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Synthesis, crystal structure and IR spectroscopy of $\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{NC})(\text{DMSO})$ and $[\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{phen})(\text{H}_2\text{O})] \cdot \text{DMA}$; (2-HIC, indole-2-carboxylic acid; phen, 1,10-phenanthroline; NC, 2,9-dimethyl-1,10-phenanthroline; DMSO, dimethyl sulfoxide; DMA, dimethyl acetamide); catalysts for the disproportionation of hydrogen peroxide

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Abstract

Two ternary complexes of manganese(II) indole-2-carboxylate (2-IC) with 2,9-dimethyl-1,10-phenanthroline (NC) and 1,10-phenanthroline (phen) in dimethyl sulfoxide (DMSO) or dimethylacetamide (DMA) were synthesized, their X-ray crystal structure and IR spectroscopy characteristics were determined. In compound $\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{NC})(\text{DMSO})$ (**1**), Mn(II) is six-coordinate by one bidentate NC ligand and two bidentate 2-IC anionic ligands. The crystal structure has revealed a seven-coordinate Mn(II) when a moderately long contact distance Mn–O (DMSO 2.643(2) Å) is included in the coordination list: the Mn(II) configuration can be described as a distorted capped octahedron. Individual molecules are linked into chains running parallel to the *a* axis by intermolecular hydrogen bonding. In compound $[\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{phen})(\text{H}_2\text{O})] \cdot \text{DMA}$ (**2**), the manganese atom is six-coordinate by one bidentate phen ligand and two 2-IC anionic ligands one of which is monodentate, and the other is bidentate. The coordination sphere is completed by one water molecule, the Mn(II) environment can be described as a very distorted octahedron. The individual molecules are associated in dimer structure by intermolecular hydrogen bonding. The crystal structure of **2** is completed by a disordered DMA solvate molecule. These two complexes are catalysts for the disproportionation of H_2O_2 in the presence of added imidazole.

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Keywords: Ternary manganese(II) complexes; 1,10-Phenanthroline; Neocuproine; Indole-2-carboxylic acid; Crystal structures; IR; Catalytic activity

1. Introduction

Manganese is known to participate in a variety of biological reactions, such as hydrogen peroxide decomposition, superoxide anion (O_2^-) dismutation, water oxidation, and ribonucleotide reduction. During the two last decades, a number of manganese-containing non-

haem catalases have been isolated and characterized [1–3], and these catalytically disproportionate hydrogen peroxide, a reaction which is important for cell detoxification. The synthesis and structural characterization of manganese(II) carboxylate complexes has been engaged, in particular the ternary complexes with added phenanthrolines, which are particularly active catalysts for this disproportionation in the presence of added base imidazole [4]. Moreover, we have shown that some ternary complexes formed by Cu(II) carboxylates and

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1,10-phenanthroline ligand exhibit biological properties (*anti-convulsant*) [5]. This prompted us to investigate the effect of adding 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (neocuproine NC) to indole-2-carboxylate as chelating agents for Mn(II).

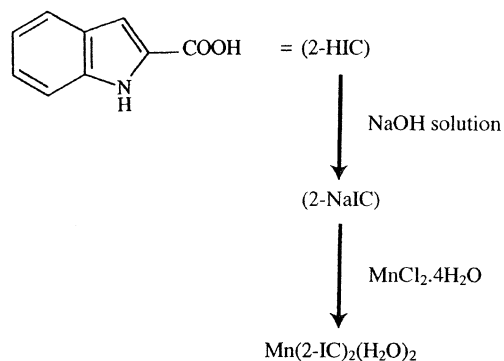
2. Results and discussion

Synthetic routes to the complexes **1–2** are shown in Schemes 1 and 2. $[\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{H}_2\text{O})_2]$ was prepared by reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with 2-NaIC after neutralizing the 2-HIC by a NaOH solution. The $[\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{H}_2\text{O})_2]$ precipitate was isolated from the filtrate (Scheme 1). This compound was dissolved in dimethyl sulfoxide (DMSO) and reacted with NC at room temperature to give $[\text{Mn}(2\text{-IC})_2(\text{NC})(\text{DMSO})]$ compound **1**. Moreover, $[\text{Mn}^{\text{II}}(2\text{-IC})_2(\text{H}_2\text{O})_2]$ reacted with phen in dimethylacetamide (DMA), at 80 °C during 15 min to give $[\text{Mn}(2\text{-IC})_2(\text{phen})(\text{H}_2\text{O})] \cdot (\text{DMA})$ compound **2** (Scheme 2).

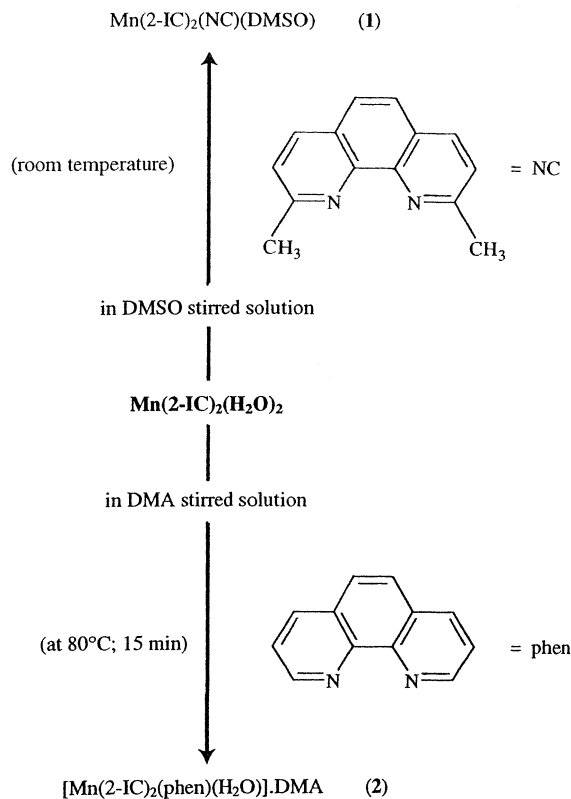
2.1. Crystal and molecular structure

The single crystal X-ray structures of compounds **1** and **2** are shown in Fig. 1(a and b) and selected interatomic data are listed in Table 1.

The asymmetric unit of bis(indole-2-carboxylato)(2,9-dimethyl-1,10-phenanthroline)(dimethyl sulfoxide)manganese(II), $[\text{Mn}(\text{C}_9\text{H}_6\text{NO}_2)_2(\text{C}_{14}\text{H}_{12}\text{N}_2)(\text{C}_2\text{H}_6\text{OS})]$ compound **1** contains one monomeric manganese complex. The Mn atom exhibits a six-coordinate environment comprising the two aromatic nitrogens from the 2,9-dimethyl-1,10-phenanthroline ligand (N21 and N30) and the two carboxylate oxygens of each chelating indole-2-carboxylate anions (O1 and O2, O11 and O12, respectively). The Mn–N bond lengths average 2.237(2) Å agree well with literature reports [6]. Among the metal–oxygen bonds to the (2-IC anionic) ligands, the Mn–O2 and Mn–O12 bonds (2.210(2) and 2.138(2) Å, respectively) seem to be reasonable values for six-coordinate Mn^{2+} [7]. In addition, the Mn–O1 [2.490(2)



Scheme 1.



Scheme 2.

Å] and Mn–O11 [2.442(2) Å] distances are greater; these values correspond to a strength attenuation for these connections which can be explained by intramolecular hydrogen bonds involving N1 and O1, N11 and O11 (Table 2(a)).

In the crystal structure of **1**, the coordination of manganese can be completed by DMSO molecule via O41 atom with a moderately long contact distance of 2.643(2) Å significantly shorter than the sum of the van der Waals radii; however, values up to 3.005 Å were reported in manganese carboxylate complexes by Rardin et al. [8]. Therefore, the manganese atom exhibits a {6+1} environment, approximately described as a distorted capped octahedron. Seven-coordinate Mn(II) complexes are relatively rare in the literature. According to this description, the Mn atom lies 0.559(1) Å out of the basal plane [O11, O12, N21, N30] with the apical positions occupied by O2 and O41 atoms [O2–Mn–O41, 160.10(8)°]; the O1 atom caps the triangular face formed by O2, O12 and N30 atoms. This very irregular geometry is imposed by the small bite angles of the indole-2-carboxylates [O1–Mn–O2, 55.53(7)°; O11–Mn–O12, 57.21(7)°] and neocuproine [N21–Mn–N30, 75.42(8)°] bidentate ligands, mainly due to the rigidity of these chelate molecules. Individual molecules are linked into chains running parallel to the *a* axis by intermolecular hydrogen bonding involving H(N1) and H(N11); in consequence, these hydrogen atoms are involved in

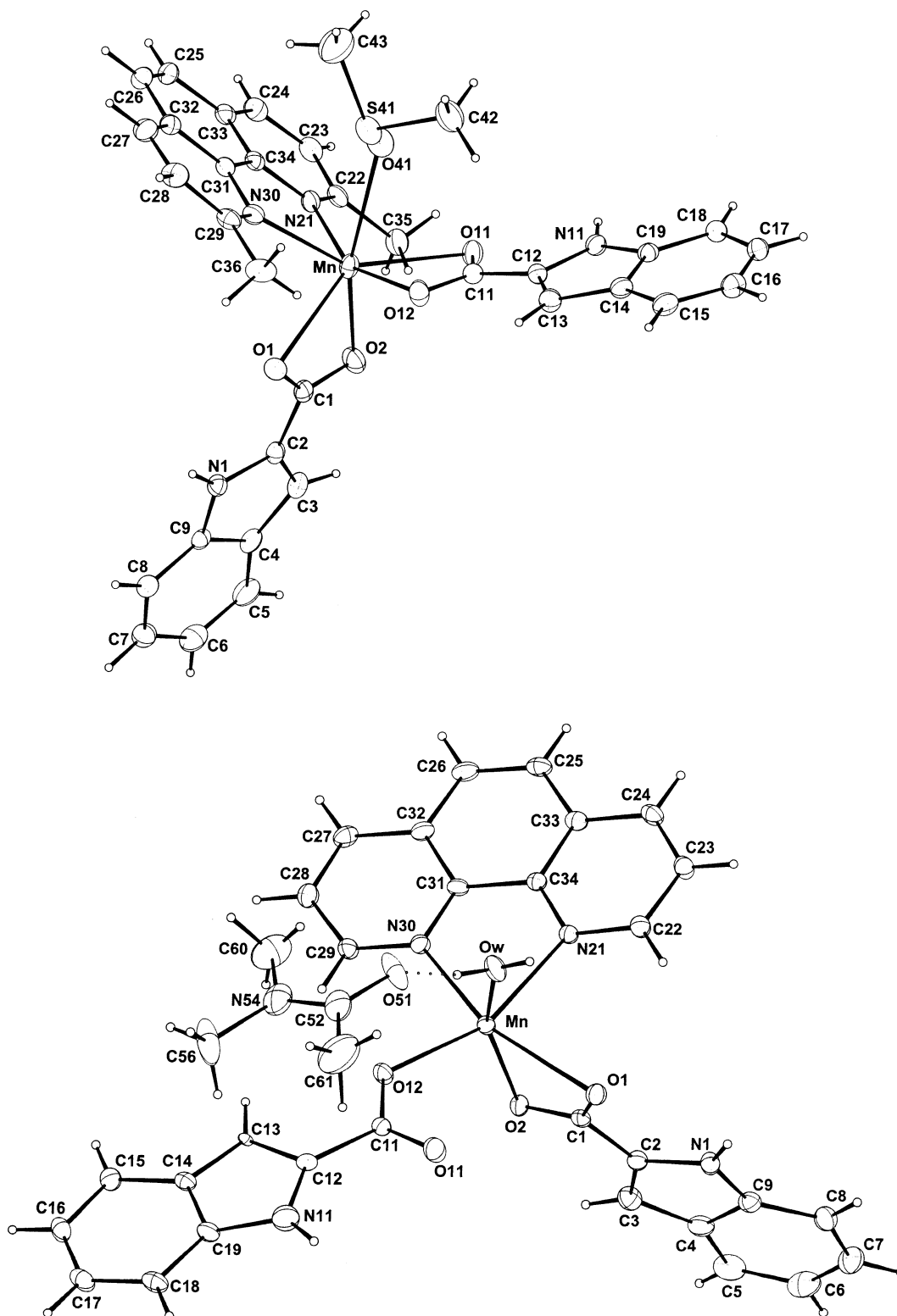


Fig. 1. (a) A perspective view of **1**, $\text{Mn}^{\text{II}}(\text{2-IC})_2(\text{NC})(\text{DMSO})$, showing 50% probability displacement ellipsoids. (b) A perspective view of **2**, $[\text{Mn}^{\text{II}}(\text{2-IC})_2(\text{phen})(\text{H}_2\text{O})]\cdot\text{DMA}$, showing 50% probability displacement ellipsoids.

bifurcated bonds (Table 2(a)). Moreover, as shown in Fig. 2(a), the chains are linked by π – π stacking interactions, which occur between neocuproine ligands related through inversion centres at $(1/2, 0, 1/2)$ and $(0,$

$1/2, 0)$ with an average spacing of $3.362(3)$ Å (Fig. 3). The bond distances and angles within the neocuproine and 2-IC anionic ligands have the expected values. The indole mean planes, P1 (N1/C2–C9) and P2 (N11/C12–

Table 1
Selected distances and angles in **1** and **2**

	1	2
<i>Distances (Å)</i>		
Mn–O11	2.442(2)	
Mn–O12	2.138(2)	2.102(2)
Mn–Ow		2.139(2)
Mn–O2	2.210(2)	2.238(2)
Mn–N30	2.242(2)	2.255(2)
Mn–N21	2.232(2)	2.337(2)
Mn–O1	2.490(2)	2.343(2)
Mn–O41	2.643(2) (contact distance)	
O1–C1	1.259(3)	1.261(3)
C1–O2	1.262(4)	1.262(3)
C1–C2	1.472(4)	1.478(3)
O11–C11	1.257(3)	1.232(3)
C11–O12	1.267(3)	1.268(3)
C11–C12	1.475(4)	1.496(3)
<i>Angles (°)</i>		
O12–Mn–Ow		92.93(7)
O12–Mn–O2	99.99(8)	97.88(7)
Ow–Mn–O21		56.09(7)
O12–Mn–N30	112.28(8)	86.56(7)
Ow–Mn–N30		102.69(7)
O2–Mn–N30	126.96(8)	99.21(6)
O12–Mn–N21	154.50(9)	157.70(7)
Ow–Mn–N21		85.25(7)
O2–Mn–N21	93.12(8)	92.44(7)
N30–Mn–N21	75.42(8)	72.25(7)
O12–Mn–O1	93.87(7)	120.56(7)
Ow–Mn–O1		98.82(7)
O2–Mn–O1	55.53(7)	57.35(5)
N30–Mn–O1	80.56(7)	144.31(7)
N21–Mn–O1	111.55(7)	81.62(6)
C1–O1–Mn	84.49(17)	87.9(1)
O1–C1–O2	121.8(3)	121.4(2)
O1–C1–C2	119.3(3)	120.5(2)
O2–C1–C2	118.7(3)	118.0(2)
C1–O2–Mn	97.28(17)	92.7(1)
O11–C11–O12	122.1(2)	125.8(2)
O11–C11–C12	119.9(3)	118.4(2)
O12–C11–C12	118.1(2)	115.8(2)
C11–O12–Mn	97.00(16)	119.2(1)
O12–Mn–O41	79.09(8)	
O2–Mn–O41	160.10(8)	
N21–Mn–O41	81.18(7)	
N30–Mn–O41	70.22(8)	
O11–Mn–O41	73.05(7)	
O1–Mn–O41	144.18(7)	

C19) (maximum deviation from the best mean plane of 0.026(2) Å for C16), make a dihedral angle of 64.82(6)°. The neocuproine is essentially planar (maximum deviation from the best mean plane of 0.057(3) Å for C28) and the Mn(II) atom is displaced from the neocuproine least-squares plane P3 (N21/C22–C29/N30/C31–C36) by 0.146(2) Å. The dihedral angles between planes P1 and P2 and P3 are 83.72(5)° and 53.10(5)°, respectively.

In compound **2**, the manganese atom is six-coordinate by one bidentate 1,10-phenanthroline ligand via N21 and N30, and two 2-IC anionic ligands one of which is

Table 2
Hydrogen-bonding geometry (Å, °)

D–H...A	D–H	H...A	D...A	D–H...A
<i>a-Compound 1</i>				
N1–H1...O1	0.84(4)	2.66(4)	2.811(3)	91(3)
N11–H11...O11	0.92(5)	2.60(4)	2.812(3)	93(3)
N1–H1...O11 ⁱ	0.84(4)	2.06(5)	2.889(3)	166(4)
N11–H11...O11 ⁱⁱ	0.92(5)	1.95(5)	2.827(3)	159(4)
<i>b-Compound 2</i>				
Ow–Hw2...O51A	0.81(4)	1.89(4)	2.659(17)	157(4)
Ow–Hw2...O51B	0.81(4)	1.90(4)	2.658(18)	155(4)
N1–H1...O1	0.86	2.65	2.839(3)	93.6
N11–H11...O11	0.86	2.97	2.965(3)	87.4
N1–H1...O51A ⁱ	0.86	2.09	2.814(18)	141.8
N1–H1...O51B ⁱ	0.86	2.11	2.872(19)	147.1
Ow–Hw1...O1 ⁱ	0.74(4)	2.01	2.734(2)	166(4)

Symmetry codes: a-Compound 1: (i) 1+x, y, z (ii) –1+x, y, z; b-Compound 2: (i) 1–x, 1–y, 1–z.

monodentate via O12 atom, and the other is bidentate via O1 and O2 atoms. The coordination sphere is completed by one water molecule. The geometry is far removed from octahedral, principally due to the 'bite' of phen and 2-IC anionic ligands. The apical positions are occupied by atoms Ow (aqua) and O2 [Ow–Mn–O2: 156.09(7)°]. The Mn atom lies 0.2079(9) Å out of the basal plane [N21/N30/O1/O12]. The degree of deviation from an ideal octahedron is appreciable with the angles of the octahedron ranging from 57.35(5)° to 120.56(7)°. The Mn–N bond lengths are slightly greater than those found in **1** but nevertheless the average 2.296(2) Å remains in the range of the values reported in the literature [6]. The Mn–Ow distance [2.139(2) Å] is of the same order of those commonly found in six-coordinate manganese(II) complexes (≈ 2.1 – 2.2 Å) [7]. Functioning as a bidentate ligand, the first 2-IC anion is coordinated to manganese(II) with a Mn–O2 distance of 2.238(2) Å, and the other carboxylate oxygen is more weakly coordinated at a longer Mn–O1 distance of 2.344(2) Å. The second 2-IC anion (monodentate ligand) coordinates Mn(II) by the O12 atom (Mn–O12: 2.102(2) Å). The bond distances and angles within the phen and 2-IC anionic ligands have the expected values. The indole mean planes, P4 (N1/C2–C9) and P5 (N11/C12–C19) (maximum deviation from the best mean plane of 0.012(2) Å for C12), make a dihedral angle of 81.50(6)°. The phen is essentially planar (maximum deviation from the best mean plane of 0.087(2) Å for C23) and the Mn(II) atom is displaced from the phen least-squares plane P6 (N21/C22–C29/N30/C31–C34) by 0.021(2) Å. The dihedral angles between planes P4 or P5 and P6 are 89.63(5)° and 9.49(8)°, respectively. The crystal structure of **2** is completed by a disordered DMA solvate molecule: O51, N54, C52, C56 atoms (and their corresponding H) being located over two sites in a statistical disorder, denoted by the suffix A or B (occupancy factor 0.50/

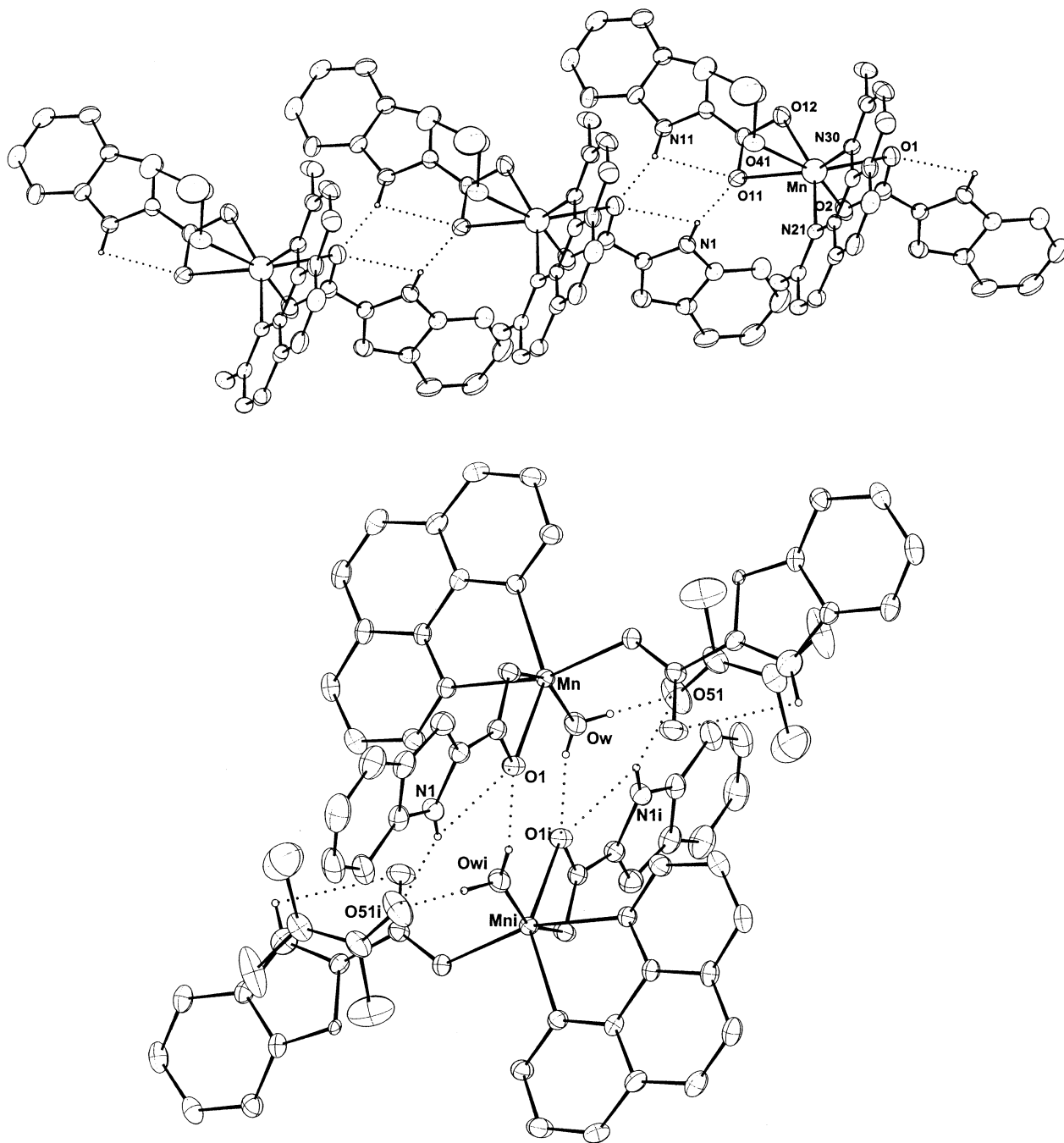


Fig. 2. (a) Individual molecules linked into chains running parallel to the a axis by intermolecular hydrogen bonding in **1**. (b) Individual molecules associated in dimer structure by intermolecular hydrogen bonding in **2**.

0.50). Each unsplit carbon atom (C60 or C61) is connected to N54 of one molecule and C52 of the other one thus playing a different role for A and B. The oxygen atom of the water molecule is hydrogen bonded to one carboxylate oxygen atom ($Ow \cdots O1^i$) of another complex molecule related by inversion centre ($i: 1-x, 1-y, 1-z$) (Table 2(b)). Thus, for **2** (and contrary to **1**), the individual molecules are associated in dimer structure by intermolecular hydrogen bonding ($Mn \cdots Mn^i$ distance: 5.616(1) Å) (Fig. 2(b)). Moreover, the

O51 (and O51ⁱ) atom of the DMA solvate molecule links by two hydrogen bonds these two complex molecules (via Ow and $N1^i$); these DMA molecules form two bridges with the dimer structure. Like in **1**, the hydrogen atom attached to N1 is involved in intermolecular (via O1 atom) and moreover in intramolecular (via DMA O51ⁱ) hydrogen bonds and thus, in a bifurcated H bond manner.

In conclusion, the versatility of the carboxylate group in the 2-IC anionic ligand is reflected in its different

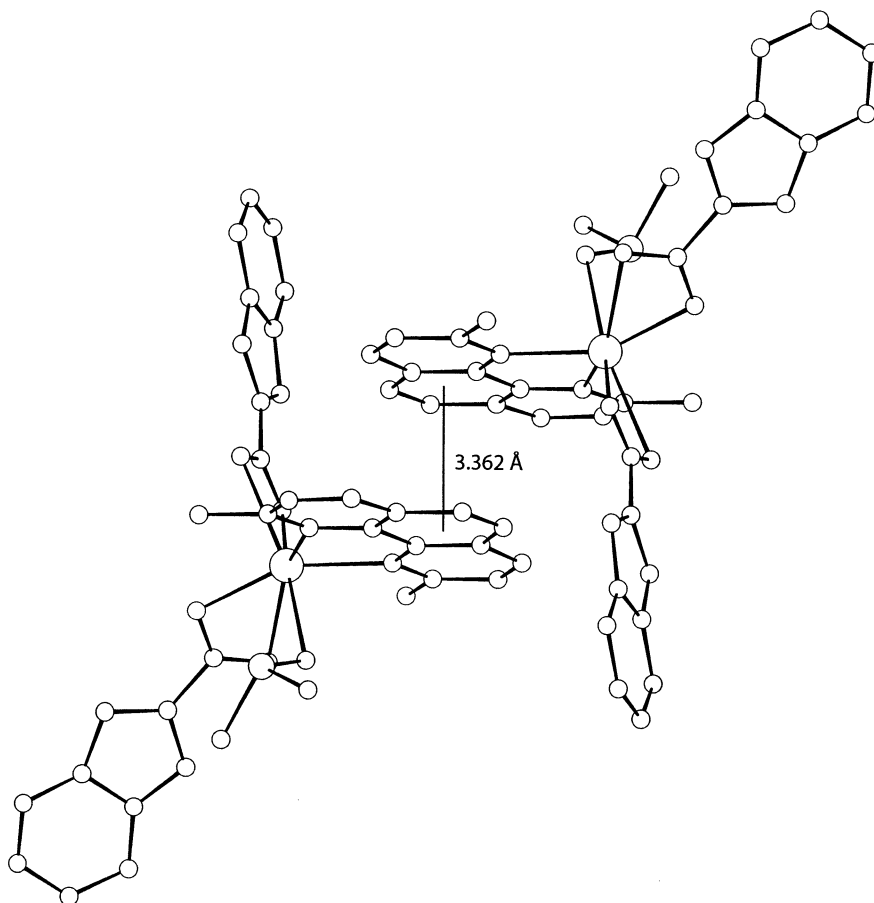


Fig. 3. π - π stacking of neocuproine ligands in **1**.

binding modes: bidentate and monodentate with two unequal C=O bonds in 2-IC anion in compound **2**, and only bidentate in compound **1** with 2 equiv. C=O bonds (within one estimated standard deviation). The preferential formation of mono or bidentate chelating mode is possibly due to steric hindrance (presence of DMA solvate in **2** and dimer structure).

2.2. IR spectroscopy

The IR spectra of **1** and **2** in KBr pellets were performed in 4000–600 cm^{-1} region, as well IR spectra of the two initial reactants: indole-2-carboxylic acid and neocuproine. We were interested in some characteristic bands: $\nu(\text{NH})$, $\nu(\text{OH})$ and $\nu(\text{OCO})$.

In the 4000–2000 cm^{-1} domain, the main bands correspond to NH and OH (Table 3). For the stretching vibration NH, two frequencies are present: free and associated $\nu(\text{NH})$. Three compounds (2-HIC, NC, and **1**) contain the free band (weak for **1**). The associated $\nu(\text{NH})$ is present in 2-HIC, **1** and **2**. The bands of **1** and **2** (broader for **2**) are shifted towards the lower frequencies in relation to 2-HIC band, with a large shift for **1**. The broad band is assigned to asymmetric $\nu_a(\text{OH})$

stretching vibrations of hydrogen bonding with the apparition of shoulder in **2** denoting the presence of bound water molecules.

The associated $\nu(\text{NH})$ and $\nu_a(\text{OH})$ frequencies can be assigned to the hydrogen bonding, either in dimer mode for 2-HIC [9] and **2** or in a polymer mode for **1** and/or formation of chelate with intramolecular bonding.

In the 2000–600 cm^{-1} domain, the different bands linked to C=O, C–O or OCO groups were observed. 2-HIC spectrum showed two strong bands corresponding, respectively, to asymmetric ν_a stretching vibrations at 1714 cm^{-1} for C=O and 1196 cm^{-1} for C–O indicating the existence of associated dimers by intermolecular hydrogen bonding and/or the formation of chelates by intramolecular hydrogen bonding [9]. In **1** and **2**, these bands disappeared by deprotonation and bonding to Mn(II).

In **1**, the asymmetric stretching vibrations $\nu_a(\text{OCO})$ appeared between 1650 and 1475 cm^{-1} , one prominent band at 1535 cm^{-1} and the symmetric stretching vibrations $\nu_s(\text{OCO})$ is attributed to the strong band at 1414 cm^{-1} . The value of $\Delta(\text{OCO})$ ($\nu_a - \nu_s$) is equal to 120 cm^{-1} which is smaller than the corresponding value

Table 3
Infrared frequencies (cm^{-1}) for 2-HIC, NC, **1** and **2** in the 4000–2000 cm^{-1} domain

Compound	Free $\nu(\text{NH})$	Associated $\nu(\text{NH})$	$\nu(\text{OH})$	Associated $\nu_a(\text{OH})$
2-HIC	3454 (w)	3352 (s)		3500–2500 (w, b)
NC	3447 (w)			
Complex 1	3500–3350 (w)	3207 (s)		3400–2500 (w, b)
Complex 2		3500–3200 (s, b)	OH water crystal shoulder 3600	3800–2600 (w, b)

Abbreviations used in this table are: s, strong; w, weak; b, broad.

in acetate (164 cm^{-1} , ionic type) [11] and similar to the corresponding values proposed by Ahuja et al. [12] in $\text{Mn}(2,2'\text{-bipyridine})(\text{acetate})_2$ and $\text{Mn}(4,4'\text{-bipyridine})(\text{acetate})_2$ bidentate complexes (Table 4, and see also [13]). The 2-IC anionic ligand exhibits a bidentate mode in **1**, consistent with the observed X-ray crystal structure.

In **2**, three strong bands correspond to $\nu(\text{OCO})$. The first band about 1610 cm^{-1} is very strong and can be assigned to $\nu_a(\text{OCO})$. The second strong band about $1422\text{--}1410 \text{ cm}^{-1}$ may be assigned to $\nu_s(\text{OCO})$. The value of $\Delta(\text{OCO})$ ($\nu_a - \nu_s$) is equal about $188\text{--}200 \text{ cm}^{-1}$, similar to values reported by several authors (see Table 4) for a monodentate mode [10,14]. The third band observed at 1536 cm^{-1} with a similar intensity can be assigned to $\nu_a(\text{OCO})$ and the separation $\Delta(\text{OCO})$ with $\nu_s(\text{OCO})$ is equal to $114\text{--}126 \text{ cm}^{-1}$ similar to values reported by several authors (see Table 4) for a bidentate mode [12]. Thus, these results agree with the presence in compound **2** of two chelating modes for the 2-IC anionic ligands: monodentate and bidentate consistent with the observed X-ray crystal structure.

2.3. Catalytic activity

Many manganese(II) complexes were found to catalyse the disproportionation of hydrogen peroxide $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ in the presence of added heterocyclic bases (pyridine, imidazole) [10,15–17]. It was suggested that these bases may be essential in the catalysis disproportionation of H_2O_2 by manganese catalase since they are known to be present in the

vicinity of active site of catalase and other manganoenzymes [18].

This catalytic activity of the compounds **1** and **2** and the effect of added imidazole were investigated for the disproportionation of hydrogen peroxide. The Fig. 4(a) presents the evolution of oxygen pressure in absence or presence of the imidazole. In absence of the imidazole, the complexes were a very weak catalyst for this reaction. To evaluate this weakness, for example in complex **2**, the initial rate v_0 (decomposition of H_2O_2) during the initial 5 min is calculated from O_2 pressure. This value is $1.58 \times 10^{-6} \text{ mol min}^{-1}$. The initial turnover rate v' (rate v_0 per mole of the complex per second) is $6.14 \times 10^{-3} \text{ s}^{-1}$; it is close to $6.25 \times 10^{-3} \text{ s}^{-1}$ for $[\text{Mn}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ [19]. Thus, the complex **2** decomposes hydrogen peroxide very weakly.

In presence of imidazole, O_2 evolution rate is increased. In **1**, an S evolution curve is observed which suggests an autocatalytic kinetic; during the initial 5 min., v_0 is equal to $2.4 \times 10^{-4} \text{ mol min}^{-1}$ and the initial turnover rate v' to 1 s^{-1} . In **2**, the curve appearance suggests the absence of autocatalytic phenomenon and is close to Devereux et al.'s [10,17] and Zhang et al.'s [16] reports. The initial rate v_0 is equal to $0.48 \times 10^{-3} \text{ mol min}^{-1}$ and the initial turnover rate v' is equal to 2 s^{-1} .

Thus, in the presence of the imidazole and in the same experimental conditions for **1** and **2**, complex **2** appears to be the most efficient catalyst over the first minute of the reaction as shown in the Fig. 4(a).

In addition, in **2**, the evolution of H_2O_2 versus time is represented respectively by $P_f - P$ and the order determination by $\ln(P_f - P)$, where P_f is the O_2 final pressure

Table 4
Infrared frequencies (cm^{-1}) for acetate, **1**, **2**, and some others Mn(II) complexes in the 1650–1400 cm^{-1} domain

Compound	$\nu_a(\text{OCO})$	$\nu_s(\text{OCO})$	$\Delta\nu$	Type	Ref.
Acetate	1578	1414	164	ionic	[11]
Complex 1	1535	1414	121	bidentate	this work
Complex 2	1610 1536	1422–1410	188–200 114–126	monodentate bidentate	this work
$\text{Mn}(2,2'\text{-bipy})(\text{acetate})_2$	1540	1410	130	bidentate	[12]
$\text{Mn}(4,4'\text{-bipy})(\text{acetate})_2$	1580	1430	150	bidentate	[12]
$\text{Mn}(\text{dipic}) \cdot 1.5\text{H}_2\text{O}$	1588	1400	188	monodentate	[10]
$(\text{NH}_4)_4[\text{Mn}(\text{citrate})_2] \cdot 2\text{H}_2\text{O}$	1621–1586	1436–1386	185–200	monodentate	[14]

Ligands abbreviations: 2,2'-bipy: 2,2'-bipyridine; 4,4'-bipy: 4,4'-bipyridine; dipic: pyridine-2,6-dicarboxylate.

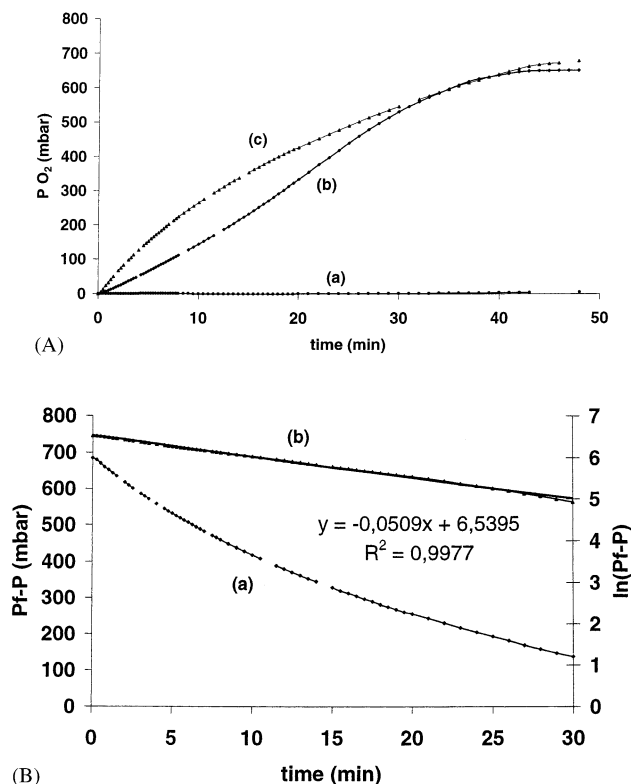


Fig. 4. (A) Hydrogen peroxide disproportionation curves in presence of complex (0.5×10^{-3} M), H_2O_2 (1.224 M), imidazole (1.25×10^{-2} M): (a) complex **2** in absence of imidazole; (b) complex **1** in presence of imidazole; (c) complex **2** in presence of imidazole. (B) Kinetic constant determination for **2**: (a) evolution of hydrogen peroxide; (b) first order for the disproportionation of hydrogen peroxide.

and P the pressure at a given time (Fig. 4(b)). After 30 min, 78% of H_2O_2 had been converted to O_2 and the order for the disproportionation of H_2O_2 was found equal to one for H_2O_2 for an imidazole/ H_2O_2 ratio equal to 10^{-2} . The rate constant is equal to 0.0509 min^{-1} . This value is similar to the rate constant calculated for a first order reaction (0.069 min^{-1}) by using a Mn(III) complex $[(ac)Mn(bbml)_2Mn(ac)] \cdot (BF_4)_2 \cdot 3.5H_2O$ (Hbbml, [bis(2-benzimidazolylmethyl)amino]ethanol; Hac, acetic acid) [16].

3. Experimental

3.1. Chemicals

Manganese(II) dichloride tetrahydrate, hydrogen peroxide, analytical grades N,N -DMA and DMSO were purchased from Prolabo, indole-2-carboxylic acid, 1,10-phenanthroline monohydrate and 2,9-dimethyl-1,10-phenanthroline hydrate from Aldrich.

3.2. Physical measurements

Infrared spectra (KBr pellet $4000\text{--}600 \text{ cm}^{-1}$) were recorded on a Bruker vector 22.

3.3. Synthesis of the complexes

3.3.1. $[Mn(C_9H_6NO_2)_2(H_2O)_2]$

Sodium indole-2-carboxylate was prepared by neutralizing indole-2-carboxylic acid (2-HIC) (1.632 g, 10 mmol) with 10 ml of 1 mol l^{-1} NaOH prepared with deionised water. To this solution was added $MnCl_2 \cdot 4H_2O$ in excess (1.979 g, 10 mmol in 10 ml of water). An immediate precipitate of diaquabis(indole-2-carboxylato)manganese(II) $[Mn^{II}(2-IC)_2(H_2O)_2]$ formed which was collected by filtration, washed several times with H_2O , and air-dried at 60°C for 24 h.

3.3.2. $[Mn(C_9H_6NO_2)_2(C_{14}H_{12}N_2)(C_2H_6OS)]$ (**1**)

Bis(indole-2-carboxylato)(2,9-dimethyl-1,10-phenanthroline)(dimethyl sulfoxide)manganese(II) **1**, was synthesized as following. 2,9-Dimethyl-1,10-phenanthroline hydrate (0.416 g, 2 mmol) was added to a stirred solution of diaquabis(indole-2-carboxylato)manganese(II) (0.823 g, 2 mmol) in 4 ml of DMSO. Under these conditions, crystals of **1** deposited in small quantities over a period of few days. Yield: 0.932 g (69.9%). Anal. Calc. for $C_{34}H_{30}MnN_4O_5S$: C, 61.72; H, 4.57; N, 8.47%. Found: C, 61.61; H, 4.61; N, 8.43%.

3.3.3. $[Mn(C_9H_6NO_2)_2(C_{12}H_8N_2)(H_2O)] \cdot (C_4H_9NO)$ (**2**)

Aquabis(indole-2-carboxylato)(1,10-phenanthroline)manganese(II) dimethylacetamide solvate **2**, was synthesized as following. 1,10-Phenanthroline monohydrate (0.396 g, 2 mmol) was added to a stirred solution of diaquabis(indole-2-carboxylato)manganese(II) (0.823 g, 2 mmol) in 20 ml of DMA and heated at 80°C during 15 min. The obtained dark yellow solution was then evaporated at room temperature. Under these conditions, crystals of **2** deposited over a period of few days. Yield: 0.850 g (64.3%). Anal. Calc. for $C_{34}H_{31}MnN_5O_6$: C, 61.82; H, 4.73; N, 10.60%. Found: C, 61.70; H, 4.75; N, 10.56%.

3.4. X-ray diffraction studies

Data for **1** and **2** were collected on a Stoe IPDS diffractometer at 180 K, with data collection and reduction using Stoe and Cie (1996) IPDS programs package [20]. All data were corrected for Lorentz-polarisation effects. Both structures were solved by direct methods using SIR-92 [21] and refined by least-squares methods on F^2 using SHELXL-97 [22]. Hydrogen atoms were inserted at calculated positions except for those on the N1 and N11 nitrogen atoms (**1**), on Ow

Table 5
Crystal data and structure refinement

Crystal parameters	Compound 1 [Mn ^{II} (2-IC) ₂ (NC)(DMSO)]	Compound 2 {[Mn ^{II} (2-IC) ₂ (phen)(H ₂ O)]·[DMA]}
Empirical formula	C ₃₄ H ₃₀ MnN ₄ O ₅ S	C ₃₄ H ₃₁ MnN ₅ O ₆
Formula mass (<i>M_r</i>)	661.62	660.58
Temperature (K)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions		
<i>a</i> (Å)	8.175(1)	10.525(1)
<i>b</i> (Å)	17.150(1)	11.211(1)
<i>c</i> (Å)	22.141(1)	13.839(2)
α (°)	90.00	88.57(2)
β (°)	100.34(1)	76.81(2)
γ (°)	90.00	72.56(1)
<i>V</i> (Å ³)	3053.8(4)	1515.2(4)
<i>Z</i>	4	2
<i>D</i> _{calc} (Mg m ⁻³)	1.439	1.448
Absorption coefficient (mm ⁻¹)	0.550	0.491
<i>F</i> (0 0 0)	1372	686
Crystal size (mm)	0.36 × 0.30 × 0.28	0.35 × 0.32 × 0.25
Description	yellow parallelepiped	yellow parallelepiped
Range for data collection (°)	2.22–26.17	2.28–26.11
Index ranges	−9 ≤ <i>h</i> , −21 ≤ <i>k</i> , −27 ≤ <i>l</i>	−12 ≤ <i>h</i> , −13 ≤ <i>k</i> , −17 ≤ <i>l</i>
Reflection collected	30285	14967
Independent reflections	5789 [<i>R</i> _{int} = 0.0520]	5520 [<i>R</i> _{int} = 0.0563]
Refinement method	full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	5789/0/413	5520/0/476
Goodness-of-fit on <i>F</i> ²	0.871	0.979
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0421	0.0440
<i>R</i> indices (all data)	0.0654	0.0563
Largest difference peak and hole (e Å ⁻³)	0.706 and −0.627	0.793 and −0.539

water molecule and C60 and C61 methyl atoms (2), which were located from the difference Fourier maps. The same isotropic thermal parameters was used for all H atoms and refined. The drawings of the molecules were realized with the help of CAMERON [23]. All programs used in the structure refinement are incorporated in the WINGX package [24]. The crystallographic data and refinement parameters are shown in Table 5.

3.5. Hydrogen peroxide disproportionation studies

In a thermostated cell at 16 °C, was stirred a mixture of water (5 ml) with 1 in a DMSO (or 2 in DMA) solution (1 ml; 4 × 10⁻³ mol l⁻¹). An aqueous imidazole solution (1 ml; 0.1 mol l⁻¹) was introduced. With a vacuum pump, an average 80 mbar pressure above the solution was obtained and measured with a pressure gauge (M.K.S. LAF 230). Then, hydrogen peroxide (1 ml; H₂O₂ 30% w/w) was introduced and the evolved oxygen was measured.

4. Supplementary material

Crystallography data have been deposited with the Cambridge Crystallographic Data centre, CCDC Nos. 199102 and 199103, respectively. Copies of this information may be obtained free of charge from, The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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