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MM2 Force Field Parameterisation, Modelling and Structure Prediction of Salen-type Monomeric and Hydrogen-Bonded Dimeric Manganese Complexes.

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Abstract: An X-ray crystallographic study on the product of the coupling reaction of **2** and **3**, revealed suprisingly that the product was cis-dialdehyde **5**, rather than trans-dialdehyde **4**. Dialdehyde **5** was employed in the synthesis of a new bis-manganese water-splitting complex, originally formulated as the hydrated derivative of **1**. However, the structure of the manganese complex derived from **5** should be revised to the hydrated complex of **7**. A molecular mechanics force field was developed and employed to model both the originally proposed bis-manganese complex **1** and the revised structure **7**. Related manganese complexes were also modelled with reasonable accuracy compared to their X-ray crystal structures.

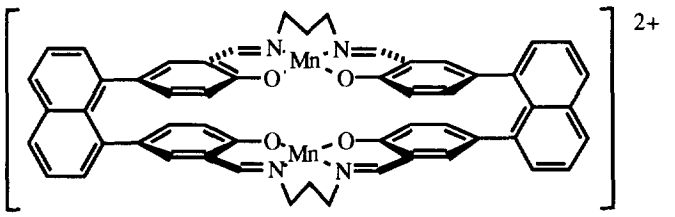
Introduction.

Manganese complexes, containing four manganese ions in a cluster, play a crucial role in the light-driven splitting of water in the photosynthetic system of green plants and cyanobacteria.[1] It has also been shown that synthetic bis-manganese complexes of Schiff base ligands, possessing an N_2O_2 donor set, are also capable of the photolytic splitting of water.[2] In contrast to the natural system which has Mn-Mn separations of *ca.* 2.7 and 3.3 Å, the synthetic bis-manganese complexes appear to self-assemble *via* di-aqua bridges to give a Mn-Mn separation of *ca.* 5 Å; whilst the synthetic complexes evolve dioxygen upon photolysis with visible light, unfortunately this is not a catalytic process.

To address this lack of catalytic activity in the synthetic bis-manganese complexes as water-splitting agents, we hypothesised that the the lack of catalytic activity might be due to a large degree in the greater Mn-Mn separation, compared to the natural complexes. In an attempt to design improved manganese-based water splitting complexes, we examined CPK (Corey-Pauling-Koltun) models of constrained manganese ligand sets, in which the manganese ions were likely to be held closer to each other than the *ca.* 5Å separation in the self-assembled synthetic systems. This resulted in proposing **1** as a likely candidate for synthesis, which was subsequently prepared and shown to exhibit water-splitting properties.[3]

However, the stereostructure reported for complex **1** (i.e. a *trans*-relationship between the imino-substituted atropisomeric 1,8-diarylnaphthalene system) could not be verified as correct due to: 1) the amorphous nature of **1**, preventing crystallisation of suitable single crystals for X-ray crystallographic analysis; and 2) the presence of paramagnetic manganese ions in the complex, preventing n.m.r. analysis.

The assignment of the *trans*-stereochemistry to **1** was based upon the notion that palladium(0) catalysed coupling of **2** to **3** would provide *trans*-diaryl **4**, rather than the *cis*-diaryl **5** (**Scheme 1**). Hence, conversion of **4** *via* the sequence previously reported[3] would lead to **1**.



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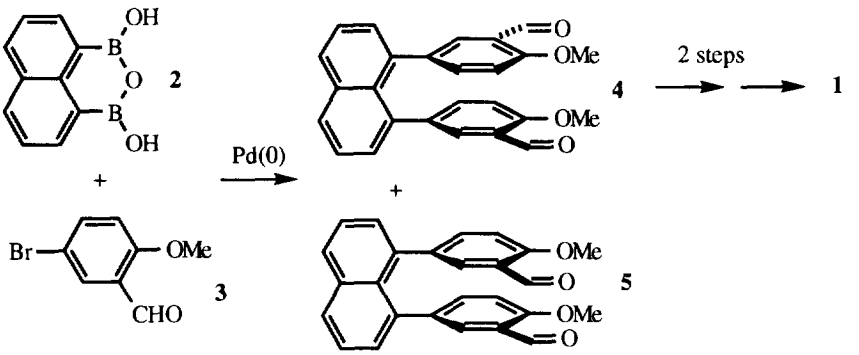
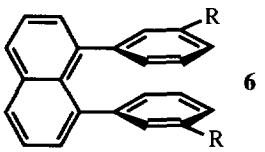
Scheme 1.



The likelihood that the major product from the coupling of **2** to **3** would be **4** has been reinforced[4] who have shown that 1,8-diarylnaphthalenes **6** prefer to exist in the *trans*-conformation shown, and that the barrier to 180 ° rotation to the *cis*-atropisomer is in the order of 16 kJmol^{-1}. Although this rotational barrier is surprisingly low,[5] one would expect the dipolar repulsion inherent in *cis*-diaryl **5**, to favour the formation of *trans*-diaryl **4**.



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However, following X-ray cystallographic determination of the structure of the product from the coupling reaction of **2** with **3**, we report herein a structure revision for the active water splitting complex previously reported to have structure **1**.[3] Also reported is a first generation molecular mechanics force field for modelling manganese complexes of tetradentate N_2O_2 Schiff-base ligands, and the use of this force field in predicting the structure of a photo-active water splitting complex.

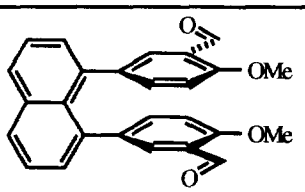
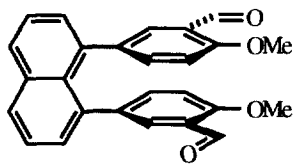
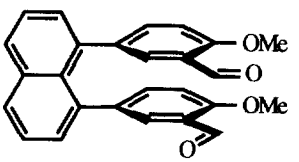
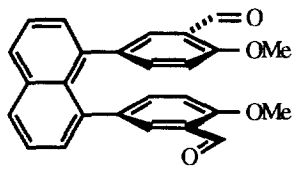
Discussion.

Structure of dialdehyde from the coupling of 2 and 3.

I. Molecular Mechanics Calculations.

In order to investigate whether the prefered conformation of the product from the reaction of **2** with **3** (**Scheme 1**) was likely to be **4** rather than **5**, molecular mechanics calculations were carried out on the dialdehyde **4** using MacroModel.[6] This was achieved using the SUMM varient[7] of the Metropolis Monte Carlo conformational search.[8] Only three true minima were found within 25 kJmol^{-1} of the lowest energy conformation (**Table 1**), which possessed the *trans*-stereochemistry as depicted by structure **4a**. The only *cis*-conformation found (i.e. **5**) was 8.57 kJmol^{-1} higher in energy than **4a**. The remaining *trans*-conformation (**4b** and **4c**) were merely Ar-CHO and Ar-OMe single bond rotational isomers of **4a**. Therefore, although the difference in energy between **4a** and **5** is not large, it is sufficient to suppose that **4** would be preferred product from the coupling of **2** and **3** under thermodynamic reaction conditions.

Table 1.

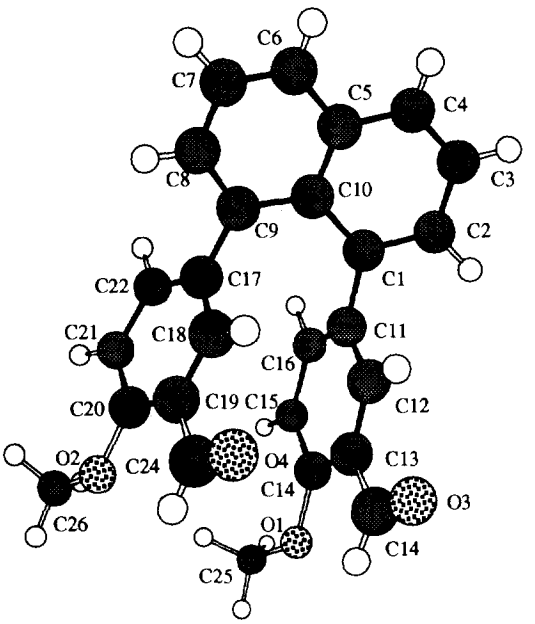
	Structure	Energy (kJmol^{-1})		Structure	Energy (kJmol^{-1})
4a		145.04	**4b**		152.92
5		153.61	**4c**		166.32

II. X-ray Crystallographic Structure Determination of **4** versus **5**.

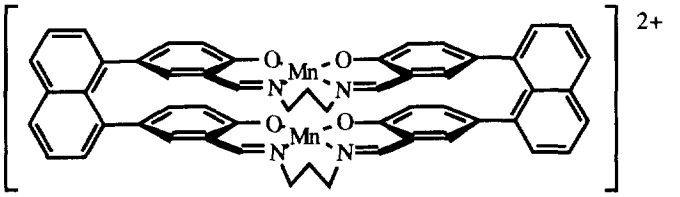
The palladium(0) catalysed coupling reaction of diboronate anhydride **2** with bromide **3** proceeds to give a single isolable dialdehyde containing product, in an unoptimised yield of 13 %.[3] This material crystallised from dichloromethane/hexane to give crystals suitable for X-ray analysis, which clearly showed (**Figure 1**) that the dialdehyde produced was the *cis*-1,8-diarylnaphthalene **5**. It is interesting to note that molecular mechanics calculations on this X-ray structure revealed it to have an energy of 168.50 kJmol^{-1}, i.e. 14.98 kJmol^{-1} higher in energy than the lowest energy *cis*-conformation of **5**. The high energy may be attributed to the alignment of the two aldehyde functions, thus causing maximal non-bonded repulsive interactions between rings. Presumably, the fact that crystallisation is preferred *via* this high energy conformer is due to the effects of crystal packing[9] on **5**.

A possible explanation for the surprising finding that the major product from the coupling reaction of **2** and **3** is the *cis*-product **5** may lie in the fact that the coupling reaction was carried out in an aqueous solution. This may allow the aldehyde functions to hydrate and cross-link *via* acetal bridges, thus directing the two aldehydes to couple in a *cis*-orientation to provide **5**. The fact that the rotation barrier of **5** to **4** would be at least 16 kJmol^{-1} (*vide supra*) would prevent interconversion of **5** to the thermodynamically stable isomer **4**. More importantly, it suggests that once the aldeyhde **5** is elaborated into a bis-manganese complex, the resulting product is more likely to possess structure **7** as its tetrahydrate, rather than **1**.

Figure 1.



As previously reported, complex **7** (as its diaqua-bridged derivative) does evolve dioxygen from water upon irradiation by visible light,[3] but this was not a catalytic process. Presumably, the deactivation of complex **7** as a water splitting complex may be due to the incorrect Mn-Mn separation. In the absence of an X-ray crystallographic structure for **7** (*vide supra*) a model was required that would provide an approximate estimation of the Mn-Mn separation in complex **7** and related systems.



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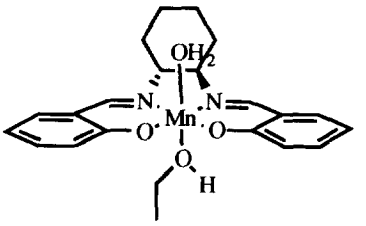
Force field parameterisation of manganese complexes.

Although the MM2 force field of Allinger *et al.*[10] was originally developed for organic molecules, more recently it has been shown that organometallic systems can also be parameterised with reasonable accuracy.[11] Indeed, this has also been successfully applied to di-μ-oxo-bridged bis-manganese complexes.[12] It was therefore reasonable to generate an initial MM2 force field for use with MacroModel for structures such as **1** and **7**, in order to estimate the Mn-Mn separations. Parameterisation of the bis-manganese complexes was therefore carried out using standard methods.[10,13]

I. Crystallographic Data (Average Bond Lengths and Angles).

Despite several X-ray crystallographic stuctures being reported[14] for salen-type manganese complexes such as **8-9**, bis-manganese complexes are much less frequent. However, such an X-ray crystal structure **10** has been obtained in these laboratories,[2b] which links *via* hydrogen bonds to form dimeric species **11** and is active as a water splitting complex and therefore provided a basic set of bond lengths and angles (See force field, **Table 2**, **Figure 2**).



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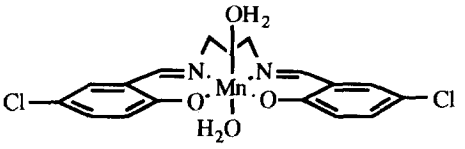

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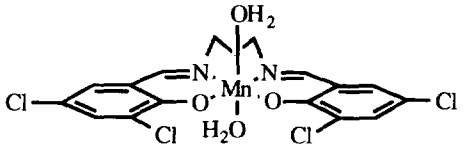

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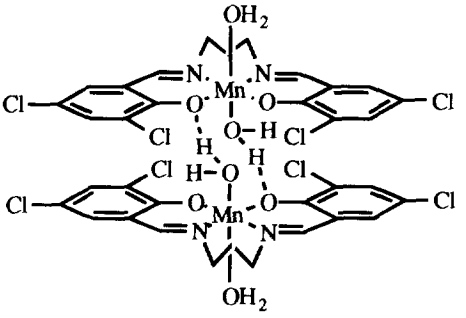

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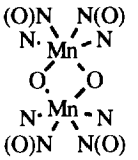
II. Vibrational Data (Force Constants).

Force and angle bending constants were added in accord with those used for similar bonds in μ-oxo bridged dimers of type **12**.[12]



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III. Van der Waals Parameters (Non-bonded Interactions).

The initial selection of the van der Waals parameters was based upon the values already used for carbon, nitrogen and oxygen in the MacroModel version of the MM2 force field. Values for manganese had to be added to the main force field and to the atom.typ file of MacroModel: 1.2700 (0.0500) Å (ε/kcalmol^{-1}).[15] Additional manganese atom descriptors were also added to the atom.typ file: molecular weight, 54.9380 g mol^{-1}; electronegativity, 1.5;[15] atom number, 27; atom type, 201.

IV. Torsional parameters.

In this first version of the manganese force field, torsional parameters have been added based upon the force field μ-oxo bridged dimers of type **12**.[12] Due to the rigidity of the poly-cyclic salen-type manganese structures typified by compounds **9** - **10** (*vide infra*), such preliminary torsional paramaters are unlikely to markedly affect the calculated structures. However, the potential energies calculated for particular structures may be affected to some degree. Refinement of these parameters, together with the substructure as a whole, will be the subject of further studies.

V. Force field.

The above parameters were combined to give a generalised substructure (**Figure 2**) force field, as shown in **Table 2**. This force field allows: 1) modelling of complexes with dimethylene, trimethylene and tetramethylene etc. bridges between the nitrogen ligands. This is a useful feature since complexes with trimethylene backbones have been shown to have the highest water splitting capacity; and 2) modelling of complexes with any common oxygen functionality in the axial coordination positions on manganese, e.g. OH_2, OR, O.COR and OSR_2 etc.

Modelling and structure prediction of manganese complexes.

The substructure force field was deliberately written to encompass both monomeric manganese complexes adhering to structures **8**-**10**,[2b,14] and bis-manganese complexes.[16] This allowed testing the accuracy of the force field on a range of different salen manganese complexes, which was achieved by Monte Carlo[8] and molecular dynamics[17] methods; the lowest energy conformations from each of the sets of calculations are summarised together with the crystal structures in **Table 3**.

It can be seen from **Table 3** that the force field provides an excellent starting point for generating reasonably accurate and meaningful structures for manganese complexes of salen-type Schiff-base ligands. The MM2 generated structures of **8** and **10** are essentially identical to their corresponding crystal structures.[14,16] The only difference lying in an altered torsion angle in the capping ethanol ligand of **8**. Some differences are observed between the MM2 generated structures of **9** and **11** and their respective X-ray derived structures.

Figure 2. (Substructure notation)

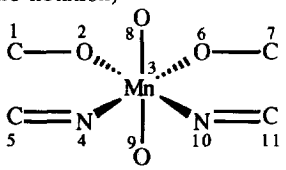
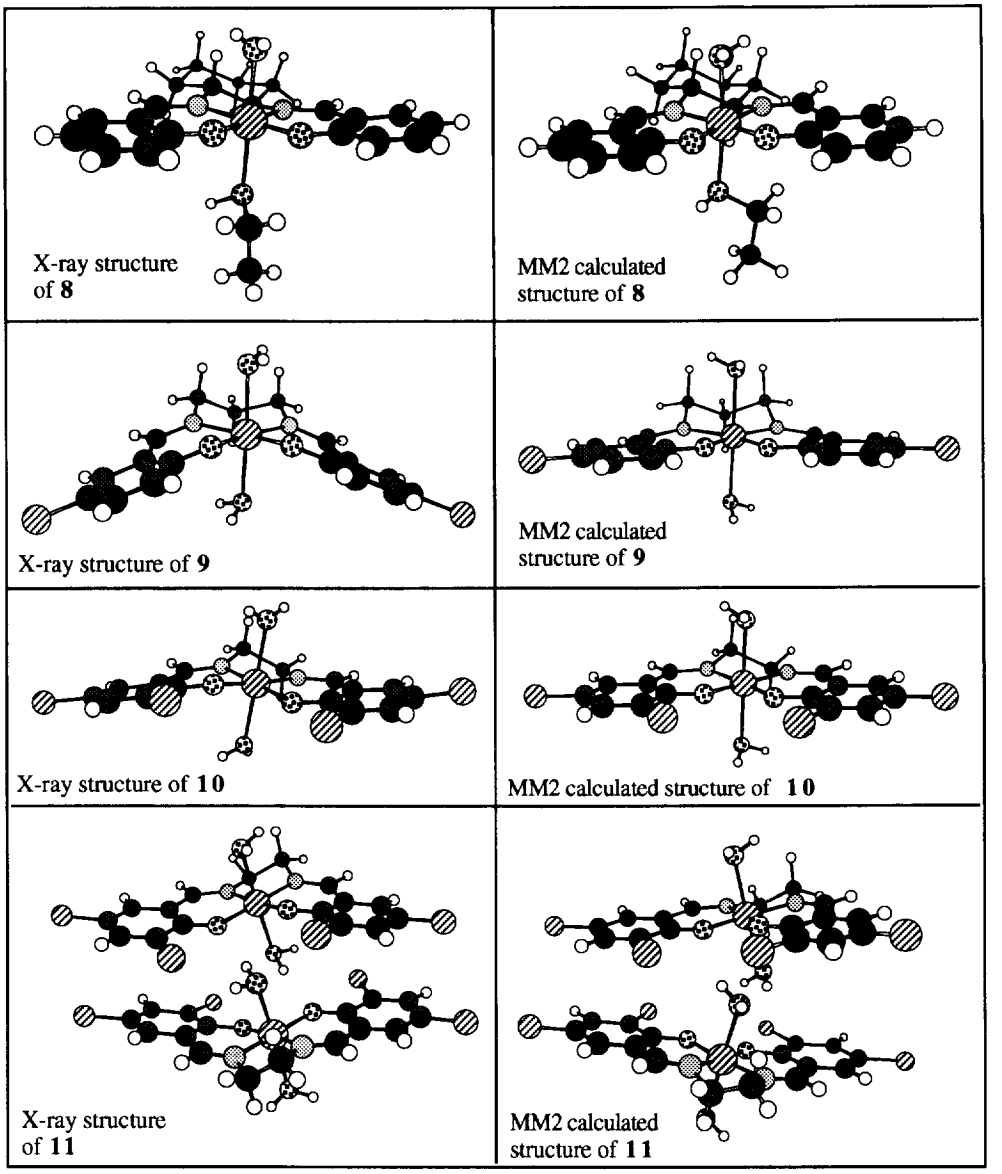


Table 2.

C Mn complex					
9 C2-O3-Mn(-N0=C2)(-O3-C2)(-O3)(-O3)-N0=C2					
-2					
1	1	2		1.3200	6.0000
1	2	3		1.8800	2.0000
1	3	4		1.9680	2.0000
1	4	5		1.2845	11.0900
1	3	6		1.8800	2.0000
1	6	7		1.3200	6.0000
1	3	9		2.2720	2.0000
1	3	8		2.2200	2.0000
1	3	10		1.9680	2.0000
1	10	11		1.2845	11.0900
1	4	C3		1.4830	0.5000
1	10	C3		1.4830	0.5000
1	8	C3		1.4780	0.5000
2	1	2	3	127.6000	0.1500
2	2	3	4	92.1000	0.1500
2	3	4	5	125.1000	0.1500
2	C3	10	3	113.9000	0.1500
2	C3	4	3	113.9000	0.1500
2	3	6	7	127.6000	0.1500
2	3	10	11	125.1000	0.1500
2	C3	4	5	120.9500	0.5500
2	C3	10	11	120.9500	0.5500
2	6	3	10	92.1000	0.1500
2	2	3	8	91.9500	0.1500
2	2	3	9	89.2000	0.1500
2	4	3	8	88.0000	0.1500
2	4	3	9	89.0000	0.1500
2	8	3	6	91.9500	0.1500
2	9	3	10	89.0000	0.1500
2	8	3	9	175.9000	0.5000
2	8	3	10	88.0000	0.1500
2	6	3	9	92.3000	0.1500
2	4	3	10	82.7000	0.1500
2	2	3	6	93.3000	0.1500
2	2	3	10	173.9500	0.1500
2	4	3	6	173.9500	0.1500
4	1	2	3 4	0.0000	2.5000 0.0000
4	2	3	4 5	0.0000	2.5000 0.0000
4	3	4	5 00	0.0000	0.0000 0.0000
4	2	3	4 C3	0.0000	0.0000 0.0000
4	3	4	C3 C3	0.0000	0.0000 0.0000
4	3	8	C3 C3	0.0000	0.0000 0.0000
4	1	2	3 6	0.0000	2.5000 0.0000
4	2	3	6 7	0.0000	2.5000 0.0000
4	3	6	7 00	0.0000	0.0000 0.0000
4	1	2	3 8	0.0000	0.0000 0.0000
4	2	3	8 00	0.0000	0.0000 0.0000
4	4	C3	C3 00	0.0000	0.0000 0.0000
4	8	C3	C3 00	0.0000	0.0000 0.0000
4	5	4	3 9	0.0000	0.0000 0.0000
4	5	4	3 8	0.0000	0.0000 0.0000
4	2	3	9 00	0.0000	0.0000 0.0000
4	4	3	8 00	0.0000	0.0000 0.0000
4	4	3	9 00	0.0000	0.0000 0.0000
4	5	4	3 10	0.0000	2.5000 0.0000
4	8	3	9 00	0.0000	0.0000 0.0000
4	C2	5	4 C3	0.0000	0.0000 0.0000
4	C3	4	3 10	0.0000	0.0000 0.0000
4	11	10	C3 H1	0.0000	0.0000 0.0000
4	11	10	C3 C3	0.0000	0.0000 0.0000
4	C3	4	5 H1	0.0000	0.0000 0.0000
4	C3	4	3 8	0.0000	0.0000 0.0000
4	3	10	C3 H1	0.0000	0.0000 0.0000
4	4	3	6 Lp	0.0000	0.0000 0.0000
4	2	3	6 Lp	0.0000	0.0000 0.0000
4	2	3	8 Lp	0.0000	0.0000 0.0000
4	8	3	9 Lp	0.0000	0.0000 0.0000
4	6	3	8 Lp	0.0000	0.0000 0.0000
4	6	3	9 Lp	0.0000	0.0000 0.0000
4	2	3	9 Lp	0.0000	0.0000 0.0000
4	8	3	6 Lp	0.0000	0.0000 0.0000
4	8	3	2 Lp	0.0000	0.0000 0.0000
4	9	3	6 Lp	0.0000	0.0000 0.0000
4	9	3	2 Lp	0.0000	0.0000 0.0000
4	3	4	5 C2	0.0000	2.5000 0.0000
4	3	2	1 C2	0.0000	2.5000 0.0000
4	C2	C2	11 10	0.0000	2.5000 0.0000
4	11	10	3 6	0.0000	2.5000 0.0000
4	7	6	3 10	0.0000	2.5000 0.0000
4	C2	C2	5 4	0.0000	2.5000 0.0000
4	3	10	11 C2	0.0000	2.5000 0.0000
4	3	6	7 C2	0.0000	2.5000 0.0000

The crystal structure of **9** shows significant deviation from planarity of the phenyl oxo and imino equitorial ligands. This effect is commonly observed, particularly in polymeric complexes[18] due to $\pi-\pi$ stacking effects and crystal packing[19] forces. The fact that such flexing is attributable to crystal packing forces is substantiated by the MM2 generated structures of the bis-manganese complexes **1** and **7** (*vide infra*). Both clearly show flexing from planarity in the Schiff base ligands, which in this case can be attributed to the constraining effects of the naphthalene framework connecting the ligands. This produces an effect which is very similar to the "winged" structure observed in the crystal structure of **9**.

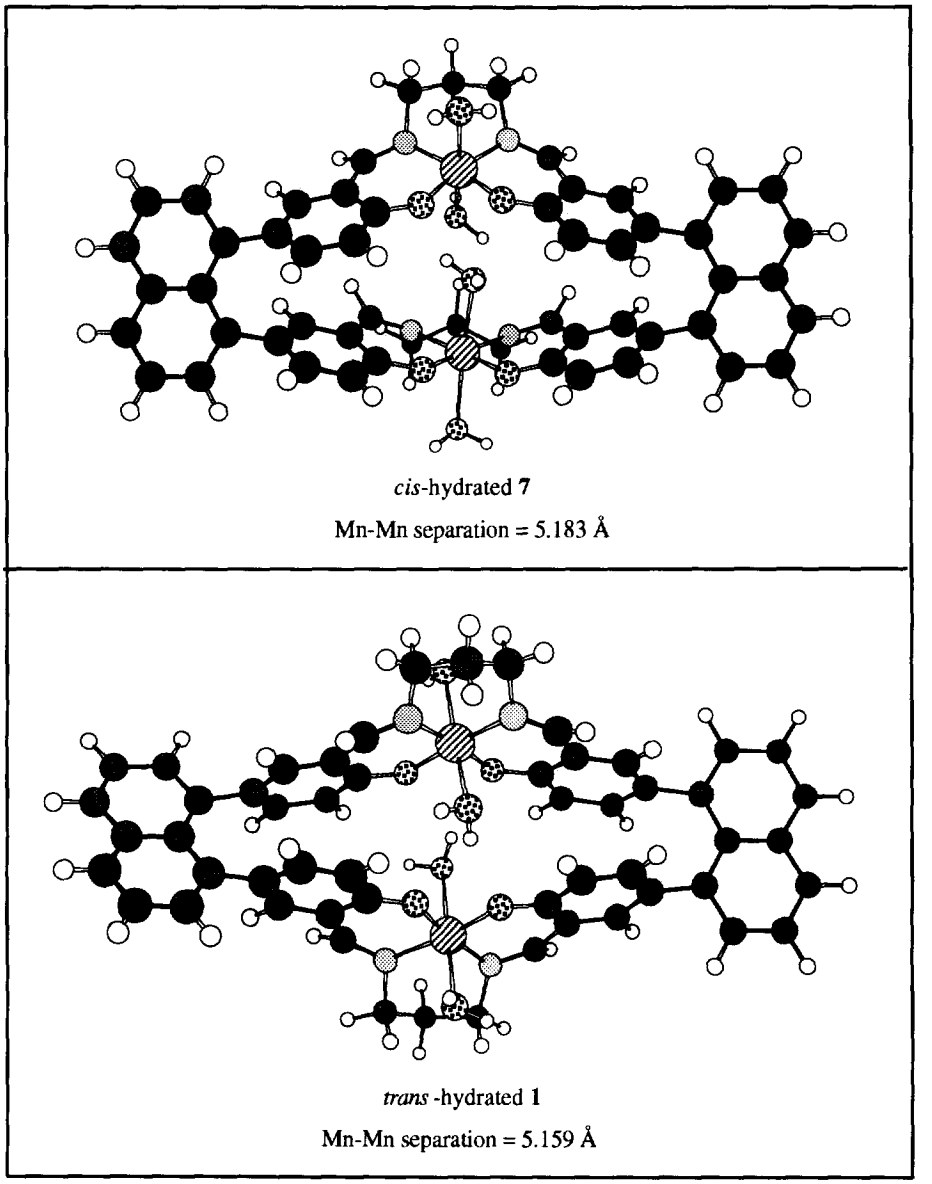
Table 3.



Structure **11** provides us with the most interesting case, since the lowest energy MM2 calculated structure shows tilting together of the Schiff base ligands in the dimer. This structure (**11**, **Table 3**) is the lowest energy structure found by Monte Carlo methods and molecular dynamics calculations, whether starting from the crystal structure or any other independantly generated structure. These diferences may again be attributable to the effects crystal packing, which may force a more orderly, parrallel arrangement of the aromatic ligands within the crystal array.

Once it was shown that the force field outlined above was suitable for modelling a range of known structures, attention was turned to examine the likely structures of synthetic complexes **7** and **1**. The resulting structures are shown in **Table 4**.

Table 4.



cis-hydrated **7**

Mn-Mn separation = 5.183 Å

trans -hydrated **1**

Mn-Mn separation = 5.159 Å

As noted previously (*vide supra*), the constraining nature of the complexes **1** and **7** leads to a flexing from planarity of the phenyl rings of the Schiff base ligands. The manganese separation observed in the calculated structures are comparable with that observed in the photo-active aqua linked dimer[2b] and it is

notable that in the absence of bridging water molecules, the manganese separations of 3.82 Å also compare very favourably with related μ-phenoxy bridged dimers that we have crystallographically characterised.[20]

Summary.

We have developed an MM2 force field for modelling and visualising the structure of salen-based manganese complexes. This force field gives a good structural approximation when compared to X-ray crystallographically derived structures and has been used to predict the structure of novel water-splitting complexes **1** and **7**. The fact that differences exist between some of the gas-phase calculated lowest energy conformations (particularly between **9** and **11**) and their crystal structures may have important implications for computer-aided design of new ligand sets in the future.

Further work on the refinement of the force field and further development of the water splitting complexes using molecular modelling to design such complexes is the subject of on-going investigations and will be reported in due course. It is worth noting that the MM2 force field reported herein should be of wide applicability to other synthetically important manganese mediated processes, such as their roles as catalysts[21] and in the modelling biosite systems.[22] Indeed, recent work on the asymmetric application of manganese[23] and other metal complexes[24] for epoxidation and related processes such as cycloproponation, aziridination and oxidation of sulfides[25] using salen-based ligands makes this force field particularly useful and modelling work particularly useful.

Experimental.

Molecular Mechanics Calculations.

All molecular mechanics calculations were carried out using either MacroModel version 3.5X or version 4.5, on Silicon Graphics Indigo or IndigoII workstations. Preliminary structures were minimised using the Batchmin subroutine, initially using SD followed by PRCG, then FMNR minimisation routines. SUMM varients of the Metropolis Monte Carlo conformational searches were carried out by allowing all single bond torsions to rotate, generating 2,000 random conformations for monomeric salen complexes and 1,000 random conformations for all other molecules, PRCG minimisation, and a 50 $kJmol^{-1}$ energy window for manganese complexes or a 25 $kJmol^{-1}$ energy window for all other structures. All structures produced were resubjected to FMNR minimisation and Mtest to check that each structure was a true minimum. Molecular dynamics calculations were carried out *via* two methods: 1) Using constant temperature runs at 300K, using a timestep of 1.0 fs. From this simulation, the average atomic coordinates were calculated over the whole 10 ps simulation; 2) By heating the molecule from 0 to 3,000K and cooling back to 0K using 1.0 fs timesteps. The difference between these two methods was negligable in all cases.

X-ray Crystallography.

Crystal Structure Determination for **5**.

Crystal Data. $C_{26}H_{20}O_4$; Fwt. 396.44; monoclinic; $P2_1/n$ (no. 14); a = 8.255(4) Å; b = 16.027(6) Å; c = 15.08(1) Å; β = 101.21(4) °; V = 1957(3) $Å^3$; Z = 4, D_{calc} 1.345 g cm^{-3}; crystal size 0.3 x 0.3 x 0.3 mm; F_{000} 832; μ(MoKα) 0.84 cm^{-1}.

Data Collection. All data were collected at ambient temperature using MoKα radiation (λ = 0.71069 Å) on a Rigaku AFC6S diffractometer using the ω/2ϑ scanning technique to a maximum 2ϑ value of 50 °. Scans of (1.00 + 0.30 tan ϑ)° were made at a speed of 4 ° min^{-1} (in ω). Of the 3337 relections which were collected, 3078 were unique (R_{int} = 0.059). An empirical absorption correction (DIFABS)[26] was applied resulting in transmission factors ranging from 0.80 to 1.19. The data were corrected for Lorentz and polarisation effects.

Structure Solution and Refinement. The structure was solved by direct methods (DIRDIF).[27] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealised positions (C-H = 0.95 Å) and were assigned isotropic thermal parameters 20 % higher than the equivalent Bvalue to the atom to which they were bonded. The final cycle of full matix least squares refinement was based on 1050 observed reflections (I > 3.00 (I)) and 271 variable parameters and converged with R = 0.051 and R_w = 0.046 ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = [(\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega F_o^2)]^{1/2}$). All claculations were performed using the TEXSAN[28] software package.

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