



ELSEVIER

Inorganica Chimica Acta 340 (2002) 197–200

**Inorganica
Chimica Acta**

www.elsevier.com/locate/ica

Note

Dinuclear iron complexes of the tridentate ligand *N,N*-bis(2-ethyl-5-methyl-imidazol-4-ylmethyl)aminopropane (biap)

M. Chiara Mimmi^a, Fabrizio Micciché^a, Huub Kooijman^b, Anthony L. Spek^b, Sabine T. Warzeska^a, Elisabeth Bouwman^{a,*}

^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

^b Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received 18 January 2002; accepted 23 April 2002

Abstract

Dinuclear iron complexes of the tridentate ligand *N,N*-bis(2-ethyl-5-methylimidazol-4-ylmethyl)aminopropane (biap) with various carboxylates as coligands have been synthesized and characterized structurally by X-ray diffraction. The three complexes can be described by the general formula $[\text{Fe}_2^{\text{III}}(\mu\text{-O})(\text{biap})_2(\text{RCOO})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_n$.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Tridentate ligand; Imidazole; Dinuclear; Crystal structures

1. Introduction

The diiron center is an important unit for several enzymes in nature [1]. One of the best-characterized dinuclear iron proteins is hemerythrin (Hr), which is involved in the transport of oxygen in a number of marine invertebrates. A large number of structural analogs comprising the dinuclear iron–oxo motif have been reported. These structural models have been obtained using tripodal nitrogen donor ligands such as triazacyclononane [2], and tris(pyrazolyl)borates [3] or linear tridentate nitrogen donor ligands such as bis(pyrid-2-ylmethyl)amine [4], bis(benzimidazol-2-ylmethyl)amine [5], or bis(imidazol-2-ylmethyl)amine [6].

The linear tridentate ligand *N,N*-bis(2-ethyl-5-methylimidazol-4-ylmethyl)aminopropane (biap) has been designed as a structural mimic for the nitrogen donors in several enzymes. Despite the steric crowd on the periphery of the ligand, the coordination compounds of Co(II), Ni(II) and Zn(II) with biap show a large variety of coordination modes [7]. The ligand biap has been used successfully in copper model complexes for nitrite reductase [8], and in structural models for mononuclear

manganese-containing enzymes [9]. It was our intention to use biap to model the histidine residues in mononuclear iron-containing enzymes, in particular iron-containing lipoxygenase. The iron ion in the active site of soybean lipoxygenase is coordinated to three nitrogens of histidine residues, one oxygen of a monodentate isoleucine and one oxygen of a weakly coordinated asparagine [10]. In combination with the sterically crowded ligand, bulky carboxylates were used with the intention to obtain mononuclear iron complexes.

2. Experimental

2.1. Materials

Starting materials were obtained from commercial sources. The synthesis of the ligand biap has been reported earlier [7].

2.2. Physical methods

FT-IR spectra were obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique ($4000\text{--}400\text{ cm}^{-1}$, res. 4 cm^{-1}). Ligand field

* Corresponding author

E-mail address: bouwman@chem.leidenuniv.nl (E. Bouwman).

spectra of the solids (300–2000 nm, diffuse reflectance) were taken on a Perkin–Elmer 330 spectrophotometer equipped with a data station. Elemental analyses were performed on a Perkin–Elmer 2400 series II analyzer.

2.3. Preparation of the complexes

Caution: organic perchlorate salts are potentially explosive. Although we have experienced no accidents, all compounds containing perchlorate should be handled with care and in small amounts.

2.3.1. $[Fe_2(\mu-O)(\mu-OBz)_2(biap)_2](ClO_4)_2(H_2O)_2$ (**1**)

$Fe^{II}(ClO_4)_2 \cdot 6H_2O$ (3 mmol, 0.764 g) was dissolved in 6 ml of methanol, and a solution of the ligand biap (3 mmol, 0.964 g) in 5 ml of methanol was added. Sodium benzoate (3 mmol, 0.432 g) was dissolved in 10 ml of methanol and added to the brown turbid mixture. Almost immediately a color change occurred, and a green precipitate was formed. The air-stable complex was collected on a glass frit and was washed with distilled water and diethyl ether. Yield: 1.025 g, 56% based on $Fe(ClO_4)_2$.

Elemental *Anal.* Calc. for $C_{48}H_{68}Cl_2Fe_2N_{10}O_{13} \cdot 2H_2O$: C, 47.58; H, 5.99; N, 11.56. Found: C, 47.05; H, 5.52; N, 11.61%. Electronic spectroscopy (solid state): 950, 648 and 377 nm. IR ν (cm^{-1}): 3586 (w), 3290 (br,w), 2970 (w), 1640 (w), 1596 (m), 1553 (s), 1538 (m), 1456 (m), 1397 (vs), 1290 (w), 1174 (w), 1156 (w), 1068 (vs), 992 (m), 907 (m), 836 (m), 738 (m), 718 (s), 676 (m), 622 (s), 527 (m), 472 (m), 452 (m), 398 (m), 328 (m).

2.3.2. $[Fe_2(\mu-O)(biap)_2(\mu-(C_6H_5)_2CHCOO)_2](ClO_4)_2$ (**2**)

To a stirred solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.254 g, 1 mmol) in 4 ml of methanol, solid biap was added (0.303 g, 1 mmol). After 15 min with stirring a solution of potassium diphenylacetate (0.25 g, 1 mmol) in 4 ml of methanol was added to the brown and cloudy reaction mixture, and almost immediately the reaction mixture turned to dark green. After 3 h with stirring some diethyl ether was carefully added and precipitation was observed. The dark green precipitate was collected by filtration. The crude product was purified by dissolution in acetonitrile. A small amount of brown powder remained, which was removed by filtration. The clear green solution was evaporated on the rotary evaporator leaving the pure product. Yield: 0.385 g, 54% based on the amount of $Fe(ClO_4)_2 \cdot 6H_2O$ used.

Elemental *Anal.* Calc. for $C_{62}H_{80}Cl_2Fe_2N_{10}O_{13} \cdot H_2O$: C, 54.20; H, 6.02; N, 10.19. Found: C, 53.52; H, 6.53; N, 10.22%. Electronic spectroscopy (solid state): 930, 642 and 358 nm. IR ν (cm^{-1}): 3254 (br,w), 2966 (w), 2923 (w), 1634 (w), 1577 (s), 1545 (m), 1494 (w), 1452 (s), 1386

(s), 1304 (w), 1249 (w), 1106 (s), 1076 (vs), 1036 (vs), 990 (m), 902 (w), 840 (w), 740 (s), 699 (s), 649 (m), 621 (s), 569 (w), 525 (m).

2.3.3. $[Fe_2(\mu-O)(biap)_2(\mu-(C_6H_5)_3CCH_2COO)_2](ClO_4)_2$ (**3**)

To a stirred solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.254 g, 1 mmol) in 4 ml of ethanol, solid biap (0.303 g, 1 mmol) was added while stirring. Almost immediately the solution turned from colorless to cloudy brown. After 30 min a solution of potassium 3,3,3-triphenylpropionate (0.34 g, 1 mmol) in 4 ml of ethanol was added. The reaction mixture was stirred for 4 h. Some diethyl ether was added inducing precipitation. The product was collected by filtration after 20 min with stirring. The dark green powder obtained was dried in vacuo. The yield was 0.40 g, 51% calculated from the amount of $Fe(ClO_4)_2 \cdot 6H_2O$ used.

Elemental *Anal.* Calc. for $C_{76}H_{92}Cl_2Fe_2N_{10}O_{13} \cdot 2H_2O$: C, 58.06; H, 6.15; N, 8.91. Found: C, 57.68; H, 6.50; N, 8.93%. Electronic spectroscopy (solid state): 930, 656 and 373 nm. IR ν (cm^{-1}): 3245 (w), 2970 (w), 2923 (w), 1636 (w), 1567 (s), 1494 (m), 1447 (s), 1400 (s, br), 1300 (m), 1106 (s), 1082 (vs), 1038 (vs), 987 (m), 905 (w), 742 (s), 699 (vs), 655 (m), 621 (s), 569 (w), 524 (m), 352 (m).

2.4. Crystal structure determination

2.4.1. Crystal data for $[Fe_2(\mu-O)(\mu-OBz)_2(biap)_2](ClO_4)_2(H_2O)_2$ (**1**)

$C_{48}H_{68}Fe_2N_{10}O_{15} \cdot 2ClO_4 \cdot 2H_2O$, $M_r = 1211.76$, monoclinic, space group $C2/c$, $a = 29.139(5)$, $b = 11.5227(18)$, $c = 21.669(4)$ Å, $\beta = 127.73(2)^\circ$, $V = 5754(2)$ Å³, $Z = 4$, $D_{calc} = 1.399$ g cm⁻³, $T = 150$ K, $\mu = 0.67$ mm⁻¹, $F(000) = 2544$.

2.4.2. Data collection and refinement

Green crystals of **1** were grown from a solution in MeOH:dmsO (10:1) by diethyl ether diffusion at room temperature. A block-shaped crystal was placed in the cold nitrogen stream of a Nonius κ CCD diffractometer on rotating anode. Data in the range $1.6 < \theta < 25.25^\circ$ were collected at 150 K, using Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0.71073$ Å). No absorption correction was applied. Intensity data of 19015 reflections were measured, of which 4933 were independent ($R_{int} = 0.0561$). The structure was solved using direct methods (SHELXS-86). Refinement on F^2 was carried out by full-matrix least-squares techniques using SHELXL-97-2. Convergence was reached at $R_1 = 0.0682$ for 3718 $F_o > 4\sigma(F_o)$, $wR_2 = 0.191$ and $S = 1.05$ for 361 parameters. Residual electron densities are between -0.87 and 1.43 e Å⁻³. The perchlorate anions display rotational disorder around one of the Cl–O bonds. A two-site disorder model was introduced to describe this

effect. All ordered non-hydrogen atoms were refined with anisotropic thermal parameters. Coordinates of N–H and O–H were freely refined, all other hydrogen atoms were included in the model on calculated positions, riding on their carrier atoms. Hydrogen atom displacement was described with a fixed isotropic parameter related to the equivalent isotropic parameter of the carrier atom. Geometrical calculations and molecular graphics were performed with PLATON [11]. From the same MeOH:dmsO (10:1) solution plate-shaped crystals were isolated. These appeared to be of the methanol solvate $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OBz})_2(\text{biap})_2](\text{ClO}_4)_2(\text{CH}_3\text{OH})_2$, the cationic unit of which shows no significant differences compared to the one described here. The data of this methanol solvate have been included in the supporting information.

3. Results and discussion

3.1. Description of the structure of $[\text{Fe}_2(\mu\text{-O})(\text{biap})_2(\mu\text{-OBz})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2$ (1)

The dinuclear molecule resides on a twofold rotation axis. Thus the asymmetric unit comprises only half a dinuclear molecule, one perchlorate ion and one water molecule. A PLATON [11] projection of the dinuclear cation $[\text{Fe}_2(\mu\text{-O})(\text{biap})_2(\mu\text{-OBz})_2]^{2+}$ is given in Fig. 1. Relevant bond lengths and angles are given in Table 1. The iron(III) ion is surrounded by a *facially* coordinating biap ligand, an oxo group and two oxygen donors of benzoate anions, resulting in an FeN_3O_3 chromophore. The amine–nitrogen of biap is coordinated *trans* to the oxo bridge. The imidazole–N to amine–N bite angles are rather small (73.5 and 76.5°) in comparison with those found in the structures of the other transition metals [7,8]. The bridging oxygen shows no residual

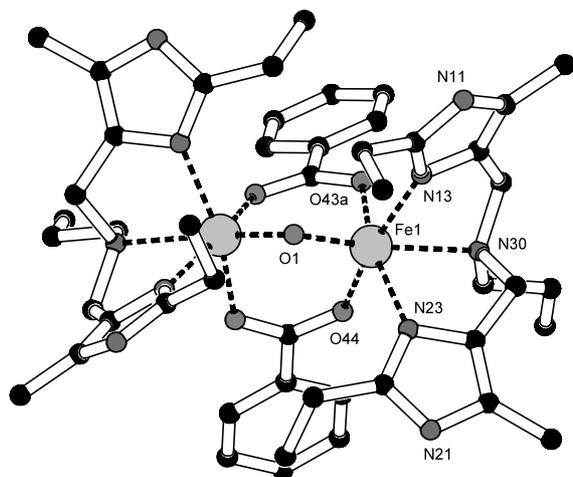


Fig. 1. PlatON projection of and selected labelling for the dinuclear cation $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OBz})_2(\text{biap})_2]^{2+}$. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles ($^\circ$) in $[\text{Fe}_2^{\text{III}}(\mu\text{-O})(\mu\text{-OBz})_2(\text{biap})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2$ (1)

Bond lengths			
Fe(1)–O(1)	1.794(2)	Fe(1)–N(23)	2.111(4)
Fe(1)–O(43a)	2.059(3)	Fe(1)–N(30)	2.348(5)
Fe(1)–O(44)	2.073(4)	Fe(1)–Fe(1)a	3.1390(15)
Fe(1)–N(13)	2.106(4)		
Bond angles			
O(1)–Fe(1)–O(43a)	98.48(15)	O(43a)–Fe(1)–N(30)	83.14(15)
O(1)–Fe(1)–O(44)	97.98(16)	O(44)–Fe(1)–N(13)	162.84(17)
O(1)–Fe(1)–N(13)	97.29(16)	O(44)–Fe(1)–N(23)	84.33(14)
O(1)–Fe(1)–N(23)	103.95(15)	O(44)–Fe(1)–N(30)	91.39(15)
O(1)–Fe(1)–N(30)	170.62(15)	N(13)–Fe(1)–N(23)	99.53(16)
O(43a)–Fe(1)–O(44)	82.12(14)	N(13)–Fe(1)–N(30)	73.49(16)
O(43a)–Fe(1)–N(13)	87.93(15)	N(23)–Fe(1)–N(30)	76.48(16)
O(43a)–Fe(1)–N(23)	155.18(16)	Fe(1)–O(1)–Fe(1)a	122.1(3)

Symmetry position: a = $-x, y, 1/2-z$.

density above $0.2 \text{ e } \text{Å}^{-3}$ at possible hydrogen sites. This observation in combination with a geometry analysis of oxo and hydroxo bridged complexes, included in the Cambridge Structural Database, strongly suggests that the bridging moiety is an oxo-group. The structure carries no unusual features in comparison with the reported structures [2–6].

Extensive hydrogen bonding occurs between the non-coordinating imidazole-nitrogens as hydrogen donors, the perchlorate oxygens as acceptors, and the water molecules both as acceptor and as donor with bonding distances in the range of 2.80 to 3.13 Å (Table 2). Through this hydrogen bonding an infinite three-dimensional network is formed.

3.2. Spectroscopy and analyses

Three similar dinuclear iron–oxo complexes have been obtained, with carboxylates of different steric properties. The bulky triphenylpropionate was chosen with the initial aim to obtain mononuclear iron complexes. However, even this sterically encumbered carboxylate does not prevent the rapid formation of a dinuclear iron complex, as has been demonstrated

Table 2
Hydrogen bond contacts in $[\text{Fe}_2(\mu\text{-O})(\mu\text{-OBz})_2(\text{biap})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2$ (1)

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A ($^\circ$)
N(11)–H(11)...O(54)b	0.80(7)	2.35(7)	3.125(10)	164(7)
N(21)–H(21)...O(60)c	0.78(5)	2.07(5)	2.823(7)	162(7)
O(60)–H(60A)...O(52)	0.82(11)	1.98(12)	2.796(18)	169(10)
O(60)–H(60B)...O(53)d	0.90(10)	1.92(10)	2.795(13)	164(12)

Only H-bonds donated to the major disorder component of ClO_4^- are listed. Symmetry positions: b = $x, 1+y, z$; c = $x, 1-y, 1/2+z$; d = $1/2-x, 1/2+y, 1/2-z$.

earlier for triphenylacetate [2]. Elemental analyses and spectroscopic data indicate that all three complexes are dinuclear Fe(III)–O–Fe(III).

The infrared spectra have been analyzed on the presence and binding mode of the carboxylates and the bridging oxo group. For a dinuclear iron complex containing two bridging carboxylates a $\Delta\nu$ value ($\Delta\nu = \nu_{\text{as}}(\text{RCOO}) - \nu_{\text{sym}}(\text{RCOO})$) comparable to the ionic one is to be expected [12]. The $\Delta\nu$ values of **1** (156 cm^{-1}) and **3** (167 cm^{-1}) are close to the ones of sodium benzoate (142 cm^{-1}) and potassium triphenylpropionate (180 cm^{-1}), respectively. These values would thus suggest complexes with bridging carboxylates. For **2** a value lower than that of potassium diphenylacetate is found (192 and 235 cm^{-1} , respectively). This could perhaps be due to an asymmetrical orientation of the phenyl groups of the carboxylate in space.

In the three mutually very similar IR spectra the asymmetric Fe–O–Fe vibrations are found at 738 (**1**), 740 (**2**) and 742 (**3**) cm^{-1} , comparable to reported values [13].

The electronic spectra of the three compounds show absorption bands in the range expected for dinuclear Fe(III) oxo complexes [14].

The variable magnetic susceptibility in the temperature range 4–350 K has been measured of compound **1** as a representative. The compound shows antiferromagnetic behavior with $J = -147 \text{ cm}^{-1}$, which is in the range found for similar dinuclear systems [13,14].

4. Comments

The present study was undertaken with the aim to synthesise mononuclear iron complexes as models for iron-containing lipxygenases. Using manganese salts, this approach has resulted in some unusual manganese complexes of which one can be regarded as a prospective model for the active centre of manganese lipxygenase [9]. However, starting from iron salts, despite the steric bulk in both the ligand and the carboxylates, dinuclear iron complexes were obtained, which can better be regarded as models for dinuclear enzymes such as hemerythrin. The spectroscopic features of the new dinuclear complexes are comparable to those of earlier reported model systems [13].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC Nos. 177574 for **1** (hydrate) and 177575 for the methanol solvate. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

This work was supported in part by the Netherlands Research Council for Chemical Sciences (NWO/CW) with financial aid from the Netherlands Technology Foundation (STW) in the Priority Programme Materials. We thank Dr. J. Reedijk for fruitful discussions, Mrs. M. Mehendale for some reproductions, and Mr. O.S. Roubeau for variable temperature magnetic susceptibility measurements. F.M. (University of Palermo, Italy) and M.C.M. (University of Pavia, Italy) were involved in the project through the Socrates student exchange programme.

References

- [1] E.I. Solomon, T.C. Brunold, M.I. Davis, J.N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A.J. Skulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* 100 (2000) 235.
- [2] J.D. Cohen, S. Payne, K.S. Hagen, J. Sanders-Loehr, *J. Am. Chem. Soc.* 119 (1997) 2960.
- [3] R.H. Beer, W.B. Tolman, S.G. Bott, S.J. Lippard, *Inorg. Chem.* 30 (1991) 2082.
- [4] S. Dick, A. Weiss, U. Wagner, F. Wagner, G. Grosse, *Z. Naturforsch., T. B* 52 (1997) 372.
- [5] P. Gomez-Romero, N. Casan-Pastor, A. Ben-Hussein, G.B. Jameson, *J. Am. Chem. Soc.* 110 (1988) 1988.
- [6] K.J. Oberhausen, J.F. Richardson, R.J. O'Brien, R.M. Buchanan, J.K. McCusker, R.J. Webb, D.N. Hendrickson, *Inorg. Chem.* 31 (1992) 1123.
- [7] E. Bouwman, B. Douzich, L. Gutierrez-Soto, M. Beretta, W.L. Driessen, J. Reedijk, G. Mendoza-Diaz, *Inorg. Chim. Acta* 304 (2000) 250.
- [8] M. Beretta, E. Bouwman, L. Casella, B. Douzich, W.L. Driessen, L. Gutierrez-Soto, E. Manzani, J. Reedijk, *Inorg. Chim. Acta* 310 (2000) 41.
- [9] S.T. Warzeska, F. Micciché, M.C. Mimmi, E. Bouwman, H. Kooijman, A.L. Spek, J. Reedijk, *J. Chem. Soc., Dalton Trans.* (2001) 3507.
- [10] W. Minor, J. Steczko, B. Stec, Z. Otwinowski, J.T. Bolin, R. Walter, B. Axelrod, *Biochemistry* 35 (1996) 10687.
- [11] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2000. Internet: <http://www.cryst.chem.uu.nl/platon>.
- [12] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.
- [13] K.B. Jensen, C.J. McKenzie, O. Simonsen, H. Toftlund, A. Hazell, *Inorg. Chim. Acta* 257 (1997) 163.
- [14] S.C. Payne, K.S. Hagen, *J. Am. Chem. Soc.* 122 (2000) 6399.