Octanuclear Iron(III) Isobutyrate Cluster With Triethanolamine Ligand

O. Botezat

Institute of Applied Physics, Academy of Sciences of Moldova, 5Academiei str., MD2028, Chisinau, Republic of Moldova, email: olgacuru@yahoo.com

Abstract: A new octanuclear iron(III) isobutyrate cluster $[Fe_8O_3(is)_6(O_2CH)_3(tea)(teaH)_3] \cdot teaH_3 \cdot (CH_3)_2CO$ (**1**) (where His = isobutyric acid; $teaH_3$ = triethanolamine) has been prepared by the interaction of smaller trinuclear isobutyrate cluster $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(CH_3CN) \cdot 2(H_2O)$ with s-triazine and triethanolamine. Single-crystal X-ray analysis revealed that **1** crystalizes in the triclinic space group *P*-1 and comprises octanuclear $[Fe_8O_3(is)_6(O_2CH)_3(tea)(teaH)_3]$ clusters and solvate $teaH_3$ and acetone molecules. The iron centers in the $\{Fe_8\}$ core are bridged by three μ_4-oxo atoms, and peripheral ligation of the core is provided by six isobutyrates and four triethanolamine ligands. Formate group is completed the coordination sphere of three metal atoms. Cluster **1** has been also characterized by elemental, infrared spectroscopy and thermogravimetric analyses.

Keywords: iron cluster, carboxylates, aminopolyalcohol ligand, structure.

1. Introduction

The design and investigation of polynuclear iron compounds with oxygen ligation continue to be of considerable interest due to their relevance to biological systems [1] and their potential serve as models for studying complex biological processes in nature. For example, a number of different polynuclear Fe oxide complexes found in non-heme metalloproteins and metalloenzymes [2]. Many metalloproteins play an important physiological role. Typical metalloproteins are proteins containing non-heme iron-transferrin, ferritin, hemosiderin, which are important in the metabolism of iron in the body. Thus, these compounds are being synthesized and examined in order to get information into the biomineralization process involved in the formation of metal core of the iron-storage protein ferritin [3]. Besides, a paramagnetic nature of Fe metals in polynuclear compounds affords interesting magnetic properties such as high-spin ground state or single molecule magnet behavior (SMM) [4, 5]. A large number of Fe-containing compounds have been synthesized and investigated over last decades [6-9]. The contribution to this area has been made by S. Baca and co-workers and consists in the preparation of new oxo/hydroxo bridged carboxylate clusters with various nuclearities $\{Fe_4\}$ [10], $\{Fe_7\}$ [11],$\{Fe_8\}$ [12], $\{Fe_{11}\}$[13], $\{Fe_{14}\}$[14] and $\{Fe_{16}\}$ [13].The clusters with higher nuclearities $\{Fe_{17}\}$ and$\{Fe_{22}\}$ have been published by R. Winpenny [15] and G. Christou [16], respectively.

For the rational preparation of the polynuclear iron compounds several approaches have been employed [17-19]. One of these approaches includes the employment of the smaller clusters in order to obtained polynuclear Fe cages with higher nuclearity. Low nuclearity clusters such as $\{Fe_2O\}$ [20, 21], $\{Fe_3O\}$ [22-24] and $\{Fe_4O_2\}$ [25, 26] are great starting materials to produce large clusters, they can be rearranged and bind to the larger systems. Herein is reported the reaction of trinuclear $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(CH_3CN) \cdot 2(H_2O)$ cluster with triethanolamine affording polynuclear octanuclear $[Fe_8O_3(is)_6(O_2CH)_3(tea)(teaH)_3] \cdot teaH_3 \cdot (acetone)$ (**1**) isobutyrate cluster. Triethanolamine is commonly found in a number of cosmetic products and used in several different medical applications. In cosmetic uses, triethanolamine is used to raise the pH of certain mixtures, as well as acting as an emulsifier [27]. Furthermore, the effect of triethanolamine on an anthralin-induced inflammation was shown [28]. The performed experiment, where patients were treated with short-contact anthralin followed by 10% triethanolamine application, revealed that triethanolamine successfully inhibited anthralin-induced inflammation. The first octanuclear iron(III) compound possessing similar structure with triethanolamine was reported by G. Christou [29], since than some structural analogues $\{Fe_8\}$ have been reported by X. Murray [30] and A. Powell [31].

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were obtained from the commercial sources and were used as received without further purification. All reactions were carried out under aerobic conditions. The precursor μ_3-oxo trinuclear Fe(III) isobutyrate $[Fe_3O(is)_6(H_2O)_3](NO_3) \cdot 2(CH_3CN) \cdot 2(H_2O)$ was prepared according to the previously published procedure [12]. Infrared spectrum for **1** was recorded on a Perkin-Elmer Spectrum One spectrometer using KBr disc in the

region 4000–400 cm^{-1}. Elemental analysis of **1** for carbon, hydrogen and nitrogen was performed using an Elementar Vario El analyzer. TGA/DTA measurements were carried out with a Mettler Toledo TGA/SDTA 851 under a stream of dry N$_2$ (60 mL min^{-1}) in the temperature range from 25 to 600°C at a heating rate of 10 K min^{-1}.

X-ray crystallography. Diffraction dataset for compound **1** was collected on a Bruker APEX II diffractometer equipped with graphite-monochromatized Mo-Kα radiation. The summary of the crystallographic parameters and structure refinement details of **1** are listed in Table 1. The structure was solved by direct methods and refined by full-matrix least squares on weighted F^2 values for all reflections using the SHELX suite of programs [32]. All non-hydrogen atoms in cluster **1** were refined with anisotropic displacement parameters, except the minor position of disordered O- and C-type atoms. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding atom. Some ethanol groups of teaH$_3$ ligands in **1** were found to be disordered; application of restraints provided reasonable geometrical parameters and thermal displacement coefficients.

2.2.   Synthesis   of [Fe$_8$O$_3$(is)$_6$(O$_2$CH)$_3$(tea)(teaH)$_3$]·teaH$_3$·(CH$_3$)$_2$CO (1)

To the solution of [Fe$_3$O(is)$_6$(H$_2$O)$_3$](NO$_3$)·2(CH$_3$CN)·2(H$_2$O) (0.212 g, 0.24 mmol) in 5mL acetonitrile were added s-triazine (0.058 g, 0.71 mmol) and teaH$_3$ (0.05 mL, 0.37 mmol). Resulted solution was stirred at room temperature during 3 hours and left for slowly evaporation. A month later 2 mL dichloromethane was added. In three weeks the obtained precipitate was dissolved in the mixture of acetone and acetonitrile (2.5:2.5 mL). The obtained red-brown crystals of **1** suitable for X-ray analysis were filtered off, washed with acetonitrile and acetone, and dried in air. (Yield: 13.2%). Elemental analysis for C$_{60}$H$_{118}$Fe$_8$N$_5$O$_{37}$: C, 36.98; H, 6.10; N, 3.59%. Found: C, 35.25; 35.24; H, 5.91; 6.31; N, 3.82; 3.74%. IR data (KBr pellet, cm^{-1}): 3355 (br), 3150 (w), 2966 (m), 2928 (sh), 2870 (m), 1629 (sh), 1576 (vs), 1471 (m), 1429 (m), 1377 (m), 1397 (m), 1094 (m), 1030(m), 1003 (w), 911 (m), 784 (w), 582 (m), 516 (m).

3. Results and Discussion

3.1. Synthesis of 1

An octanuclear cluster **1** was prepared using soft conditions: the solution of the μ$_3$-oxo trinuclear iron(III) isobutyrate in acetonitrile solution with s-triazine and triethanolamine was stirred at room temperature, followed by the addition of dichloromethane. The obtained precipitate was recrystallized from the mixture of solvents (acetone and acetonitrile), giving red-brown crystals of [Fe$_8$O$_3$(is)$_6$(O$_2$CH)$_3$(tea)(teaH)$_3$]·teaH$_3$·(CH$_3$)$_2$CO (**1**). The additional amount of **1** was extracted with acetone and acetonitrile several times from the precipitate. The presence of s-triazine in the reaction is a prerequisite for the preparation of crystals of **1**.

3.2. Infrared spectroscopy

The IR spectrum of **1** displays the O−H stretching vibration at 3355 cm^{-1}, which corresponds to ethanol groups in teaH$_3$. Strong and broad bands of the coordinated asymmetric and symmetric carboxylate groups are observed at 1576 cm^{-1} and 1429 cm^{-1}, respectively. The C−H asymmetric and symmetric stretching vibrations of isobutyric groups show peaks in the range of 2966–2870 cm^{-1}, while the asymmetric and symmetric bending vibrations for these methyl groups produce a strong single band in the region of 1471 cm^{-1} and a doublet at 1377 cm^{-1}, respectively. The absorption peak found at 1629 cm^{-1} corresponds to C=O stretching vibrations of solvate acetone molecule in **1**.

3.3. Thermogravimetric analysis

The TGA data shows that the first weight loss of cluster **1** (Figure 1) begins at 40 °C and lasts up to 217 °C, corresponding to removal of solvent acetone and triethanolamine molecules (found: 10.05 %; calcd: 10.55%). The second step is accompanied by an endothermic peak at 236°C that indicates the loss of three formate and three isobutyrate groups (found: 20.13%; calcd: 20.35%). The next two consecutive steps in the range 300-410°C of TGA curve show an exothermic peak at 317°C that indicates the loss of remaining carboxylate ligands and all coordinated triethanolamine groups (found: 41.43%; calcd: 43.5%) with residual weight of 32.39 % suggests the final product of iron oxides (calcd: 35.7%).

3.4. Structure of 1

Single-crystal X-ray analysis revealed that **1** crystalizes in the triclinic space group *P*-1 and contains an octanuclear [Fe$_8$O$_3$(is)$_6$(O$_2$CH)$_3$(tea)(teaH)$_3$] cluster and solvate teaH$_3$ and acetone molecules. The {Fe$_8$} core comprises two almost equilateral and parallel Fe$_3$ triangles (Fe…Fe separations are 5.058(1), 5.083(1), 5.127(1) Å and 5.170(1), 5.225(1), 5.299(1) Å, dihedral angle between the planes of triangles is 1.91°), giving the appearance of a six-pointed star (Figure 2). Each triangle is capped by fourth iron atom, which displaces from the plane of triangle at 0.465 and 0.791 Å and situated at the distances 2.968-2.984 and 3.108-3.130 Å, respectively, from the iron atoms in the vertexes of triangle. The distance of 2.947(1) Å between these capped iron atoms is the shortest Fe…Fe distance in the cluster. Selected bond distances are given in Table 2. The Fe(III) centers are bridged by three μ$_4$-oxo, six isobutyrates and four triethanolamine ligands: three doubly deprotonated (teaH^{2-}) that coordinate in η^2:η^2:η^1:μ$_3$−bonding mode and one triply deprotonated (tea^{3-}) coordinating in η^2:η^2:η^2:η^1:μ$_4$−bonding mode. Three monodentate formate groups in **1** complete the coordination spheres of three Fe(III) atoms from one triangle. The replacement of these monodentate ligands can permit further linkage to form higher dimensionality clusters and cluster-based polymeric networks.
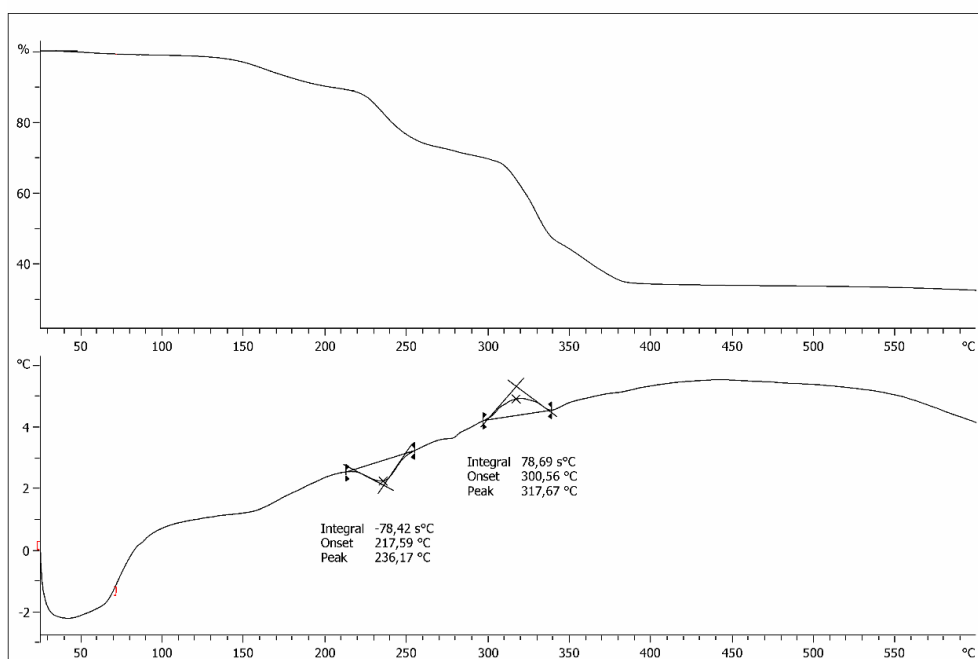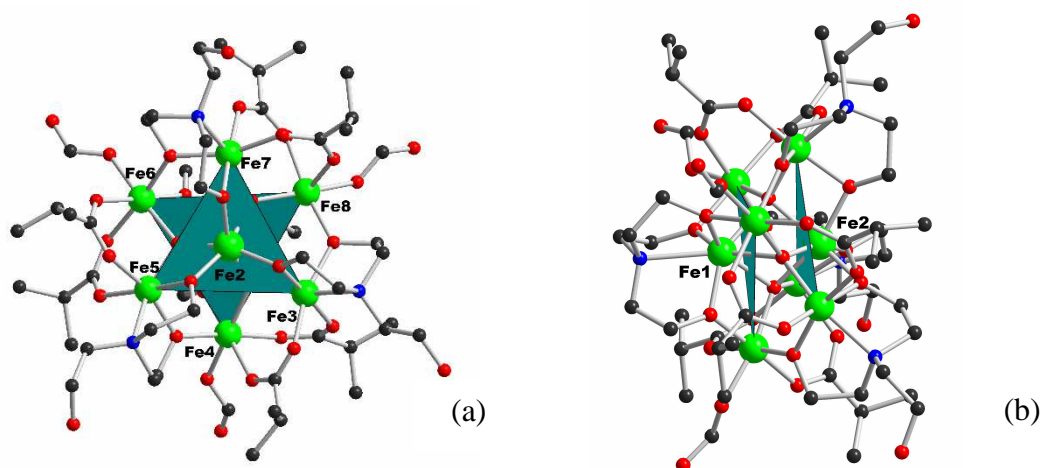
Figure 1. The thermogravimetric spectrum of 1

Figure 2. Molecular structure of $[Fe_8O_3(is)_6(O_2CH)_3(tea)(teaH)_3]$(1): top view (a) and side view (b). Two triangles are highlighted in aquamarine color. Colour definition: Fe, bright green spheres; N, blue; O, red and C, black balls. Hydrogen atoms and solvent molecules were omitted for clarity

All Fe(III) centers, except one (Fe1) are hexa-coordinated, displaying a distorted octahedral coordination sphere. The Fe(III) atoms in cluster have different coordination environments: Fe4, Fe6 and Fe8 atoms from one of above mentioned triangle have an O_6 donor set being coordinated by a μ_4-O^{2-} atom, three O atoms from two bridging isobutyrates and one monodentate formate group, and two O atoms from one doubly deprotonated (teaH^{2-}) and one triply deprotonated (tea^{3-}) ligands. Each of the Fe3, Fe5 and Fe7 atoms from another triangle have an O_5N donor set arising from one μ_4-O^{2-} atom, two O atoms from two bridging isobutyrates, and two O atoms and one N

atom from one teaH^{2-}. One of the central iron atoms (Fe1) is coordinated by three μ_4-O^{2-} atoms, three alkoxide O atoms and one N atom from one tea^{3-}, while another central iron atom (Fe2) is coordinated *via* three μ_4-O^{2-} atoms, three alkoxide O atoms from three teaH^{2-}. The Fe–O bond distances are in the range of 1.931(2)-2.477(2) Å (Fe–μ_4-O: 1.940(2)-2.232(2) Å, Fe–O_{carb}: 1.985(2)-2.086(2) Å, and Fe–O_{tea}: 1.931(2)-1.993(2) Å. The Fe–N distances range from 2.243(2) to 2.267(2) Å for teaH^{2-} ligands and equals 2.477(2) Å for teaH^{3-}. Packing diagram of **1** is shown in Figure 3.
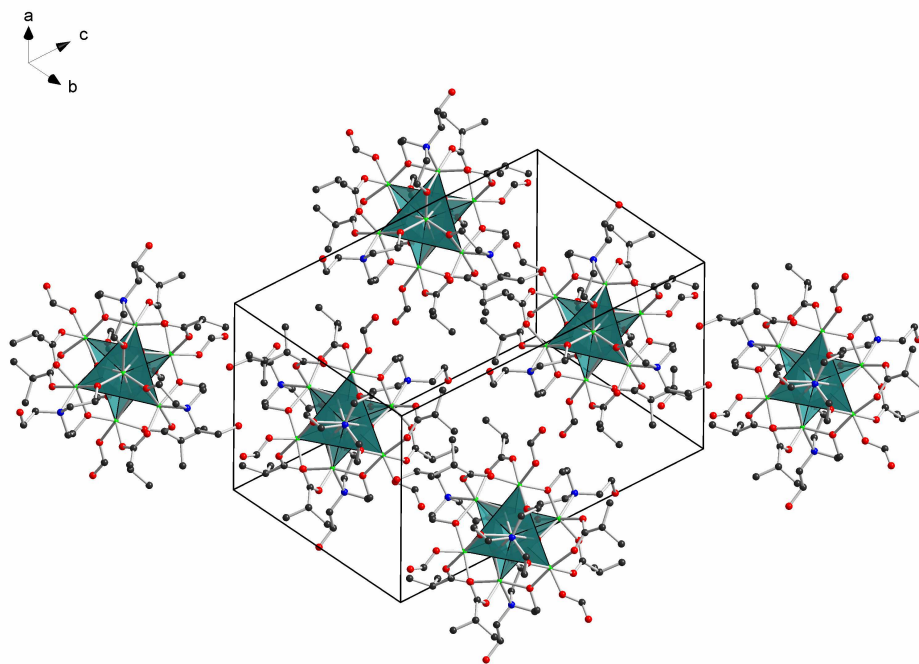
Figure 3. View of the packing in 1. Hydrogen atoms, solvate teaH$_3$ and acetone molecules are omitted for clarity

TABLE 1. The main crystallographic data of 1

	1
Empirical formula	C$_{60}$H$_{118}$Fe$_8$N$_5$O$_{37}$
Temperature (K)	123
Mr/g mol^{-1}	1948.32
Crystal system	Triclinic
Space group	*P*-1
a (Å)	14.5428(9)
b(Å)	14.6907(9)
c (Å)	20.5757(13)
α (°)	73.1080(10)
β (°)	76.6520(10)
γ (°)	88.6330(10)
Z	2
V(Å^3)	4088.17
μ (mm^{-1})	1.468
$F(000)$	2018
D(calc) [g/cm^3]	1.575
reflns collected/reflns unique	39608/18580 [R_{int} = 0.031]
Reflections[I>2$\sigma(I)$]	14252
R1, wR2 [I>2$\sigma(I)$]	0.0399, 0.1230

TABLE 2. Selected bond distances (Å) for 1

Fe1–O1	2.211(2)	Fe3–O26	1.964(2)	Fe6–O15	2.066(2)
Fe1–O2	2.281(2)	Fe3–N2	2.243(2)	Fe6–O17	2.037(2)
Fe1–O3	2.232(2)	Fe4–O1	1.967(2)	Fe6–O19	1.985(2)
Fe1–O4	1.945(2)	Fe4–O5	1.965(2)	Fe6–O30	1.995(2)
Fe1–O5	1.947(2)	Fe4–O8	2.086(2)	Fe7–O3	1.948(2)
Fe1–O6	1.931(2)	Fe4–O10	2.041(2)	Fe7–O18	1.980(2)
Fe1–N1	2.477(2)	Fe4–O11	1.970(2)	Fe7–O19	1.980(2)
Fe2–O1	2.082(2)	Fe4–O28	2.023(2)	Fe7–O21	2.047(2)
Fe2–O2	2.054(2)	Fe5–O2	1.940(2)	Fe7–O23	1.998(3)
Fe2–O3	2.060(2)	Fe5–O11	1.993(2)	Fe7–N4	2.267(2)
Fe2–O12	1.939(2)	Fe5–O12	1.979(2)	Fe8–O3	1.973(2)
Fe2–O18	1.960(2)	Fe5–O14	1.985(2)	Fe8–O4	1.965(2)
Fe2–O26	1.931(2)	Fe5–O16	2.046(2)	Fe8–O22	2.040(2)
Fe3–O1	1.952(2)	Fe5–N3	2.248(3)	Fe8–O24	2.069(3)
Fe3–O7	1.995(2)	Fe6–O2	1.967(2)	Fe8–O25	1.979(2)
Fe3–O9	2.033(3)	Fe6–O6	1.963(2)	Fe8–O32	2.010(2)
Fe3–O25	1.982(2)				

4. Conclusions

In summary, an octanuclear Fe(III) isobutyrate cluster with triethanolamine ligand $[Fe_8O_3(is)_6(O_2CH)_3(tea)(teaH)_3] \cdot teaH_3 \cdot (CH_3)_2CO$ (**1**) has been synthesized and structurally characterized by a single crystal X-ray method. Cluster **1** consists of $\{Fe_8\}$ core in which iron atoms have different O_6, O_5N, or O_6N coordination surrounding and triethanolamine ligand performs different structural functions. Characteristic peaks in the IR spectrum confirms the presence of coordinating organic ligands in the structure. Thermogravimetric analysis showed that cluster **1** loses its weight at 40 °C and completely decomposes reaching a temperature of 410°C.

REFERENCES

1. Crichton R.R., *Angew. Chem., Int. Ed. Engl.*, 12, **1973**, 57-65.
2. Fontecave M., Menage S. and Duboc-Toia C., *Coord. Chem. Rev*., 178–180, **1998**, 1555-1572.
3. Taft K.L., Papaefthymiou G.C. and Lippard S.J., *Science*, 259, **1993**, 1302-1305.
4. Wernsdorfer W., Sessoli R., Caneschi A., Gatteschi D. and Cornia, A., *Lett.*, 50, **2000**, 552-558.
5. Cornia A., Fabretti A.C., Garrisi P., Mortalo C., Bonacchi D., Gatteschi D., Sessoli R., Sorace L., Wernsdorfer W. and Barra A.L., *Angew. Chem. Int. Ed.*, 43, **2004**, 1136-1139.
6. Ferguson A., Thomas L.H. and Murrie M., *Polyhedron*, 52, **2013**, 227-2337.
7. Canada-Vilalta C., O'Brien T.A., Pink M., Davidson E.R. and Christou G., *Inorg. Chem*., 42(24), **2003**, 7819-7829.
8. Khanra S., Helliwell M., Tuna F., McInnes E.J.L. and Winpenny R.E.P., *Dalton Trans.*, **2009**, 6166-6174.
9. Bagai R., Abboud K. A. and Christou G., *Chem. Commun.*, **2007**, 3359-3361.
10. Baca S.G., Filippova I.G., Keene T.D., Botezat O., Malaestean I.L., Stoeckli-Evans H., Kravtsov V. Ch., Chumacov I., Liu S.-X. and Decurtins S., *Eur. J. Inorg. Chem*., **2011**, 356-367.
11. Baca S.G., Botezat O., Filippova I., Speldrich M., Jeanneau E., and Kögerler P., *Z. Anorg. Allg. Chem.*, 637, **2011**, 821-823.
12. Botezat O., van Leusen J., Kravtsov V.Ch., Ellern A., Kögerler P. and Baca S.G., *Dalton Trans*., 44, **2015**, 20753-20762.
13. Baca S.G., Speldrich M., van Leusen J., Ellern A. and Kögerler P., *Dalton Trans.*, 44, **2015**, 7777-7780.
14. Baca S.G., Speldrich M., Ellern A. and Kögerler P., *Materials,* 4, **2011**, 300-310.
15. Parsons S., Solan G.A. and Winpenny R.E.P., *J. Chem. Soc., Chem. Commun*., **1995**, 1987-1988.
16. Foguet-Albiol D., Abboud K. A. and Christou G., *Chem. Commun.*, **2005**, 4282-4284.
17. Winpenny R.E.P., *J. Chem. Soc. Dalton Trans*., **2002**, 1-10.
18. Gorun S.M. and Lippard S J., *Nature*, 319, **1986**, 666-668.
19. Gorun S.M., Papaefthymiou G.C., Frankel R.B. and Lippard S.J., *J. Am. Chem. Soc.*, 109, **1987**, 3337-3348.
20. Slep L.D., Mijovilovich A., Meyer-Klaucke W., Weyhermuller T., Bill E., Bothe E., Neese F. and Wieghardt K., *J. Am. Chem. Soc*., 125, **2003**, 15554-15570.
21. Ookubo T., Sugimoto H., Nagayama T., Masuda H., Sato T., Tanaka K., Maeda Y., Okawa H., Hayashi Y., Uehara A. and Suzuki M.J., *Am. Chem. Soc*., 118, **1996**, 701-702.
22. Overgaard J., Larsen F.K., Schiott B. and Iversen BB., *J. Am. Chem. Soc.,* 125, **2003**, 11088-11099.
23. Raptopoulou C.P., Sanakis Y., Boudalis A.K. and Psychais V., *Polyhedron*, **2005**, 24711-24721.
24. Boudalis A.K., Sanakis Y., Raptopoulou C.P., Terzis A., Tuchagues J.P., and Perlepes S.P., *Polyhedron,* 24, **2005**, 1540-1548.
25. Tanase T., Inoue C., Ota E., Yano S., Takahashi M. and Takeda M., Inorg. Chim. Acta, 297, 2000, 18-26.
26. Celenligil-Cetin R., Staples R. J. and Stavropoulos P., *Inorg. Chem.,* 39, **2000**, 5838–5846.
27. Fiume M.M., Heldreth B., Bergfeld W.F., Belsito D.V., Hill R.A., Klaassen C.D., Liebler D., Marks J.G., Shank R.C., Slaga T.J., Snyder P W., and Andersen F.A., *Int. J. of Toxicology*, 32, 59S-83S.
28. Ramsay B., Lawrence C. M., Bruce J. M., and Shuster S., *J. Am. Acad. Dermatol.*, 23, **1990**, 73-76.
29. Murugesu M., Abboud K. A. and Christou G., *Dalton Trans.,* **2003**, 4552-4556.
30. Jones L.F., Jensen P., Moubaraki B., Berry K.J., Boas J.F., Pilbrow J.R. and Murray K.S.J., *Mater. Chem.*, 16, **2006**, 2690-2697.
31. Ako A.M., Waldmann O., Mereacre V., Klöwer F., Hewitt I.J., Anson C.E., Güdel H.U. and Powell A.K., *Inorg. Chem.,* 46, **2007**, 756-766.
32. Sheldrick G.M., *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 64, **2008**, 112-122.