Synthesis and Structural Characterization of Iron(III) Complexes with 2-Hydroxyphenones

Maria Lalia-Kantouri,*^[a] Theodor Dimitriadis,^[a] Christos D. Papadopoulos,^[a] Maria Gdaniec,^[b] Agnieszka Czapik,^[b] and Antonios G. Hatzidimitriou^[a]

Keywords: Iron chelates; 2-Hydroxyphenones; Crystal structure; Thermochemistry

Abstract. Four iron(III) complexes [Fe(2-OH-phenone)₃] (1-4), in which 2-OH-phenone is the anion of the ligands 2-OH-aceto-phenone(Hapo) (1'), 2-OH-propiophenone(Hppo) (2'), 2-OH-benzophenone(Hbpo) (3') and 2-OH, 4-OCH₃-benzophenone(Hopo) (4'), were synthesized and characterized by physicochemical and spectral (IR, UV/Vis, Mössbauer) data. The X-ray diffraction study of compound 2, tris(2-hydroxypropiophenone)iron(III)

 $[Fe(ppo)_3]$ revealed a facial octahedral arrangement of the ligands around the iron(III) atom. The thermal decomposition for the compounds 2 and 4 was studied in nitrogen atmosphere, from ambient temperature to 1000 °C, by using the TG/DTG-DTA technique. The compounds are very stable at ambient temperature but unstable upon heating giving as residue carbonaceous iron oxide.

1. Introduction

Among all metals, iron earns a relevant position due to its indispensability in life, since it takes part in processes such as oxygen transport and electron transfer and DNA syntheses. Iron metal complexes with oxygen atoms possess a variety of structures and are of current interest not only in bioinorganic chemistry [1] (the iron storage protein ferritin has been extensively studied as a biological prototype in the organic systems [2]) but also in material science, since they can find technological applications due to their promising magnetic, electronic and catalytic properties [3, 4], that are related to their structural characterization.

Besides, the strong coordinating properties of 2-hydroxyphenones or 2-hydroxy-benzaldehydes (salicylaldehyde, saloH) and their derivatives with 3d transition metals have stimulated research in these compounds, which find applications in both pure [5] and applied chemistry fields, especially in extractive metallurgy as analytical reagents [6]. These ligands are known to coordinate in a bidentate manner with divalent transition metals in the mono-anionic form, adopting square-planar arrangement, [Zn(salo)₂], [Zn-5-Br-salo] [7], [Cu(5-Br-salo)₂] [8a], [Fe(salo)₂] [8b] or

- P.O.Box 135, Aristotle University Thessaloniki-54124, Greece [b] Faculty of Chemistry
- Adam Mickiewicz University 60780 Poznán, Poland

with vanadium octahedral coordination [VO(3-OCH₃salo)₂(H₂O)] [9]. The bidentate coordination mode of the ligand 3-OCH₃-saloH is retained when mixed-ligands are involved, e.g. [Co(salo)₂(α -diimine)] (α -diimine is a bipyridine or phenanthroline molecule) [10, 11], but there is no reference of any salicylaldehyde or 2-hydroxy-phenone complex with trivalent 3d metal structurally characterized. However, it was recently found by us that under proper conditions, 3-OCH₃-salicylaldehyde can coordinate with Fe^{III} ions in two different modes as bridging ligand, forming polynuclear complexes [12].

For a better understanding of the bonds and properties in these complexes we have recently initiated a research project with the metal ions cobalt(II, III) or iron(III) and ligands with nitrogen and/or oxygen donor atoms [13]. In this paper, our approach to the field concerns the synthesis and characterization (physicochemical and spectroscopic by IR, UV/Vis, Mössbauer methods) of four iron(III) complexes with the general formula [Fe(2-OH-phenone)₃] (1-4). The crystal and molecular structure for one compound, $[Fe(ppo)_3]$ (2), was studied by X-ray diffraction analysis. The deprotonated ligands ppo⁻ coordinate to the Fe^{III} ion with the bidentate chelating mode from the carbonyl and phenolic oxygens adopting an octahedral arrangement. The thermal stability and decomposition mode for two of the new complexes (2 and 4) were studied in nitrogen atmosphere by using TG/DTG-DTA technique.

The 2-OH-phenones presented in this work have the molecular formula 2-OH- $C_6H_4C(R)O$, in which $R = CH_3$, C_2H_5 or C_6H_5 , commonly known and abbreviated as 2-OH-acetophenone(Hapo) (1'), 2-OH-propiophenone(Hppo)



^{*} Prof. Dr. M. Lalia-Kantouri E-Mail: lalia@chem.auth.gr

[[]a] Department of Chemistry Lab. of Inorganic Chemistry

(2'), 2-OH-benzophenone(Hbpo) (3') and 2-OH, 4-OCH₃-benzophenone(Hopo) (4'), respectively (Scheme 1).





2. Experimental Section

2.1. Materials

2-Hydroxyphenone ligands 1'-4', FeCl₃·6H₂O and NaSCN were obtained as reagent grade from Aldrich and used as received. For physical measurements solvents of "extra pure" quality were obtained from Fluka and used without further purification.

2.2. Instrumentation and Analytical Procedures

Microanalyses were carried out with a Perkin-Elmer 240 B CHN microanalyzer and Perkin-Elmer 5100 PC Atomic Absorption Spectrophotometer for the metal content.

Infrared spectra were recorded with a Perkin-Elmer 1600 FT-IR spectrometer in KBr discs at room temperature and are reported in cm⁻¹. Electronic absorption spectra in CH₃CN solutions were obtained with a Shimatzu 160 A spectrometer. Molar conductivities were measured in CH₃CN solutions, employing a WTW conductivity bridge and a calibrated dip type cell. Magnetic susceptibility measurements on powdered samples were performed at 25 °C employing the Faraday method on a home-build balance calibrated against Hg[Co(SCN)₄].

⁵⁷Fe Mössbauer spectra were obtained at room temperature with a conventional constant acceleration spectrometer using a ⁵⁷Co(Rh-matrix) source. The spectrometer was calibrated with a metallic α -Fe spectrum at room temperature and the isomer shift values are given relative to metallic iron at room temperature.

The thermal behavior of the title compounds was studied in nitrogen with the simultaneous TG/DTG-DTA technique, over the temperature range ambient—to—1000 °C, using a Setaram Model Setsys-1200 thermogravimetric analyzer. The samples, with a mass of about 12 mg were heated in platinum crucibles, at a heating rate 10 °C/min.

2.3. Preparation of the Complexes [FeL₃]

2.3.1. Preparation of $[Fe(apo)_3]$ (1)

A freshly prepared methanol solution of Fe(SCN)₃, [derived from the reaction of FeCl₃·6H₂O (270.5 mg, 1 mmol) and NaSCN (243 mg, 3 mmol) after the elimination by filtration of the white NaCl] was added dropwise to a stirred methanol solution of 2-OHacetophenone (Hapo, 408 mg, 3 mmol) in the presence of excess sodium methoxide (CH₃ONa, 162 mg, 3 mmol) at room temperature. The color of the solution turned gradually darker and after 2 hours to dark red. The solution mixture was left at rest and a few days later dark red microcrystals of compound 1 were formed. The microcrystals obtained were collected by filtration, washed with ethyl ether, dried in vacuo and recrystallized from dichloromethane. The resulting solid analyzed as Anal. Calc. % for 1 ($C_{24}H_{21}O_6Fe$): C: 62.23 (calcd. 62.47), H: 4.52 (calcd. 4.55); Fe: 12.03 (calcd. 12.13). Yield 267 mg, 58 %. The conductivity in freshly prepared CH₃CN solutions was found equal to 16 µS/cm, denoting the neutral character of the compound. The magnetic value at room temp. (μ_{eff}) for compound 1 was found equal to 2.26 μ_{B} . IR (KBr), selected peaks: 1603 vs, 1342 m, 604 m cm $^{-1}$.

2.3.2. Preparation of $[Fe(ppo)_3]$ (2)

The procedure followed was the same as described above, by replacing only the ligand 2-OH-acetophenone, by 2-OH-propiophenone (Hppo, 450 mg 3 mmol). The microcrystalline compound obtained analyzed as Anal. Calc. % for **2** ($C_{27}H_{27}O_6Fe$): C: 63.94 (calcd. 64.41), H: 5.35 (calcd. 5.36); Fe: 11.02 (calcd. 11.20). Yield 276 mg, 55 %. Conductivity in CH₃CN solutions was equal to 14 µS/cm and $\mu_{eff} = 2.63 \,\mu_{B}$. IR (KBr), selected peaks: 1602 s, 1341 m, 603 m cm⁻¹.

2.3.3. Preparation of $[Fe(bpo)_3]$ (3)

The procedure followed was the same as described above, by replacing only the ligand 2-OH-acetophenone, by 2-OH-benzophenone (Hbpo, 594 mg, 3 mmol). The microcrystalline compound obtained analyzed as Anal. Calc. % for **3** (C₃₉H₂₇O₆Fe): C: 71.83 (calcd. 72.33), H: 4.15 (calcd. 4.17); Fe: 8.63 (calcd. 8.65). Yield 297.6 mg, 46 %. Conductivity in CH₃CN 12 µS/ cm and $\mu_{\rm eff} = 2.67 \,\mu_{\rm B}$. IR (KBr), selected peaks: 1608 s, 1368 m, 604 m cm⁻¹.

2.3.4. Preparation of $[Fe(opo)_3]$ (4)

The procedure followed was the same as described above, by replacing only the ligand 2-OH-acetophenone, by 2-OH-4-OCH₃benzophenone (Hopo, 684 mg, 3 mmol). The microcrystalline compound obtained analyzed as Anal. Calc. % for 4 (C₄₂H₃₃O₉Fe): C: 67.84 (calcd. 68.38), H: 4.42 (calcd. 4.47); Fe: 7.50 (calcd.7.59). Yield 309.5 mg, 42 %. Conductivity in CH₃CN 15 μ S/ cm and $\mu_{\rm eff} = 2.59 \,\mu_{\rm B}$. IR (KBr), selected peaks: 2837 m, 1607 s, 1371 m, 604 m cm⁻¹.

2.4. X-ray Crystallography

Single crystals of the $[Fe(ppo)_3]$ were obtained by recrystallization from dichloromethane solution at ambient temperature. Diffraction data were collected at 130 K with a KumaCCD single-crystal diffractometer equipped with an Oxford Cryostream device. Data collection and reduction were performed with CrysAlis CCD [14] and CrysAlis RED [14], respectively. As initial attempts to solve the crystal structure in different trigonal space groups and a P lattice were unsuccessful, twinning was considered as a source of the failure. More careful analysis of the diffraction pattern pointed to an obverse/reverse twinning [15]. In layers with 1 = 3n only every third reflection was observed, whereas in all the other layers one third of the reflections was absent (a typical manifestation of the obverse/ reverse twinning) and therefore data integration was repeated on an R lattice. The structure was solved in the space group $R\overline{3}$ by direct methods with the SHELXS-97 program [16] and refined by full-matrix least-squares method on F^2 with SHELXL-97 [17]. In the refinement process obverse/reverse twinning was taken into account with the help of the "HKLF 5" instruction of SHELXL-97. The BASF parameter refined to 0.420(2). Hydrogen atoms bound to carbon atoms were generated geometrically in idealized positions. Their displacement parameters were set equal to $1.5U_{eq}(C)$ for the methyl groups and $1.2U_{eq}(C)$ for the remaining hydrogen atoms. The crystal data and some details of data collection and structure refinement are given in Table 1. CCDC-713969 contains the supplementary crystallographic data for this paper.

Table 1. Crystal data for [Fe(ppo)₃].

Empirical formula	$(C_9H_9O_2)_3Fe$	
Formula weight	503.34	
Temperature /K	130 (2)	
Wavelength /Å	0.71073	
Crystal system	trigonal	
Space group	R3	
Unit cell dimensions		
a /Å	13.3184(1)	
b /Å	13.3184(1)	
c /Å	46.4459(9)	
Volume /Å ³	7134.80(16)	
Ζ	12	
Density calculated $/g \cdot cm^{-3}$	1.406	
F(000)	3156	
Crystal size /mm	$0.2 \times 0.2 \times 0.15$	
θ range for data collection /°	4.16-25.02	
Limiting indices	$-15 \le h \le 7, -7 \le k \le 15,$	
	$-54 \le l \le 55$	
Reflection collected / unique	13978 / 2797	
Data / restraints / parameters	2797 / 0 / 206	
Completeness $\theta = 25.02^{\circ}$	99.4 %	
Goodness-of-fit on F^2	1.131	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0404, wR_2 = 0.0923$	
R indices (all data)	$R_1 = 0.0510, wR_2 = 0.0975$	
$\Delta_{ homax}$ and $\Delta_{ homin}$ /e·Å ⁻³	0.506 and -0.512	

3. Results and Discussion

3.1. Synthesis and Characterization

The reaction of a methanol solution of Fe(SCN)₃ with the anion of a 2-OH-phenone ligand, in a metal-to-ligand ratio 1:3 [Equation (1)], in air at room temperature, led to the formation of four dark red microcrystalline iron compounds. They are stable in air, soluble in almost all organic solvents but insoluble in ethyl ether and water. Their elemental analyses and the absence of electrical conductivity in CH₃CN solutions ($\Lambda_M \approx 14 \,\mu$ S/cm) indicated neutral compounds of the general formula [Fe(2-OH-phenone)₃]. Their magnetic moments at room temperature ($\mu_{eff} = 2.49 \,\mu_{B}$), corroborate with low-spin octahedral coordination of the iron(III) ion [18].

$$Fe(SCN)_3 + 3 (2-OH-phenoneH) + 3 CH_3ONa \rightarrow [Fe(2-OH-phenone)_3] + 3 CH_3OH + 3 NaSCN (1)$$

The coordination mode and the arrangement around the metal ion of the 2-hydroxy-phenone ligands in the newly prepared complexes were examined by different spectroscopic methods (IR and electronic excitation spectra, as well as Mössbauer for one representative complex).

3.2. Infrared Spectra (IR)

From a plethora of discrete bands in the IR spectra of the compounds studied we selected those that are important for the elucidation of the coordination mode of the ligands with the metal ion.

In the spectra of the free 2-hydroxyphenone ligands the intense bands stemming from the stretching and bending vibrational modes of the phenolic OH around 3200 cm⁻¹ and 1410 cm^{-1} , respectively, disappear from the spectra of all complexes indicating the ligand deprotonation [19]. Also, the bands originating from the C-O stretching vibrations at 1245-1285 cm⁻¹ in the complexes exhibit positive shifts at 1342-1385 cm⁻¹, whereas their intensity is enhanced appreciably denoting coordination through the carbonyl oxygen of the phenone ligand. The band at ~1660 cm⁻¹ attributable to the carbonyl bond v(C=O) of the free ligand, upon coordination, in the complexes is shifted to lower frequencies at $\sim 1603 \text{ cm}^{-1}$ thus denoting the bidentate mono-anionic character of the studied hydroxyl-phenone ligands. The medium intensity bands at about 604 cm^{-1} are attributed to the Fe-O coordination bonds [20].

3.3. Electronic Spectra (UVIVis)

The UV/Vis spectra of all compounds studied in CH₃CN solutions presented five dominant bands in the region 200–1000 nm. The intense bands in the ultraviolet region, appearing at around 220 nm (Band I), 265 nm (Band II), and 330 nm (Band III), were assigned to $\pi^* \leftarrow \pi$ or $\pi^* \leftarrow \eta$ intra ligand transitions, evidence arising from the position and intensity, as well as from the comparison with the corresponding free 2-hydroxy-phenones spectra.

In the visible region the band appearing at around $\sim 430 \text{ nm}$ (Band IV) with the shoulder at $\sim 480 \text{ nm}$ (Band V) can be assigned to charge transfer, probably from phenolate ligand to metal (LMCT), responsible for the deep red color of the compounds [21, 22].

The expected band at ~ 600 nm due to the (d-d) metal transition is not apparent in the spectra of these complexes, probably obscured from the more intense CT band. A rep-

resentative UV/Vis spectrum for the compound [Fe(apo)₃] is given in Figure 1.



Figure 1. Electronic excitation (UV/Vis) spectrum for the compound [Fe(apo)₃], $C = 10^{-4}$ M in CH₃CN.

3.4. Mössbauer

The RT Mössbauer spectrum of the compound $[Fe(ppo)_3]$ (Figure 2) consists of one non-equivalent doublet with hyperfine parameters (isomer shift value δ (Fe) = 0.28 mm/s and quadrupolar splitting ΔEq = 0.66 mm/s) corresponding to Fe^{III} in distorted octahedral environment with probability of low-spin complexes [23].



Figure 2. Mössbauer spectrum of the compound $[Fe(ppo)_3]$ at room temp.

3.5. Crystal Structure of $[Fe(ppo)_3]$ (2)

 $[Fe(ppo)_3]$ crystallizes in the space group $R\overline{3}$ with two symmetry independent molecules in the unit cell, A and B, situated on a threefold axis (Figure 3). The ppo ligand is a bidentate *O*,*O* donor, with one oxygen atom belonging to the phenolate group and the second oxygen atom to the carbonyl group and therefore the tris-chelate $[Fe(ppo)_3]$ molecules could, in principle, assume meridional and facial arrangements. However, C_3 symmetry of the complex molecules in the studied crystal allows for facial isomers only.

In both symmetry independent molecules, the FeO₆ units show distorted octahedral arrangement (Table 2) with the trans O-Fe-O angles of 165.42(8)° and 168.21(8)° in molecules A and B, respectively. Larger distortions in the molecule A are also observed for the cis O-Fe-O angles which fall in the range $80.53(8) - 100.13(7)^\circ$. The equatorial coordination planes present no deviation within the experimental error for the atoms forming them and both Fe^{III} ions are placed slightly lower with distances 0.13 and 0.17 Å. The corresponding Fe-O distances in both molecules are equal within an experimental error, with the mean Fe-O(phenolato) length of 1.914(2) Å significantly shorter than the mean Fe-O(carbonyl) distance, 2.070(2) A. This arrangement is in a good agreement with that observed in some complexes formed by Fe^{III} with salicylate-based tripodal ligands [24]. A significantly smaller difference between the distances of the metal ion to phenolato and carbonyl oxygen atoms was observed in the meridional [Ru(s alo_{3} complex [25].

Table 2. Selected interatomic distances /Å and angles $/^{\circ}$ for $[Fe(ppo)_3]$.

Bond/angle	Molecule A	Molecule B
Fe1-01	1.9135(19)	1.9155(19)
Fe1-O2	2.0766(19)	2.0632(19)
O1-C1	1.313(3)	1.312(3)
O2-C7	1.244(3)	1.252(3)
O1-Fe1-O1 ⁽ⁱ⁾	100.13(7)	96.94(7)
O1-Fe1-O2	86.07(8)	85.72(7)
$O1 - Fe1 - O2^{(i)}$	91.66(8)	94.13(8)
O1-Fe1-O2(ii)	165.42(8)	168.21(8)
O2-Fe1-O2 ⁽ⁱⁱ⁾	80.53(8)	82.63(8)

Symmetry codes: (i) 1-y, 1 + x-y, z; (ii) 1-x + y, 1-x, z.

The crystal packing is shown in Figure 4a. Two types of (0001) layers, composed solely of similarly arranged molecules A or B, alternate along the z axis (Figure 4b-d). The crystal structure is mainly stabilized by $C-H-\pi$ interactions between the phenyl rings belonging to the same layer and by C-H····O(phenolate) interactions between the molecules from neighboring layers.

3.6. Thermal Behavior

The decomposition mode of the complexes $[Fe(ppo)_3]$ and $[Fe(opo)_3]$ was studied in nitrogen atmosphere by using the simultaneous thermogravimetric and differential thermal analysis technique (TG/DTG-DTA) from ambient temperature up to 1000 °C. The thermal decomposition mode of the two complexes under investigation seems to follow similar models. Representative thermoanalytical curves are depicted for $[Fe(ppo)_3]$ in Figure 5. It is obvious that there is no crystallized water or alcohol solvent molecule in the compound. The melting, deduced from the sharp intense endothermic peak on DTA curve at 205 °C, was followed





Figure 3. Ortep plot of the two symmetry independent molecules of $[Fe(ppo)_3]$ with 50 % probability ellipsoids. Atomic labels are shown for asymmetric unit and hydrogen atoms have been omitted for clarity.

immediately by decomposition. The first decomposition stage proceeds with a sudden and considerable mass loss (30 %) with maximum decomposition rate (DTGmax) at 250 °C, which is attributed to the elimination of one Hppo ligand molecule (29.62 % calcd.). The second stage, separated in several steps as deduced from the DTG curve, follows successively with the rupture of both coordination bonds and bonds inside the ligands. The experimental mass loss for this stage (36 %) involves possibly elimination of a second ligand plus one ethane molecule from the third one at DTG maxima 300 and 350 °C (35.60 % calcd.).



Figure 5. Thermoanalytical (TG/DTG-DTA) curves for compound [Fe(ppo)₃] in nitrogen.



Figure 4. Crystal packing of $[Fe(ppo)_3]$: (a) view along the z axis; (b) view along the b axis showing alternating layers of molecules A and B and arrangement of the molecules within the layers for molecules A (c) and B (d). Hydrogen atoms have been omitted for clarity.

The intermediates formed are further decomposed at 700 °C leading to the formation of carbonaceous (4 % in carbon) iron oxide, Fe_2O_3 , confirmed by its infrared spectrum and X-ray diffraction pattern as final product at 1000 °C [26, 27].

4. Conclusions

The characterization of the newly synthesized iron(III) complexes [Fe(2-OH-phenone)₃] was made by stoichiometric analysis, molar conductivity and magnetic measurements at room temperature. The infrared spectroscopic data gave evidence for the bidentate coordination mode (through the phenolate and carbonyl oxygen atoms) of the 2-hydroxyphenone ligands, whereas Mössbauer data verified the trivalent character of the iron atom in the studied complexes. The X-ray study of complex **2** revealed a facial octahedral arrangement of the ppo⁻ ligands around the iron(III) atom. The thermal data of the complexes **2** and **4**, in nitrogen, gave as residues at 1000 °C the carbonaceous oxide Fe₂O₃.

References

- a) S. Tanase, E. Bouwman, G. J. Long, A. M. Shahin, R. de Gelder, A. M. Mills, L. A. Spek, J. Reedijk, *Polyhedron* 2005, 24, 41; b) X. Xu, H. L. Persson, D. R. Richardson, *Mol. Pharmacol.* 2005, 68, 261.
- [2] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, J. Am. Chem. Soc. 1994, 116, 823.
- [3] a) P. Chaudhuri, *Coord. Chem. Rev.* 2003, 243, 143; b) M. Soler,
 W. Wernsdorfer, K. Folting, M. Pink, G. Christou, *J. Am. Chem. Soc.* 2004, 126, 2156.
- [4] L. Bénisvy, J.-C. Chottard, J. Marrot, Y. Li, Eur. J. Inorg. Chem. 2005, 999.
- [5] R. N. Prasad, A. Agrawal, J. Ind. Chem. Soc. 2006, 83, 75.
- [6] K. Fujinaga, Y. Sakaguchi, T. Tsuruhara, Y. Seike, M. Oku-
- mura, Solvent Extract. Res. Develop. 2001, 144.
 [7] a) Z.-Y. Xiong, L.-J. Liu, Acta Crystallogr., Sect. E 2005, 61, m863; b) Q. Chen, Acta Crystallogr., Sect. E 2006, 62, m56.
- [8] a) Y.-X. Sun, G.-Z. Gao, Acta Crystallogr., Sect. E 2005, 61, m354; b) Y.-M. Yang, P.-C. Lu, T.-T. Zhu, C.-H. Liu, Acta Crystallogr., Sect. E, 2007, 63, m1613.

- [9] J. C. Pessoa, I. Cavaco, I. Correia, I. Tomaz, T. Duarte, P. M. Matias, J. Inorg. Biochem. 2000, 80, 35.
- [10] C. D. Papadopoulos, A. G. Hatzidimitriou, G. P. Voutsas, M. Lalia-Kantouri, *Polyhedron* 2007, 26, 1077.
- [11] C. D. Papadopoulos, M. Lalia-Kantouri, J. Jaud, A. G. Hatzidimitriou, *Inorg. Chim. Acta* 2007, 360, 3581.
- [12] M. Lalia-Kantouri, C. D. Papadopoulos, A. G. Hatzidimitriou, S. Skoulika, *Struct. Chem.* 2008, in press, DOI: 10.1007/ s11224-008-9397-5.
- [13] C. D. Papadopoulos, Ph. D. Thesis, Aristotle University of Thessaloniki, Greece 2007.
- [14] Oxford Diffraction. CrysAlis CCD and CrysAlis RED Ver. 1.171.31. Oxford Diffraction Ltd., Abingdon, Oxfordshire, England 2006.
- [15] a) R. Herbst-Irmer, G. M. Sheldrick, Acta Crystallogr, Sect. B 2002, 58, 477; b) G. M. Sheldrick, Acta Crystallogr, Sect. A: Found. Crystallogr. 2008, 64, 112.
- [16] G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Göttingen, Germany 1997.
- [17] a) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany 1997; b) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.
- [18] a) V. Paredes-Garcia, R. O. Latorre, E. Spodine, *Polyhedron* 2004, 23, 1869; b) A. Earnshaw; B. N. Figgis, J. Lewis, *J. Chem. Soc.* 1966, *A*, 1656.
- [19] R. M. Silverstein, G. C. Bassler, G. Morvill, *Spectrometric Identification of Organic Compounds*, 6th ed., Wiley, New York 1998, p. 87.
- [20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Part B, Wiley-Interscience, New York **1986**, p. 172.
- [21] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam 1984, p. 452.
- [22] V. Paredes-García, D. Venegas-Yazigi, R. O. Latorre, E. Spodine, *Polyhedron* 2006, 25, 2026.
- [23] G. Long, *Mössbauer spectroscopy*, Applied to Inorganic Chemistry, Plenum Press, N. York **1984**, p. 43.
- [24] S. M. Cohen, M. Meyer, K. N. Raymond, J. Am. Chem. Soc. 1998, 120, 6277.
- [25] N. Bag, G. K. Lahiri, S. Bhattacharya, L. R. Falvello, A. Chakravorty, *Inorg. Chem.* 1988, 27, 4396.
- [26] P. S. Thomas, D. Hirschausen, R. E. White, J. P. Guerbois, A. S. Ray, J. Therm. Anal. Cal. 2003, 72, 769.
- [27] R. K. Verma, L. Verma, M. Ranjan, B. P. Verma, S. C. Mojumdar, J. Therm. Anal. Cal. 2008, 94, 27.

Received: January 20, 2009 Published Online: April 8, 2009