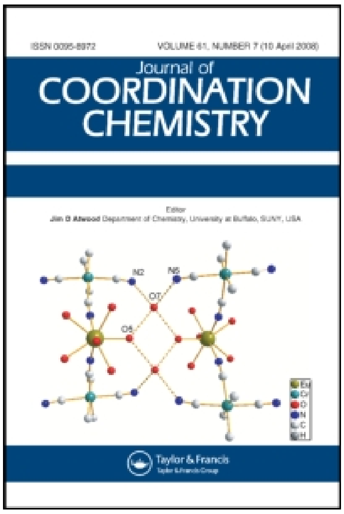

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A new capped iron(III) trinuclear benzoate cluster

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The new cluster $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ was prepared and characterized by atomic absorption, elemental analysis, mass spectrometry, Mössbauer, IR, UV-vis and EPR spectroscopies. Structural information was obtained from quantum mechanics calculations using the molecular mechanics (MM+) approach. This cluster has only one labile coordination site suitable for ligand substitution and can be used as a starting material to the rational assemble of polynuclear compounds.

Keywords: Iron(III); Benzoate; Cluster; *o*-Phenanthroline

1. Introduction

The iron acetate cluster was first isolated in 1909 by Weinland and Gussmann [1] although at the time they were not able to propose the correct formula. Since then, trinuclear oxo-centered carboxylate complexes have been extensively investigated as models of electronic and magnetic extended interactions [2–5] and as homogeneous catalysts [6]. As an important building block to supramolecular chemistry [7–10], the literature presents some examples of hexanuclear complexes prepared by reacting two trinuclear units in the presence of a bridging (ambidentate) ligand as illustrated in scheme 1. This approach uses a monodentate auxiliary ligand such as pyridine to produce an asymmetric cluster of the type $[M_3O(RCO_2)(py)_2(solv)]^+$ in order to protect two of the three substitution sites. The problem is that, up to the present, there is no direct synthesis of the asymmetric clusters and it involves a multi-step procedure usually with low overall yields [8]. First the symmetric complex $[M_3O(RCO_2)(solv)_3]^+$ is prepared followed by its reduction and further reaction with CO yielding $[M_3O(RCO_2)(solv)_2(CO)]$. This complex undergoes a substitution reaction of the solvent molecules by pyridine, for example, and finally after this, the corresponding

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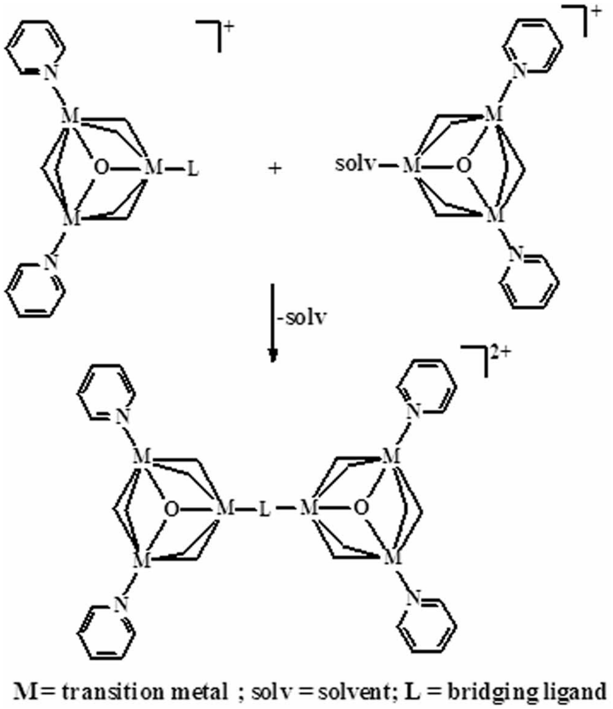
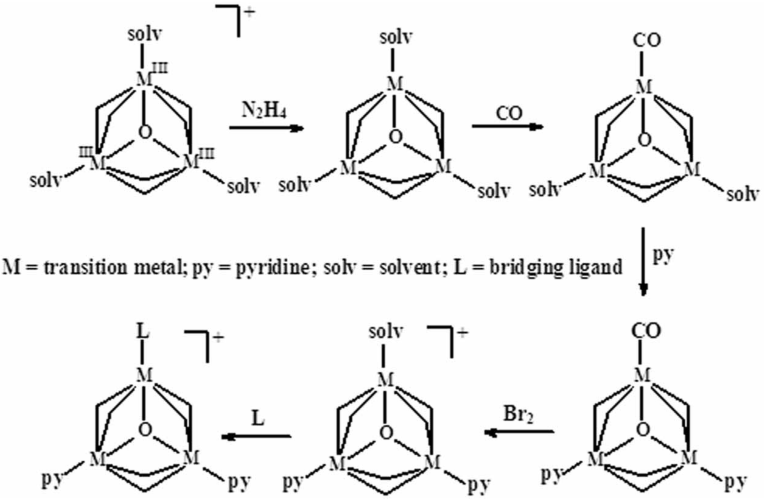


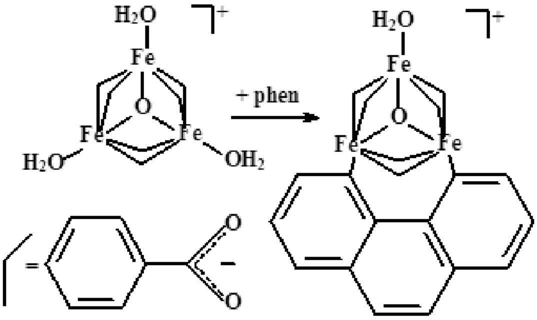
Scheme 1. Synthetic approach to ligand-bridged hexanuclear carboxylate clusters.



Scheme 2. Classic synthetic pathway to substitution in trinuclear carboxylate clusters.

$[M_3O(RCO_2)(py)_2(CO)]$ species are oxidized with bromine to eliminate the CO ligand (scheme 2).

Herein we present a single pot, high yield synthetic route to obtain $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ (scheme 3). This compound contains the strong



Scheme 3. Representation of $[Fe_3O(C_7H_5O_2)_6(H_2O)(phen)]^+$.

chelating agent phen = *o*-phenanthroline, which blocks the sixth coordination sites of two iron centers, leaving the third iron(III) ion coordinated to a labile water molecule capable of undergoing further substitution reactions. It is, therefore, an important precursor to more rational and straightforward preparations of polynuclear complexes.

2. Experimental

2.1. *Syntheses*

2.1.1. $[Fe_3O(C_7H_5O_2)_6(H_2O)_3]NO_3$. This compound was prepared with a modification of the method described elsewhere [11]. $Fe(NO_3)_3 \cdot 9H_2O$ (32.3 g, 80 mmol) was dissolved in 100 mL of water and mixed under stirring with 23.6 g (164 mmol in 100 mL of water) of sodium benzoate. A light reddish solid was isolated by filtration, washed with water and vacuum dried. After recrystalization from acetonitrile, the yield was 27 g (97%). Anal. Calcd for $C_{42}H_{36}NO_{19}Fe_3$(%): C, 49.2; H, 3.5; N, 1.4. Found: C, 48.3; H, 3.7; N, 1.3.

2.1.2. $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$. To a hot acetonitrile solution of $[Fe_3O(C_7H_5O_2)_6(H_2O)_3]NO_3$ (1.0 g, 0.96 mmol in 20 mL of the solvent) was added under stirring 0.17 g (0.96 mmol) of *o*-phenanthroline dissolved in 5 mL of acetonitrile. A brown powder was recovered by filtration after cooling to room temperature. The solid was washed with acetonitrile and vacuum dried. Yield was 1.1 g (98%). Anal. Calcd for $C_{54}H_{40}N_3O_{17}Fe_3$(%): C, 55.4; H, 3.4; N, 3.6; Fe, 14.3. Found: C, 55.5; H, 3.6; N, 3.8; Fe, 14.1.

2.2. *Physical measurements and instrumentation*

Mass spectrum. The sample was dissolved in CH_2Cl_2 and analyzed directly by electrospray ionization on a ZQ (Micromass, UK) single quadrupole mass spectrometer. Mössbauer data were recorded from solid samples at 298 and 80 K using an ES-Technology MS105 spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix. Spectra were referenced against iron foil at 298 K and parameters obtained by fitting the spectrum with Lorentzian lines, errors were $\leq \pm 0.01\ mm\,s^{-1}$. X-band electron paramagnetic resonance (epr) spectra were recorded on a Bruker ESP300-E instrument from solid samples of the complex at 77 K. Infrared spectra were obtained with a Varian Excalibur series spectrophotometer in the region 4000–400 cm^{-1} as nujol mulls spread on KBr windows. Electronic spectra in the UV-vis range (190–820 nm) were obtained on a Hewlett-Packard Model 8452A diode-array spectrophotometer in ethanol solutions. Molecular modeling calculations were carried out using the HyperChem 7.1 package, from Hypercube Inc., Gainesville, USA. Geometry optimization was carried out using the MM+ method, with a gradient of 4×10^{-5} kcal as a convergence criterion. Desert Analytics, USA, handled microanalyses. Metal content was determined by atomic absorption.

3. Results and discussion

3.1. *Mass and infrared spectra*

The mass spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ was recorded in CH_2Cl_2 solution and exhibits a peak at $m/z = 910.1$ (27%) corresponding to the species $[Fe_3O(C_7H_5O_2)_6]^+$ after loss of phen and H_2O molecules, and is consistent with the triangular structure of the complex.

Infrared spectra of complex $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ showed main bands at (cm^{-1}): 1598 (ν_{asym} COO^-), 1408 (ν_{sym} COO), 1350 (sym bend CH_3), 1022 (ν_{sym} NO_3^-), 718 (πC–H), 665 and 633 (in plane and out-of-plane bend COO^-, respectively) and at 469 (ν_{as} M_3O). The difference in frequency between the antisymmetric and symmetric stretching modes of the carboxylate group supports the presence of bridging coordinated benzoate in the complex [12–14].

3.2. *Mössbauer spectrum*

The Mössbauer spectrum at 298 K of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ (figure 1) exhibits three nested doublets of approximately equal intensity. Isomer shifts (i.s.), quadrupole splittings (q.s.) and half-width at half-maxima (h.w.h.m.) were observed at: 0.40, 0.40, 0.40; 1.03, 0.76, 0.44 and 0.15, 0.13, 0.17 $mm\,s^{-1}$, respectively, and are consistent with three high-spin iron(III) sites in slightly different environments. The parameters at 80 K are 0.49, 0.51, 0.53; 1.14, 0.85, 0.51; 0.12, 0.15, 0.16 $mm\,s^{-1}$. Typical values of i.s., q.s. and h.w.h.m. for $[Fe_3O(CH_3CO_2)_6(L)_3]NO_3$ ($L = H_2O$, and pyridine derivatives), at room temperature, range from 0.36–0.48, 059–0.80 and 0.14–0.25 $mm\,s^{-1}$, respectively [14].

3.3. *UV-visible spectrum and electron paramagnetic resonance (epr)*

The UV-visible spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ in ethanol (figure 2) exhibited an intense band at 410 nm assigned to a (benzoate, μ-O) $p_\pi \rightarrow d_\pi(Fe^{III})$ charge transfer and a ligand field transition at 460 nm.

The epr spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ (figure 3) showed signals at $g = 8.0$ and 4.3, typical of high spin ($S = 5/2$) Fe^{III} in rhombic complexes. These high g-values have also been attributed to zero-field splitting effects. The $g = 2.0$ signal and the broad shape at lower magnetic fields indicate intermolecular interactions in the solid state [15].

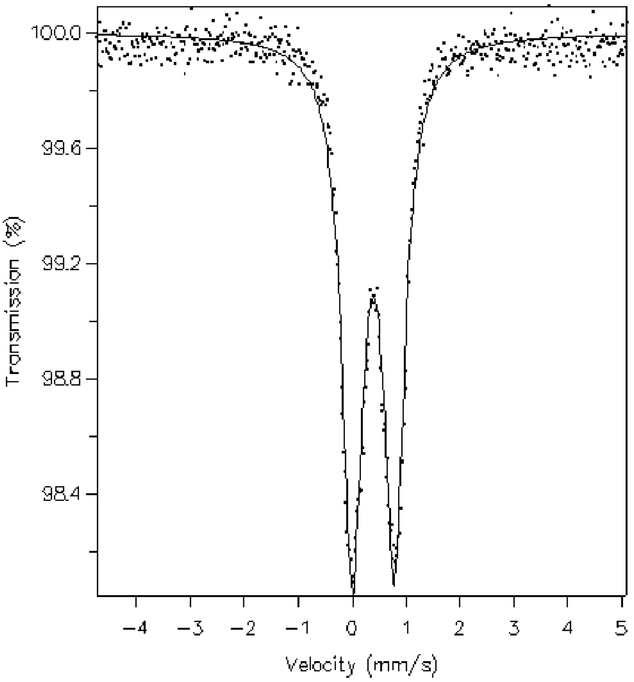


Figure 1. Mössbauer spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ at 298 K. The solid line is a fit to three nested doublets of equal intensity.

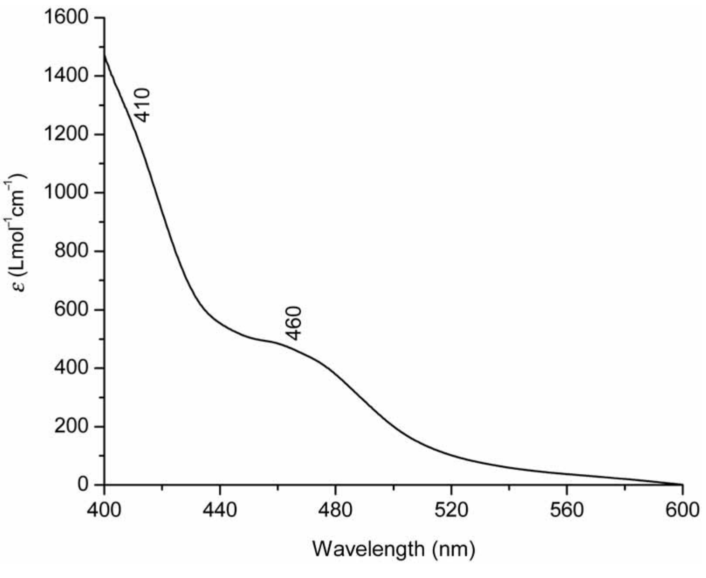


Figure 2. UV-vis spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ in ethanol.

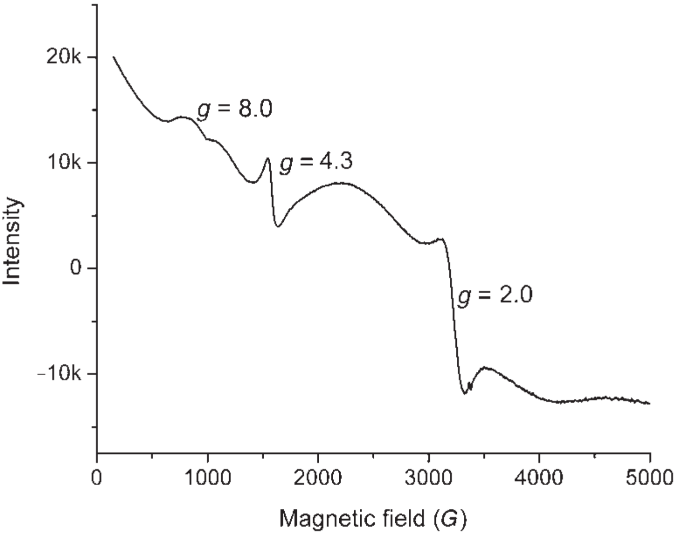
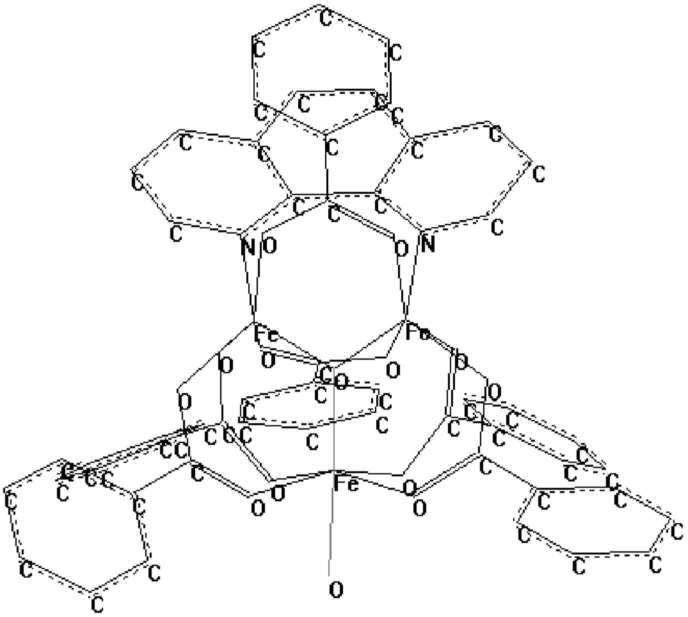


Figure 3. EPR spectrum of $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$ at 77 K.



Scheme 4. Molecular mechanics (MM+) optimized configuration of $[Fe_3O(C_7H_5O_2)_6(H_2O)(phen)]^+$.

3.4. *Molecular mechanics (MM+)*

Molecular modeling was carried out using the MM+ method of HYPERCHEM. The optimized geometry for the complex is given in scheme 4. The benzoato ligands are coordinated through the usual $\mu_2:\eta^1:\eta^1$, with two of the iron(III) ions having an O_5N coordination environment while the third has an O_6 one. The central oxygen

Table 1. Calculated mean bond distances (Å) and angles (°) for $[Fe_3O(C_7H_5O_2)_6(phen)(H_2O)]NO_3$.

Bond distance	(Å)	Bond angle	(°)
$Fe–O_{(H_2O)}$	1.8707	$Fe–O_{(central)}–Fe$	111.17
$Fe–O_{(central)}$	1.8232	$O_{(H_2O)}–Fe–O_{(COO^-)}$	80.44
$Fe–O_{(COO^-)}$	1.8271	$O_{(H_2O)}–Fe–O_{(central)}$	162.50
Fe–N	1.9012		

atom bridges the three iron ions forming a core $[Fe_3(\mu_3\text{-}O)]$ that is not planar. Main bond distances were calculated at 1.8707 Å for the axial $Fe–O(H_2O)$ and at 1.8232 Å (mean value) for $Fe–O_{central}$. The crystal structure analysis of another benzoate cluster, $[Fe_3O(C_7H_5O_2)_5(salox)(MeOH)_2] \cdot 1.25MeOH \cdot 1.05H_2O$ [15] (salox = salicylaldoximato ligand) revealed mean distances at 2.090 Å for Fe–O(MeOH) and 1.894 Å for $Fe–O_{central}$. Other relevant angles and bond distances are given in table 1.

3.5. *Final remarks*

The analytical and spectroscopic data supported the synthesis of a new tri-iron benzoate cluster. The route is currently being tested in our laboratory to prepare heterometallic clusters with first-row transition metals such as nickel and cobalt and mixed benzoate-acetate compounds as well. Substitution reactions are also being carried out in an attempt to isolate new polynuclear carboxylate complexes.

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References

[1] R. Weinland, E. Gussmann. *Berichte der Deutschen Chemischen Gessellsschaft*, **42**, 2997 (1909).

[2] R.W. Wu, S.K.A. Koske, R.P. White, C.E. Anson, U.A. Jayasooriya, R.D. Cannon. *J. Chem. Soc. Chem. Commun.*, 1657 (1994).

[3] T.C. Jovmir, C.I. Turta, S.G. Shova, Y.A. Simonov, M. Gdaniec, I.I. Bulgac, I.G. Cadelnic, F. Filoti. *J. Struc. Chem.*, **40**, 905 (1999).

[4] T. Nakamoto, M. Katada, H. Sano. *Inorg. Chim. Acta*, **291**, 127 (1999).

[5] R.D. Cannon, R.P. White. *Prog. Inorg. Chem.*, **36**, 195 (1988).

[6] S. Murata, M. Miura, M. Nomura. *J. Chem. Soc., Perkin Trans.*, **2**, 617 (1989).

[7] M. Murugesu, K.A. Abboud, G. Christou. *Polyhedron*, **23**, 2779 (2004).

[8] H.E. Toma, K. Araki, A.D.P. Alexiou, S. Nikolau, S. Dovidauskas. *Coord. Chem. Rev.*, **219–221**, 187 (2001).

[9] C.D. Chandlet, C. Roger, M.J. Hampden-Smith. *Chem. Rev.*, **93**, 1205 (1993).

[10] G. Christou. *Acc. Chem. Res.*, **22**, 328 (1989).

[11] F.E. Sowrey, C. Tilford, S. Wolcadlo, C.E. Anson, A.K. Powell, S.M. Bennington, W. Montfrooij, U.A. Jayasooriya, R.D. Cannon. *J. Chem. Soc., Dalton Trans.*, 862 (2001).

[12] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 60, John Wiley, New York (1997).

[13] M.L. Johnson, D.B. Powell, R.D. Cannon. *Spectrochim. Acta*, **37A**, 995 (1981).

[14] C. Fernandes, E. Stadler, V. Drago, C.J. Cunha, I.H. Kuwabara. *Spectrochim. Acta*, **52A**, 1815 (1996).

[15] C.P. Raptopoulou, Y. Sanakis, A.K. Boudalis, V. Psycharis. *Polyhedron*, **24**, 711 (2005).