DALTON
FULL PAPER

Tuning the coordination mode in mononuclear manganese complexes by changing the steric bulk of the carboxylates

Sabine T. Warzeska,[a] Fabrizio Miccichè,[a] M. Chiara Mimmi,[a] Elisabeth Bouwman,*[a] Huub Kooijman,[b] Anthony L. Spek[b] and Jan Reedijk[a]

[a] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*
[b] *Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 6th June 2001, Accepted 3rd October 2001
First published as an Advance Article on the web 8th November 2001

Three mononuclear manganese complexes of the tridentate ligand biap [= *N*,*N*-bis(2-ethyl-5-methylimidazol-4-ylmethyl)aminopropane] with various carboxylates as co-ligands have been synthesized and structurally characterised by X-ray diffraction. All three complexes can be described by the general formula $[Mn^{II}(biap)(RCOO)_2(H_2O)_n]$ ($n = 0$, 1). The manganese(II) ion in $[Mn^{II}(biap)(C_6H_5COO)_2]$ (**1**) is five coordinated by three nitrogen donors from biap and two oxygen donors of monodentate benzoate molecules. This monodentate binding mode is confirmed by IR analysis. In the compound $[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (**2**), the manganese ion is coordinated in a distorted octahedron with an additional water molecule as the sixth ligand. This aqua ligand forms strong intramolecular hydrogen bonds to both carboxylate groups as is reflected in the IR. Finally the manganese ion in the complex $[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]$ (**3**) is again five coordinated with triphenylpropionate as coordinating counter ion. In **3** both carboxylates are bound monodentately, but one shows a semi coordination of the free oxygen to the manganese center (Mn–O = 3.169 Å). Both carboxylates are involved in hydrogen bonding albeit to a different degree. This asymmetric binding mode is reflected in the IR spectrum, which shows two pairs of carboxylate vibrations. The structural differences of the three complexes are expressed by the very different X-band EPR spectra of the solid compounds. In solution, however, all three complexes are most likely octahedrally coordinated as indicated by their similar EPR spectra in frozen MeOH–EtOH solution.

Introduction

To date five different mononuclear manganese enzymes are known:[1] manganese superoxide dismutase (MnSOD), manganese peroxidase (MnP), manganese dioxygenase and the recently discovered manganese lipoxygenase (MnLO)[2] and oxalate oxidase.[3,4] In all these enzymes the manganese ion is believed to shuttle between the Mn(II) and Mn(III) oxidation state, catalysing one-electron redox reactions. Except for manganese peroxidase, a unique enzyme in many respects that will not be discussed further here, and the oxalate oxidases all the other enzymes also exist in an iron-containing form. MnSOD contains a trigonal bipyramidal coordinated manganese ion in the active site.[5] The coordination sphere consists of three histidines, an aspartate and a water, or hydroxide, molecule. Germin is a manganese-containing enzyme with oxalate oxidase and superoxide dismutase activities.[3] The manganese(II) ion is in an octahedral geometry comprising three histidines, a glutamate and two water molecules.[3] The active-site structure of the remaining two enzymes is not known as yet. Structure proposals are based on structural similarities between the manganese and iron-containing enzymes (see Fig. 1). For the Mn(II) dioxygenase a square-pyramidal arrangement of two histidines, a glutamate and two water molecules, like in the corresponding extradiol Fe(II) dioxygenases might be possible.[6] Recently a manganese lipoxygenase has been discovered[2] and also in this case a structure analogous to the iron-containing soy bean lipoxygenase (LO) is a topic of discussion.[7] The iron ion in the active site of LO is coordinated to three nitrogens of histidine residues, one oxygen of a monodentate isoleucine and one oxygen of a weakly coordinated asparagine.[8] A water molecule, stabilised by a hydrogen bond with the non-coordinated carboxylate oxygen of isoleucine, completes the distorted octahedral coordination sphere.[8] In summary, the manganese ions in all three enzymes are believed to be coordinated by imidazoles, carboxylates and water molecules as ligands in varying coordination geometries.

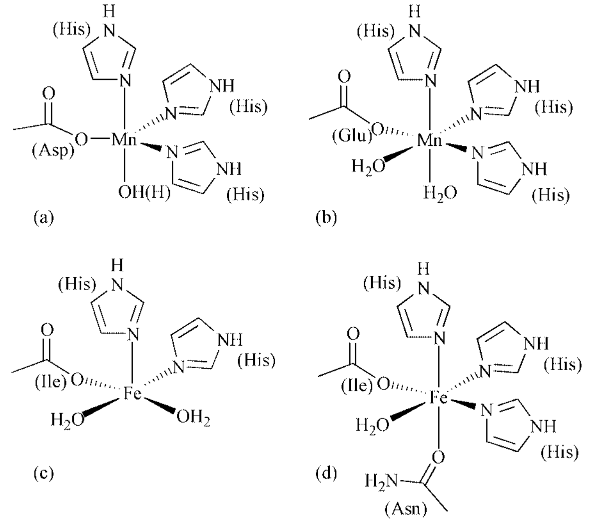

Fig. 1 Comparison of the active sites of manganese(II) superoxide dismutase (a), manganese(II) oxalate oxidase (b), extradiol iron(II) dioxygenase (c) and iron(II) lipoxygenase-1 (d).

The 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 crowding at the periphery of the ligand, the coordination

DOI: 10.1039/b104975p

compounds of Co(II), Ni(II) and Zn(II) with biap show a large variety of coordination modes.[9] Recently biap has been used successfully in copper model complexes for nitrite reductase.[10] In the present study, biap is used to model the histidine residues in manganese containing enzymes. To study the influence of the carboxylates on the coordination mode of the Mn(II) complexes several carboxylates with different steric requirements have been used.

Experimental

Materials

Manganese(II) perchlorate hexahydrate, sodium benzoate, diphenylacetic acid, and 3,3,3-triphenylpropionic acid were obtained from Acros. The ligand biap was synthesised according to published methods.[9] All reagents were used without further purification. The complex syntheses were carried out in an inert atmosphere to prevent oxidation to Mn^{III}.

CAUTION! Organic perchlorate salts are potentially explosive. Although we have experienced no accidents so far, all compounds containing perchlorate should be handled with care and in small amounts.

Syntheses

$[Mn^{II}(biap)(C_6H_5COO)_2]$ (1). A solution of biap (1 mmol, 0.30 g in 1 ml MeOH) was added to a solution of $Mn(ClO_4)_2\cdot 6H_2O$ (1 mmol, 0.36 g) in 2 ml MeOH while stirring, resulting in a clear pale yellow solution. Sodium benzoate (2 mmol, 0.29 g) was dissolved in 3 ml of distilled H_2O and added to the reagents mixture, provoking the precipitation of **1**·H_2O [0.46 g, 74% based on $Mn(ClO_4)_2$] as an air-stable white powder. μ_{eff} = 5.70 μ_B (at 22 °C). Anal. calc. for **1**·H_2O: $C_{31}H_{41}MnN_5O_5$: C, 60.2; H, 6.7; N, 11.3. Found: C, 60.0; H, 6.2; N, 11.6%. IR ($\tilde{\nu}$/cm^{-1}): 3126 (m), 3062 (m), 2932 (m), 2874 (m), 1597 (s), 1538 (s), 1455 (m), 1385 (vs), 1171 (w), 1080 (w), 1065 (m), 1045 (m), 1023 (m), 802 (m), 713 (vs), 645 (s), 539 (m), 418 (s).

$[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (2). 0.36 g of $Mn(ClO_4)_2\cdot 6H_2O$ (1 mmol) was dissolved in 2 ml of methanol to give a colourless solution. With stirring a solution of biap in methanol was added (0.30 g, 1 mmol in 2 ml MeOH). After ten minutes with stirring the methanolic solution of diphenylacetic acid (0.21 g, 1 mmol in 2 ml MeOH) and several drops of triethylamine were added to the colourless reaction mixture. The clear solution was stirred for four hours at room temperature. By slowly adding 20 ml of distilled water a white precipitation formed. After half an hour with stirring the precipitate was collected by filtration in air. A white air-stable powder resulted. It was washed with some water and a small amount of acetone and dried *in vacuo*. The yield of **2** was 70% (0.28 g), calculated from the amount of diphenylacetic acid used. μ_{eff} = 5.88 μ_B (at 22 °C). Anal. calc. for $C_{45}H_{53}MnN_5O_5$: C, 67.7; H, 6.7; N, 8.8. Found: C, 67.0; H, 6.2; N, 9.0%. IR ($\tilde{\nu}$/cm^{-1}): 3027 (s), 2973 (s), 1590 (s), 1386 (s), 1435 (m), 1496 (m), 715 (s), 695 (s).

$[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]$ (3). To a stirred solution of $Mn(ClO_4)_2\cdot 6H_2O$ (0.36 g, 1 mmol in 2 ml of EtOH), the biap containing solution was added (0.30 g, 1 mmol in 2 ml of EtOH) and a colourless reaction mixture resulted. After 10 minutes with stirring a solution of 3,3,3-triphenylpropionic acid (0.30 g, 1 mmol) in 3 ml of EtOH containing some drops of triethylamine was added. The colourless reaction mixture was stirred for 14 hours. At the end of this period, about 20 ml of distilled water was added drop-by-drop resulting in a white precipitate. After 30 minutes with stirring, the precipitate was collected by filtration in air. It was washed with some water and dried *in vacuo*, yielding 0.24 g (48% based on acid) of **3**. μ_{eff} = 5.87 μ_B (at 22 °C). Anal. calc. for $C_{59}H_{63}MnN_5O_4$: C, 73.7; H, 6.6; N, 7.3, Mn, 5.7. Found: C, 73.9; H, 6.9; N, 7.6; Mn, 5.6%. IR ($\tilde{\nu}$/cm^{-1}): 3055 (w), 2967 (w), 1636 (m), 1609 (s), 1559 (s), 1494 (m), 1447 (s), 1410 (s), 1386 (s), 1080 (m), 1045 (m), 762 (m), 744 (m), 698 (s). Recrystallisation from DMF led to another white manganese(II) complex (**3b**) as characterised by the differences in IR. μ_{eff} = 5.75 μ_B (at 22 °C). IR ($\tilde{\nu}$/cm^{-1}): 3053 (w), 2920 (w), 2832 (w), 1596 (s), 1557 (s), 1540 (s), 1491 (m), 1468 (m), 1456(w), 1445 (w), 1394 (s), 1084 (m), 1056 (m), 755 (m), 696 (s).

Methods and instrumentation

FTIR spectra were obtained on a Perkin-Elmer Paragon 1000 FTIR spectophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000–400 cm^{-1}, 4 cm^{-1} resolution). Elemental Analyses were performed on a Perkin-Elmer 2400 Series II analyzer. X-Band EPR spectra were recorded on a Jeol RE2x electron spin resonance spectrometer using DPPH (diphenylpicrylhydrazyl, $g = 2.0036$) as a standard. Manganese analysis was carried out complexometrically with Na_2H_2EDTA as the complexing agent.

X-Ray structure determination

Crystals of suitable size were placed in the cold nitrogen stream of a Nonius-KappaCCD diffractometer on a rotating anode. Data in the range $1.6° < \theta < 25.25°$ were collected at 150 K, using Mo-Kα radiation (graphite monochromator, λ = 0.71073 Å). No absorption correction was applied. The structures were solved by direct methods or Patterson methods, as indicated below. Refinement on F^2 was carried out by full-matrix least-squares techniques using SHELXL-97.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of those in the disordered solvent of **1**. Hydrogen atoms were included in the model at calculated positions, riding on their carrier atoms unless stated otherwise. Hydrogen atom displacement was described with a fixed isotropic parameter related to the equivalent isotropic parameter of the carrier atom. Pertinent data for each of the structure determinations are given in Table 1.

CCDC reference numbers 153639, 165397 and 165398.

See http://www.rsc.org/suppdata/dt/b1/b104975p/ for crystallographic data in CIF or other electronic format.

$[Mn^{II}(biap)(C_6H_5COO)_2]\cdot 0.4EtOH$ (1·0.4EtOH). Crystals of **1**·0.4EtOH suitable for X-ray structure determination could be grown from an ethanol–dimethylsulfoxide (10 : 1) solution of **1** by diethyl ether diffusion at room temperature. Data were collected on a crystal of dimensions 0.1 × 0.2 × 0.3 mm. The structure was solved by automated direct methods (SHELXS-86).[12] The Mn ion is located on a crystallographic 2-fold rotation axis which results in a disorder of the propyl and methylene moieties bound to the tertiary amine nitrogen. The crystal packing can accommodate both orientations of the propyl moiety without intermolecular collisions. The structure contains an ethanol solvent molecule in the lattice. This molecule is also situated on a crystallographic 2-fold axis, and is therefore disordered.

In the crystal packing, the disordered region contains either two propyl moieties or a disordered ethanol molecule.

$[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (2). Single crystals of this compound have been obtained from a solution of MeOH, acetone and water (2 : 1 : 1) by slow evaporation in air. A block shaped crystal of dimensions 0.10 × 0.15 × 0.20 mm was used for data collection. The structure was solved by automated direct methods (SHELXS-86).[12] The measured crystal turned out to be a non-merohedral twin. The twin operation is a 2-fold rotation axis parallel to c^*, which causes overlap of crystallographically unrelated reflections in the zones $h_1 = 5n$. This

Table 1 Crystallographic data for $[Mn^{II}(biap)(C_6H_5COO)_2]\cdot 0.4EtOH$ (**1**·0.4EtOH), $[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (**2**) and $[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]\cdot H_2O$ (**3**·H_2O)

	1·0.4 EtOH	**2**	**3**·H_2O
Empirical formula	$C_{31.8}H_{41.4}MnN_5O_{4.4}$	$C_{45}H_{53}MnN_5O_5$	$C_{59}H_{63}MnN_5O_5$
FW	619.07	798.86	979.10
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pccn* (no. 56)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)
a/Å	21.073(3)	9.756(1)	9.743(1)
b/Å	8.964(1)	19.356(3)	15.554(2)
c/Å	16.568(1)	22.421(4)	17.412(3)
a/°	—	—	78.23(1)
β/°	—	92.59(1)	87.74(2)
γ/°	—	—	84.03(2)
V/Å^3	3129.5(6)	4230(1)	2568.7(7)
Z	4	4	2
D_c/g cm^{-3}	1.3139(3)	1.2546(3)	1.2659(3)
No. of measured reflections	9760	55995	25581
No. of unique reflections	2820 (R_{int} = 0.0443)	14934 (R_{int} = 0.0878)	8943 (R_{int} = 0.0738)
No. of parameters	217	1027	657
μ(Mo-Kα)/mm^{-1}	0.47	0.362	0.311
GOF	1.068	1.054	1.047
wR_2 (all data)[a]	0.1678	0.1019	0.1167
$R_1[F_o > 4\sigma(F_o)]$[a]	0.0591	0.0487	0.0559

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

Table 2 Selected bond distances (Å) and angles (°) at the manganese centre for $[Mn^{II}(biap)(C_6H_5COO)_2]\cdot 0.4EtOH$ (**1**·0.4EtOH), $[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (**2**) and $[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]\cdot H_2O$ (**3**·H_2O)

	1[a]	**2**		**3**
		Mn1	Mn2	
Mn1–N13	2.191(4)	2.228(3)	2.236(3)	2.150(3)
Mn1–N23	2.191(4)	2.171(3)	2.195(3)	2.140(3)
Mn1–N30	2.397(3)	2.415(3)	2.418(3)	2.502(3)
Mn1–O41	2.083(3)	2.150(2)	2.160(2)	2.079(2)
Mn1–O42	3.121(4)			3.169(2)
Mn1–O61	2.083(3)	2.125(2)	2.117(2)	2.061(2)
Mn1–O62	3.121(4)			3.551(2)
Mn1–O1		2.262(3)	2.277(3)	
O41–Mn1–O61	105.1(1)	94.1(1)	92.0(1)	92.2(1)
O41–Mn1–N13	98.9(1)	164.1(1)	161.2(1)	126.1(1)
O41–Mn1–N23	100.4(1)	85.7(1)	86.1(1)	120.8(1)
O41–Mn1–N30	127.5(1)	94.6(1)	92.0(1)	90.3(1)
N13–Mn1–N23	148.0(1)	99.2(1)	100.0(1)	103.6(1)
N13–Mn1–N30	74.0(1)	72.2(1)	72.4(1)	73.1(1)
N23–Mn1–N30	74.0(1)	75.9(1)	76.8(1)	74.0(1)
O61–Mn1–N13	100.4(1)	99.6(1)	103.4(1)	111.0(1)
O61–Mn1–N23	98.9(1)	102.2(1)	104.4(1)	98.6(1)
O61–Mn1–N30	127.5(1)	170.9(1)	175.8(1)	172.4(1)
O1–Mn1–O41		84.0(1)	84.2(1)	
O1–Mn1–O61		93.3(1)	91.6(1)	
O1–Mn1–N13		87.2(1)	84.8(1)	
O1–Mn1–N23		161.9(1)	161.5(1)	
O1–Mn1–N30		90.2(1)	87.8(1)	

[a] Due to the location of **1** on the 2-fold axis, N23 = N13a (1/2 − x, 3/2 − y, z), O61 = O41a (1/2 − x, 3/2 − y, z), O62 = O42a (1/2 − x, 3/2 − y, z).

overlap was taken into account during refinement with SHELXL-97.[11] The crystal was also an inversion twin. The water hydrogen atoms were located on a difference Fourier map and included in a rigid group with the oxygen as pivot atom.

$[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]\cdot H_2O$ (3·H_2O). Crystals of **3**·H_2O could be obtained by recrystallisation of the crude product from ethanol (97%). Data were collected on a crystal of dimensions 0.05 × 0.15 × 0.35 mm. The structure was solved using Patterson methods (DIRDIF99).[13] The crystal structure contains a co-crystallised water molecule. The water and N–H hydrogens were located on a difference Fourier map; their coordinates were included as parameters in the refinement.

Results and discussion

Synthesis of the complexes

The complex syntheses have to be carried out in an inert atmosphere. The aqueous manganese containing solutions rapidly turn brown when the reaction is performed in air, indicating the formation of higher oxidation state complexes. The manganese(II) complexes, once isolated, seem to be quite resistant to oxidation, they are stable in air in the solid state for a prolonged period of time. Furthermore, the complexes seem to be resistant to electrochemical oxidation (see below), however, this could be due to the non-aqueous conditions used in cyclic voltammetry.

The syntheses have not been optimised in terms of yields. It appears that the use of an alkali salt of the carboxylate ligand has a positive effect on the isolated yield of the complex. For the complexes **2** and **3**, however, a substoichiometric amount of the corresponding acid was used, primarily because it was assumed that the bulk of these carboxylates would preclude the binding of two such moieties to the metal centre. It was intended that the binding of only one carboxylate would result in the formation of possible models for those active sites in enzymes in which only one carboxylate group and two water molecules are bound to the metal ion. Unexpectedly, it appeared that two carboxylates bind to the manganese(II) ion in complexes **2** and **3**.

Description of the structures

$[Mn^{II}(biap)(C_6H_5COO)_2]\cdot 0.4EtOH$ (1·0.4EtOH). Selected bond distances and angles are listed in Table 2. The structure of the complex is shown in Fig. 2. The crystal structure consists of a neutral, mononuclear manganese(II) complex. The Mn(II) ion is five coordinated in an N_3O_2 donor set. The ligand biap is coordinated meridionally to the central manganese ion in an almost planar conformation. Both benzoate anions act as monodentate co-ligands. Attempts to analyse the coordination sphere by the method of Addison and Reedijk *et al.*[14] or the method described by Holmes[15] both led to intermediate results. The τ descriptor[14] of 0.34 is closest to a distorted square-pyramidal coordination sphere. In this description the apex of the square pyramid would be O41 or, for symmetry reasons,

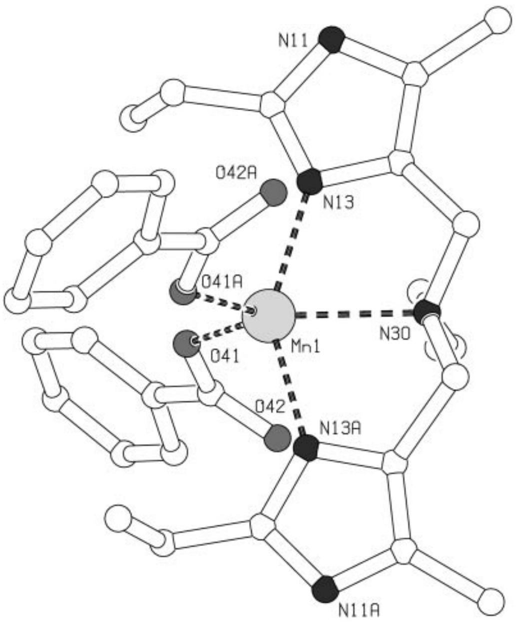

Fig. 2 Projection of **1**, only one of the disordered components (related by crystallographic symmetry; see Experimental section) is shown. All hydrogen atoms have been omitted for clarity.

O41a. With a dihedral angle δ_{24} of 36.88° on the other hand the structure would be better described as distorted *TBPY* geometry,[15] with the imidazole nitrogens occupying the axial positions. In any case these analyses stress that the coordination sphere is severely distorted. The small bite angle of the ligand [N13–Mn1–N13a = 148.0(1)°] in the manganese complex in comparison to the related copper complexes (N13–Cu1–N23 = 161.6/162.9°),[10] and the larger ionic radius of the manganese ion forces the metal ion into this distorted coordination geometry.

The non-coordinated carboxylate O42 accepts an intermolecular hydrogen bond from atom N11 of a neighbouring molecule [O ··· N distance 2.806(4) Å] and a long hydrogen bond from the disordered ethanol solvent [O ··· O distance 3.16(3) Å]. One might also consider a weak interaction to the central metal atom [O42 ··· Mn1: 3.121(4) Å, *i.e.* 0.55 Å shorter than the sum of the contact radii].

Interestingly, two very similar mononuclear complexes $[Mn(bba)(OAc)_2]$ [bba = bis(benzimidazol-2-ylmethyl)amine][16] and $[Mn(terpy)(dmb)_2]$ (terpy = 6′,2″-terpyridine, dmb = 2,6-dimethoxybenzoate)[17] have been synthesised and characterised by single crystal X-ray diffraction. Also in these two complexes the manganese ion is five coordinated with an N_3O_2 donor set, the tridentate nitrogen donating ligands are coordinated meridionally and the coordinated carboxylates are bound in a monodentate manner. Both complexes also exhibit very irregular coordination geometries, which are neither *TBPY* nor *SPY*. In $[Mn(bba)(OAc)_2]$ an additional interaction of one of the unbound oxygens to the manganese ion is present, the Mn–O distance (2.62 Å) is much shorter than in **1**.

$[Mn^{II}(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$ (2). A drawing of the crystal structure of **2** is shown in Fig. 3, selected interatomic distances and bond angles are listed in Table 2. The asymmetric unit contains two independent molecules of $[Mn(II)(biap)((C_6H_5)_2CHCOO)_2(H_2O)]$. The only major difference between these molecules is a 180° rotation along one of the $C–CPh_2$ bonds. The remaining parts of the molecules are related by a non-crystallographic inversion operation. The three nitrogen-donor atoms from the ligand biap are folded around the manganese ion in a facial fashion with an angle of 61° between the imidazole planes. Both carboxylates are coordinated in a monodentate coordination mode, one carboxylate *trans* to the amine-N, the other *trans* to an imidazole-N. A water molecule occupies the sixth position in the distorted octahedron *trans* to imidazole. This aqua ligand forms strong intramolecular hydrogen bonds to the non-coordinated oxygen of each carboxylate group (O ··· O distance 2.72–2.76 Å). Another hydrogen bonding interaction is present between the carboxylates and the imidazole N–H of neighbouring molecules (O ··· N distances 2.77–2.80 Å), thus forming a two-dimensional network parallel to the *a*,*b* plane. The bond distances around the metal ion are normal for divalent manganese ions in an octahedral geometry, although the distance from the manganese ion to the tertiary amine is rather long [Mn1–N30: 2.415(3) Å; Mn2 ··· N130: 2.418(3) Å]. The octahedral geometry around the manganese ion is severely distorted. This distortion is dictated by the bite angle of the biap ligand in combination with the large ionic radius of Mn(II) resulting in bond angles N13–Mn1–N30 and N23–Mn1–N30 in both independent molecules significantly smaller than 90°.

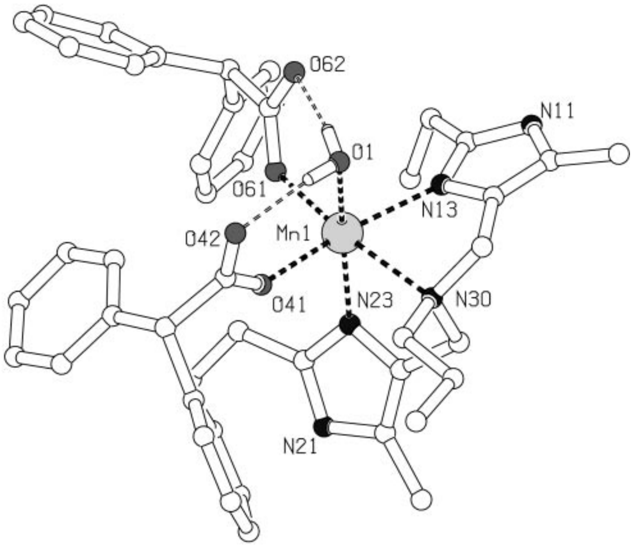

Fig. 3 Projection of **2**, only one of the two independent molecules is shown. All hydrogen atoms except H(1) and H(2) of the water molecule have been omitted for clarity.

Octahedral mononuclear manganese(II) complexes with carboxylate containing ligands in a N_3O_3 donor set are quite rare in the literature. One example is the manganese(II) complex $[Mn(Hquin)_3]^-$ (H_2quin = 2,3-pyridinedicarboxylic acid), in which the chelating ligand is bound with one pyridine nitrogen atom and a monodentate carboxylate.[18]

$[Mn^{II}(biap)((C_6H_5)_3CCH_2COO)_2]\cdot H_2O$ ($3\cdot H_2O$). In the complex $3\cdot H_2O$ the manganese ion is five coordinated in an N_3O_2 donor set as depicted in Fig. 4. The ligand biap is coordinated facially with an angle between the imidazole planes of 72.2(2)°. The coordination sphere can best be described as distorted trigonal bipyramidal. This is also confirmed by the parameters $\tau = 0.77$ and $\delta_{24} = 47.97$. In the trigonal bipyramid the axial positions are occupied by the amine nitrogen and O61, whereas the imidazole nitrogens and O41 occupy the equatorial positions. In a first approximation both carboxylates are coordinated in a monodentate fashion, but one might discuss a semi-coordination of O42 to Mn1 [Mn1 ··· O42: 3.169(2) Å] since this distance is significantly (0.5 Å) shorter than the sum of the van der Waals radii. The other carboxylate is clearly monodentate [Mn1 ··· O62: 3.551(2) Å]. The two “free” carboxylate oxygens O42 and O62 also show differences in their participation in hydrogen bonds. O42 accepts a hydrogen bond from a neighbouring imidazole N–H [O42 ··· N21: 2.794(4) Å] and from the lattice water molecule [O42 ··· O94: 2.967(4) Å]. On the other hand O62 accepts only one short hydrogen bond from the water molecule O94 [O62 ··· O94: 2.658(4) Å]. The

Table 3 Carboxyl stretching frequencies (in cm^{-1}) of the complexes **1**, **2**, **3**, **3b** and of the alkali salts of the carboxylates

	1	Na(PhCOO)	**2**	K(Ph_2CHCOO)	**3**		**3b**	K(Ph_3CCH_2COO)
$\nu_a(CO_2)$	1549	1547	1590	1595	1609	1596	1560	1564
$\nu_s(CO_2)$	1386	1405	1383	1360	1391	1394	1408	1384
$\Delta\nu$	163	142	207	235	218	202	152	180

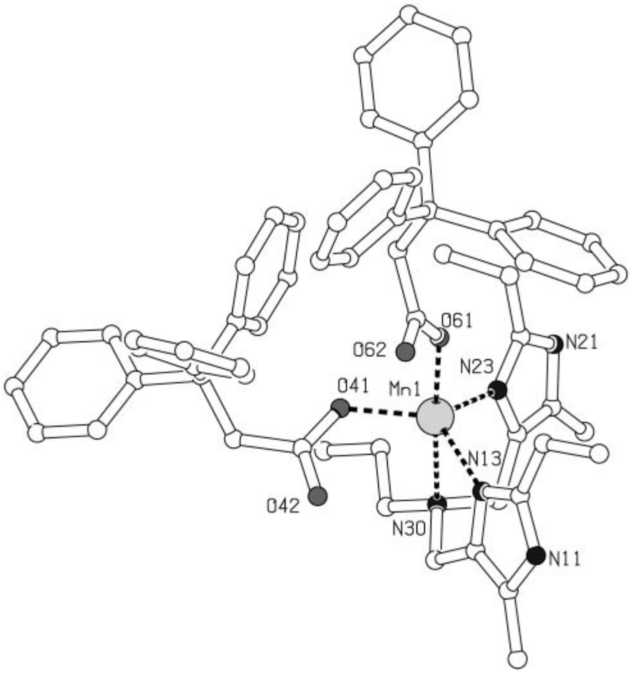

Fig. 4 Projection of **3**. All hydrogen atoms have been omitted for clarity.

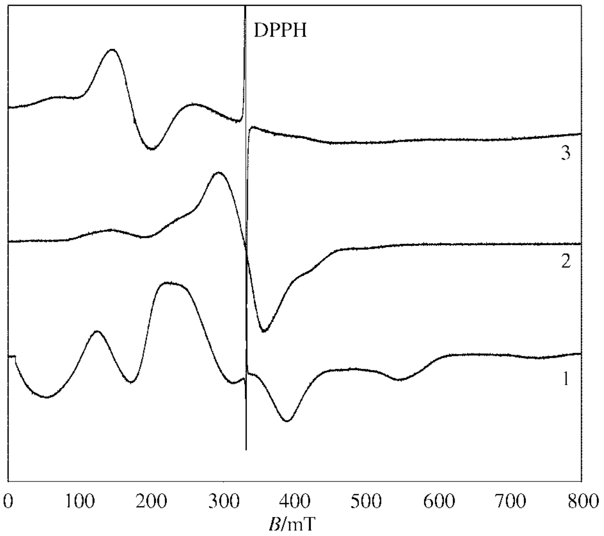

Fig. 5 EPR spectra of polycrystalline samples of **1**, **2** and **3** at the X-band frequency.

hydrogen bond network is completed by hydrogen bonds donated from the imidazole N–H to the oxygen of the lattice water molecule [O94 ··· N11: 2.754(4) Å]. All these hydrogen bonds result in a chain parallel to the *a*-axis.

Comparison of the structures

It is interesting to compare the coordination sphere of the present complexes [Mn(biap)($RCOO)_2(H_2O)_n$] ($n = 0$, 1) with respect to the growing steric bulk of the carboxylates. The complexes seem to follow two strategies in response to the steric stress. The first one is a different folding of biap. The *mer* conformation is much more space filling than the *fac* conformation. Despite the larger carboxylate group in **2**, the *fac* conformation of biap even allows the binding of a sixth ligand. The second strategy is to reduce the coordination number from 6 to 5 again, with biap remaining in the *fac* conformation as realized in **3**.

It is noteworthy that all non-coordinated carboxylate oxygens in the three structures are involved in extensive hydrogen bonding, both intra- and inter-molecularly, thereby adding to the stability of the complexes. This hydrogen bonding clearly affects the infrared stretching frequencies of the carboxylate groups and indeed the interpretation of the IR data is not straightforward.

Spectroscopic properties of the complexes

The antisymmetric and symmetric stretching modes of the carboxylates dominate the infrared spectra of the manganese complexes **1**–**3**. The carboxyl stretching frequencies of the complexes and their corresponding sodium/potassium salts are listed in Table 3. A comparison between the $\Delta\nu$ value [$\Delta\nu = \nu_a(COO) - \nu_s(COO)$] of the corresponding sodium or potassium salts of the carboxylates and the $\Delta\nu$ value of the complexes gives interesting insights into the binding mode of the carboxylate ion. Deacon and Phillips[19] analysed a number of carboxylate containing complexes and arrived at the following conclusions:

- Monodentate carboxylates show $\Delta\nu$ values which are much larger than that of the ionic carboxylate ($\Delta\nu - \Delta\nu_{ionic} > 50$ cm^{-1});
- Chelating (didentate) carboxylates exhibit $\Delta\nu$ values which are significantly less than the ionic values ($\Delta\nu_{ionic} - \Delta\nu > 50$ cm^{-1});
- Bridging carboxylates exhibit $\Delta\nu$ values that are close to the ionic values ($\Delta\nu_{ionic} - \Delta\nu \approx 0$ cm^{-1}).

The $\Delta\nu$ values of **1** and **2** are close to those of sodium benzoate and potassium diphenylacetate, respectively. These values would thus suggest polynuclear complexes with bridging carboxylates, although the monodentate binding mode of the carboxylates has been confirmed by X-ray analysis. However, in our case this unusual $\Delta\nu$ value must be due to the strong hydrogen bonds in the complexes; such strong bonds have been described before for other complexes.[20,21] These hydrogen bonds are more predominant in **2** than in **1**, where only intermolecular hydrogen bonds are found. In fact the carboxylates in **2** can be considered as *bridging* between the metal centre and the water molecule. Interestingly, in **3** two different pairs of carboxyl stretching frequencies are found. This is probably due to the two different binding modes of the coordinated carboxylates.

Recrystallisation of **3** in a DMF–H_2O mixture results in a different manganese(II) species **3b**. In **3b** only one pair of carboxyl stretching frequencies is observed. This might suggest that in **3b** a solvent molecule is bound as a sixth ligand resulting in a structure similar to **2**, or that the carboxylates are bound more symmetrically as in **1**.

The complexes **1**, **2** and **3** were all expected to show signals in the EPR spectra due to the presence of Mn(II). Therefore the X-band EPR spectra of the three complexes were recorded in a powdered sample (Fig. 5) and in a MeOH–EtOH (9 : 1) glass at 77 K (Fig. 6). The EPR spectrum of **2** shows a broad pattern around $g \approx 2$ typical for manganese(II) in a distorted octahedral environment.[22] The EPR signals of **1** and **3** are even more complicated due to zero-field splitting effects. A detailed analysis of the EPR behaviour at various frequencies is beyond the scope of the present study and will be described elsewhere.

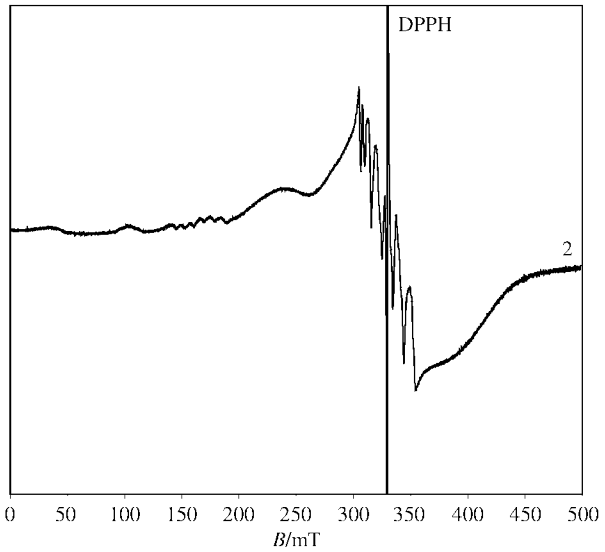

Fig. 6 EPR spectra of a frozen solution of **2** in MeOH–EtOH (9 : 1) at the X-band frequency.

The spectra of the complexes in frozen solution are all quite similar. The signals are better resolved and show an additional ^{55}Mn 6-line pattern, visible on a few of the main bands (A_{Mn} = 9 ± 1 mT). Only for the octahedral complex **2** do the solid state and frozen solution spectra resemble one another (Fig. 6). Given the similarity between the solution spectra of the three complexes, it is therefore also likely that the five coordinated complexes **1** and **3** bind a sixth ligand in solution. The solution spectra of the complexes show a striking resemblance to that of barley oxalate oxidase.[4]

The electrochemical properties of the complexes have been studied in dry and degassed DMF. Although the synthesis of the complexes has to be carried out in an inert atmosphere, the complexes appear to be remarkably stable towards oxidation. Within the potential window of DMF all the complexes were found to be electrochemically inactive. The discrepancy with the oxidation sensitivity during synthesis may be attributed to the use of strictly anhydrous conditions in the cyclic voltammetry.

Conclusions

The results presented in this paper show that in complexes of the general formula $[Mn(biap)(RCOO)_2(H_2O)_n]$ ($n = 0$, 1) a variety of structures is possible. The differences in the three structures discussed is mainly caused by the coordination mode of biap (*fac* or *mer*), the absence or presence of a sixth ligand, the tendency of the free carboxylate oxygen to bind to the metal ion and the possible formation of inter- and intra-molecular hydrogen bonds. The three structures can be distinguished by X-ray crystallography, IR analysis and EPR spectroscopy. In solution, however, it seems that all the complexes are able to bind a sixth ligand to form an octahedral complex independent of the bulk of the coordinated carboxylates.

From the studies described above it is clear that extreme care has to be taken in assignment of the binding mode of carboxylate groups based on infrared studies alone. The presence of strong hydrogen bridges will affect the stretching frequencies of the carboxylates to such an extent that solid statements on their origin cannot be made. The coordinating groups used in this study are similar to those found in mononuclear manganese enzymes (imidazoles, carboxylates, water). The coordination numbers 5 and 6 could be realized using these donors. The same coordination numbers are believed to play an important role in the catalytic cycle of the manganese enzymes. The coordination mode of the carboxylates, and even more their ability to form hydrogen bridges to assist neighbouring groups, seems to be crucial for tuning the coordination number of the manganese centres. Complex **2** in particular can be regarded as a close structural model of manganese containing oxalate oxidase and of iron containing lipoxygenase. Both in **2** and in the enzyme the nitrogen donors are bound facially in the octahedron and both structures contain a monodentate carboxylate, which accepts a hydrogen bond from the coordinated water molecule. The second carboxylate group in **2** simulates the weakly coordinated amide of asparagine.

Acknowledgements

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. 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.

References

1 N. A. Law, M. T. Caudle and V. L. Pecoraro, *Adv. Inorg. Chem.*, 1999, **46**, 305 and references cited therein.
2 C. Su and E. H. Oliw, *J. Biol. Chem.*, 1998, **273**, 13072.
3 E. J. Woo, J. M. Dunwell, P. W. Goodenough, A. C. Marvier and R. W. Pickersgill, *Nat. Struct. Biol.*, 2000, **7**, 1036.
4 L. Requena and S. Bornemann, *Biochem. J.*, 1999, **343**, 185.
5 G. E. Borgstahl, H. E. Parge, M. J. Hickey, W. F. Beyer, Jr., R. A. Hallewell and J. A. Trainer, *Cell*, 1992, **71**, 107.
6 S. Han, L. D. Eltis, K. N. Timmis, S. W. Muchmore and J. T. Bolin, *Science*, 1995, **270**, 976.
7 C. Su, M. Sahlin and E. H. Oliw, *J. Biol. Chem.*, 2000, **275**, 18830.
8 W. Minor, J. Steczko, B. Stec, Z. Otwinowski, J. T. Bolin, R. Walter and B. Axelrod, *Biochemistry*, 1996, **35**, 10687.
9 E. Bouwman, B. Douziech, L. Gutierrez-Soto, M. Beretta, W. L. Driessen, J. Reedijk and G. Mendoza-Díaz, *Inorg. Chim. Acta*, 2000, **304**, 250.
10 M. Beretta, E. Bouwman, L. Casella, B. Douziech, W. L. Driessen, L. Gutierrez-Soto, E. Manzani and J. Reedijk, *Inorg. Chim. Acta*, 2000, **310**, 41.
11 G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, 1997.
12 G. M. Sheldrick, SHELXS-86, Program for crystal structure determination, University of Göttingen, Germany, 1986.
13 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, DIRDIF99 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
14 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
15 R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119.
16 H. Adams, N. A. Bailey, J. D. Crane and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1990, 1727.
17 L. S. Erre, G. Micera, E. Garribba and A. Cs. Bényei, *New J. Chem.*, 2000, **24**, 725.
18 M. A. S. Goher, A. A. Youssef, Z. Y. Zhou and T. C. W. Mak, *Polyhedron*, 1993, **12**, 1871.
19 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
20 L. S. Erre, G. Micera, F. Cariati, G. Ciani, A. Sironi, H. Kozlowski and J. Baranowski, *J. Chem. Soc., Dalton Trans.*, 1988, 363.
21 T. Glowiak, H. Kozlowski, L. S. Erre and G. Micera, *Inorg. Chim. Acta*, 1995, **236**, 149.
22 R. D. Dowsing, B. Nieuwenhuijse and J. Reedijk, *Inorg. Chim. Acta*, 1971, **5**, 301.