Table 4. The increase in the average Fe–O–Fe bridging angles (α) from 101.7 in **a** to 125.4 in **d** is connected with a decrease in the antiferromagnetic exchange coupling constant (J) from -10.8 to -7.7 cm^{-1} . **d** has the largest average Fe–O–Fe bridging angle and the smallest J constant (see Table 4). The average Fe–O bond lengths of **a**, **b**, **c**, **d** and of the investigated compound are almost identical, the difference of the Fe–O bond lengths between present work and **b** being 0.011 Å , the difference of the J constant 3.3 cm^{-1} . The data strongly indicate that variations in the Fe–O–Fe bridging angles and Fe–O bond lengths do not play a dominant role in determining the degree of antiferromagnetic exchange in these compounds.

In recent years several attempts were made to combine the structural and magnetic properties of a large number of Fe(III)–O(R)–Fe(III)-systems using simple empirical correlations. In 1991 Gorun and Lippard [8] established a semi-empirical correlation of magnetic and structural data for dinuclear oxygen-bridged iron(III) complexes which are double or triply bridged by O²⁻, OR⁻, OPh⁻, OH⁻ or O₂X⁻ (*i.e.* acetate, sulfate, phosphate, arsenate *etc.*), relating the magnitude of the exchange coupling constant J with a single structural parameter P :

$$-J = A \cdot \exp(B \cdot P) \quad (2)$$

Using the reported values for A (8.763×10^{11}) and B (-12.663) and the value $P = 1.956 \text{ Å}$ as found in

the present study, a value of $J_{\text{calc}} = -15.3 \text{ cm}^{-1}$ is obtained in fair agreement with $J_{\text{obs}} = -11.3 \text{ cm}^{-1}$.

Conclusion

We have investigated the structural and magnetic properties of a dinuclear Fe(III) Schiff base complex asymmetrically bridged by a phenoxo and a methoxo group. The iron(III) centers are weakly antiferromagnetically coupled with a J value in the range so far ob-

served ($7 \leq |J| \leq 17 \text{ cm}^{-1}$) for other iron(III) complexes involving Fe_2O_2 bridging units [10, 35–38]. The magnitude of the Fe–O–Fe bridging angles and of the Fe–O bond lengths has no noticeable influence on the exchange coupling in the $\text{Fe}_2\text{L}(\text{OCH}_3)\text{Cl}_2$ compounds. The variation of the strength of the superexchange interaction cannot be explained completely by the structural features of dinuclear iron(III) complexes.

- [1] S. J. Lippard, *Angew. Chem.* **100**, 353 (1988).
 [2] D. M. Kurtz, *Chem. Rev.* **90**, 585 (1990).
 [3] L. Que (Jr.), A. E. True, *Progr. Inorg. Chem.* **38**, 97 (1990).
 [4] S. Sheriff, W. A. Hendrickson, J. L. Smith, *J. Mol. Biol.* **273** (1987).
 [5] R. E. Stenkamp, L. C. Sieker, L. H. Jesen, *J. Am. Chem. Soc.* **106**, 618 (1994).
 [6] A. C. Rosenzweig, C. A. Frederick, S. J. Lippard, P. Nordlund, *Nature* **336**, 537 (1993).
 [7] A. C. Rosenzweig, P. Nordlund, P. M. Takahara, C. A. Frederick, S. J. Lippard, *J. Chem. Biol.* **2**, 409 (1995).
 [8] S. M. Gorun, S. J. Lippard, *Inorg. Chem.* **30**, 1625 (1991).
 [9] B. Chiari, O. Piovesena, T. Tarantelli, P. E. Zanazzi, *Inorg. Chem.* **21**, 1396 (1982).
 [10] B. Chiari, O. Piovesena, T. Tarantelli, P. E. Zanazzi, *Inorg. Chem.* **21**, 2444 (1982).
 [11] P. J. Hay, J. C. Thibault, R. J. Hoffmann, *J. Am. Chem. Soc.* **97**, 4884 (1975).
 [12] R. E. Norman, S. Yan, L. Que (Jr.), G. Backes, J. Ling, J. Sanders-Loehr, J. H. Zhang, C. J. O'Connor, *J. Am. Chem. Soc.* **112**, 1554 (1990).
 [13] R. E. Norman, R. C. Holz, S. Ménage, C. J. O'Connor, J. H. Zhang, L. Que (Jr.), *Inorg. Chem.* **29**, 4629 (1990).
 [14] S. M. Gorun, S. Lippard, *Inorg. Chem.* **30**, 1625 (1991).
 [15] H. Weihe, H. U. Güdel, *J. Am. Chem. Soc.* **119**, 6539 (1997).
 [16] A. Elmali, Y. Elerman, C. T. Zeyrek, I. Svoboda, *Z. Naturforsch.* **58b**, 433 (2003).
 [17] A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, *J. Mol. Struct.* **516**, 43 (2000).
 [18] A. Elmali, Y. Elerman, I. Svoboda, *Z. Naturforsch.* **56b**, 897 (2001).
 [19] A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, K. Griesar, W. Haase, *Z. Naturforsch.* **48b**, 313 (1993).
 [20] A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, K. Griesar, W. Haase, *Z. Naturforsch.* **49b**, 365 (1994).
 [21] A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, *J. Mol. Struct.* **516**, 43 (2000).
 [22] A. Elmali, Y. Elerman, I. Svoboda, *Z. Naturforsch.* **56b**, 897 (2001).
 [23] A. Elmali, Y. Elerman, I. Svoboda, H. Fuess, K. Griesar, W. Haase, *Z. Naturforsch.* **48b**, 313 (1993).
 [24] C. T. Zeyrek, A. Elmali, Y. Elerman, *Z. Naturforsch.* in press (2005).
 [25] Enraf-Nonius diffractometer control software, Release 5.1, Enraf-Nonius, Delft, Netherlands (1993).
 [26] G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, Univ. of Göttingen, Germany (1997).
 [27] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, Univ. of Göttingen, Germany (1997).
 [28] L. J. Farrugia, ORTEP III. *J. Appl. Crystallogr.* **30**, 565 (1997).
 [29] Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-271906. E-mail: deposit@ccdc.cam.
 [30] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim (1973).
 [31] W. R. Scheidt, D. K. Geiger, R. K. Hayes, G. Lang, *J. Am. Chem. Soc.* **105**, 2625 (1983).
 [32] C. T. Zeyrek, A. Elmali, Y. Elerman, *Z. Naturforsch.* **60b**, 520 (2005).
 [33] G. C. Percy, D. A. Thornton, *J. Inorg. Nucl. Chem.* **34**, 3369 (1972).
 [34] A. Syamal, K. S. Kale, *Inorg. Chem.* **18**, 992 (1979).
 [35] J. T. Wroblewski, G. J. Long, *Inorg. Chem.* **16**, 2752 (1977).
 [36] J. A. Bertrand, P. G. Eller, *Inorg. Chem.* **13**, 125 (1974).
 [37] B. Chiari, O. Piovesena, T. Tarantelli, P. E. Zanazzi, *Inorg. Chem.* **21**, 2781 (1983).
 [38] R. Werner, S. Ostrovsky, K. Griesar, W. Haase, *Inorg. Chim. Acta*, **326**, 78 (2001).