



Single-crystal-to-single-crystal Transformation of the Dichloromethane Solvate of the Schiff Base Manganese(III) Complex to a Solvent Free Material

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(Received: 10 August 1999; in final form: 1 December 1999)

Abstract. The chloride complex of Mn(III) with an optically active Schiff base derived from 3,5-*tert*-butyl-salicyl aldehyde and (*1R,3S*)-1,2,2-trimethylcyclopentane-1,3-diamine crystallizes as a 1 : 1 solvate (**I**) with CH₂Cl₂ and transforms at room temperature to a solvent-free compound (**II**) without destruction of the crystals. Two X-ray diffraction experiments carried out on the same crystal at 120 K revealed that the guest CH₂Cl₂ molecules are completely enclosed in the host matrix and that drastic conformational changes of the complex molecules occur during removal of solvent. A possible mechanism of the crystal transformation is discussed. The spectral evidence on association of the metal complex with dichloromethane in solution are demonstrated.

Key words: chiral Schiff base ligand, manganese(III) complex, X-ray structure, crystal transformation, dichloromethane.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. 82271 (49 pages).

1. Introduction

Interest in the synthesis of optically active, tetradentate Schiff bases comes from a catalytic activity in enantioselective epoxidation reactions exhibited by their metal complexes [1–4]. We have recently described the synthesis of a new Schiff base, derived from 3,5-di-*t*-butyl-salicyl aldehyde and (*1R,3S*)-1,2,2-trimethylcyclopentane-1,3-diamine (*t*^{Bu}SalcamH₂) and the spectral characterisation of its metal complexes [5]. When we tried to determine the structure of the chloride complex of Mn(III) with this ligand by single crystal X-ray analysis we unexpectedly discovered that the complex crystallized as an unstable

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dichloromethane-solvate which lost solvent so quickly that initially we had ignored the solvent presence. The solvated-crystals lacked transparency but retained both the external morphology and the single-crystalline nature throughout the solvent loss. As single-crystal to single-crystal processes without disruption of the lattice are rarely observed in molecular crystals we thought the investigation of our crystals could provide more information on the mechanism of such crystal-crystal transformations. In this paper we report on the crystal and molecular structures of (*t*^{Bu}Salcam)MnCl · CH₂Cl₂ (**I**) and (*t*^{Bu}Salcam)MnCl (**II**), determined from two X-ray diffraction studies carried out on the *same* crystal specimen.

2. Experimental

2.1. PREPARATION AND CRYSTALLIZATION

The synthesis of the (*t*^{Bu}Salcam)MnCl complex was performed as described previously [5]. Single crystals of the solvate compound (*t*^{Bu}Salcam)MnCl · CH₂Cl₂ (**I**) were obtained upon recrystallization from a mixture of CH₂Cl₂ and hexane at 275 K. Crystals were bright brown plates.

2.2. X-RAY CRYSTALLOGRAPHIC ANALYSIS

For the crystallographic experiment a crystal of **I** with dimensions 1.0 × 0.6 × 0.2 mm was immersed in oil and quickly cooled with nitrogen. Over more than one month of the diffractometer measurement at low temperature no significant deterioration of crystal (**I**) was detected. Subsequently the crystal was warmed up to room temperature allowing the solvent to escape and the second data collection was performed at low temperature. A loss of quality of the diffraction pattern was found. The solvent-free crystal (**II**) diffracted weakly and the reflection profiles were diffuse in contrast to those of **I**, which were sharp and well defined. Data were collected on a KUMA KM-4 diffractometer with graphite-monochromatized Mo-K_α radiation employing the ω-2θ scan method. Lattice parameters were determined from 81 reflections (14° < 2θ < 24°) for **I** and from 25 reflections (12° < 2θ < 18°) for **II**. The three standard reflections measured every 100 reflections showed negligible intensity decay. Details of the two diffraction experiments are presented in Table I, and the positional and thermal parameters are included in the supplementary material. The data sets were corrected for Lorentz and polarization effects and analytical absorption corrections were applied. The structures were solved by direct methods with SHELXS86 [6] and refined using SHELXL97 [7]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms and hydrogen atoms were calculated using a riding model with U(iso) equal to 1.2 U(eq) of the parent atoms. Scattering factors were taken from [8].

Refinement of **I** was complicated by apparent disorder of the three independent guest CH₂Cl₂ molecules. Only the disorder of one molecule could be resolved

Table I. Crystal data and experimental details

Compound	I	II
Formula	C ₃₈ H ₅₆ ClMnN ₂ O ₂ ·CH ₂ Cl ₂	C ₃₈ H ₅₆ ClMnN ₂ O ₂
Formula weight	748.16	663.24
Temperature (K)	120	120
Wavelength (Å)	0.71069	0.71069
Crystal system	Orthorhombic	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions		
<i>a</i> (Å)	10.516(9)	10.44(3)
<i>b</i> (Å)	48.81(3)	15.20(4)
<i>c</i> (Å)	23.92(2)	23.42(7)
<i>V</i> (Å ³)	12278(17)	3716(18)
<i>Z</i>	12	4
<i>D</i> _{calc} (Mg m ⁻³)	1.214	1.185
Absorption coefficient (mm ⁻¹)	0.552	0.460
<i>F</i> (000)	4776	1424
Reflections collected	13817	6218
Independent reflections	11212 [R _{int} = 0.0195]	5321 [R _{int} = 0.060]
Observed reflections [I > 2σ(I)]	7442	3081
Theta range for data collection (°)	2 to 24	2 to 25
Index ranges	-12 → <i>h</i> → 12 0 → <i>k</i> → 49 0 → <i>l</i> → 25	-12 → <i>h</i> → 12 -17 → <i>k</i> → 18 -27 → <i>l</i> → 27
Refinement method	Full-matrix least-squares on F ²	
Data/parameters	11212/1279.	5321/396
Goodnes-of-fit on F ²	1.086	1.071
Final R indices [I > 2σ(I)]	R = 0.0521, wR ² = 0.1424	R = 0.0679, wR ² = 0.1822
R indices (all data)	R = 0.0944, wR ² = 0.1686	R = 0.1186, wR ² = 0.2037
Flack parameter	-0.05(3)	-0.01(5)
Largest diff. peak and hole (e Å ⁻³)	1.26 and -0.50	0.58 and -0.40

into two alternative positions of one chlorine atom, Cl(3B) and Cl(4B), with occupancies of 0.66 and 0.34, respectively. Anisotropic refinement gave extremely elongated displacement ellipsoids for all guest chlorine atoms and one fairly high residual peak (1.26 e · Å⁻³) at a distance of 1.92 Å from the C(9C) atom which corresponds to a chlorine with a low occupancy. The disorder of the guest molecules seemed to be largely rotational, but a small amount of displacive disorder was also present. The latter may be related to the tendency of the solvated crystal to undergo transformation to a solvent-free crystal. Some anomalies, such as the

spread in values of chemically equivalent bond distances, a poor geometry of *t*-butyl groups and unrealistic displacement parameters of a few carbon atoms, found in the structure of the host molecules, may be attributed to the slight disorder of the flexible Schiff base ligands, an imperfect modelling of the guest disorder or to the poor quality of our data. Refinement of **II** showed the rotational disorder of *t*-butyl groups complicated by the fact that the metal complex molecules in the crystal had slightly different positions, orientation and probably conformation. Because many attempts to model this disorder remained unsatisfactory the refinement was by a single conformation with large anisotropic parameters. As a result, the geometrical parameters of this averaged structure are of a small precision; in particular the geometries of *t*-butyl groups and aromatic rings are meaningless.

2.3. SPECTRAL MEASUREMENTS

UV-Vis and CD spectra were obtained for 1.5×10^{-3} mol/dm³ manganese(III) complex solutions in a mixed solvent (toluene/dichloromethane) using Cary-5 and JASCO 600 J instruments, respectively. The ¹H NMR spectra were obtained as previously [5]. For that method the equilibrium constant for the association: $({}^t\text{BuSalcam})\text{MnCl} + n \text{CD}_2\text{Cl}_2 \rightleftharpoons ({}^t\text{BuSalcam})\text{MnCl} \cdot n \text{CD}_2\text{Cl}_2$ was determined by titration of a 0.021 mol/dm³ solution of the metal complex in toluene-*d*₈ with a 0.021 mol/dm³ solution of the metal complex in CH₂Cl₂, observing the respective chemical shift changes. The overlaid relevant fragments of solvent-dependent CD and ¹H NMR spectra of $({}^t\text{BuSalcam})\text{MnCl}$, the CD spectrum of $({}^t\text{BuSalcam})\text{MnCl}$ in toluene and dichloromethane, and the plot of $\log(n_1/n_2)$ vs $\log[\text{S}]$ (where n_1 and n_2 are the molar fractions of $({}^t\text{BuSalcam})\text{MnCl} \cdot (\text{CD}_2\text{Cl}_2)$ and $({}^t\text{BuSalcam})\text{MnCl}$, respectively, and [S] is the concentration of CD₂Cl₂ in toluene-*d*₈) are included in the supplementary material.

3. Result and Discussion

The structural formula of the $({}^t\text{BuSalcam})\text{MnCl}$ complex and the numbering scheme for the four complex molecules in the two compounds presented here are shown in Figure 1.

The asymmetric unit of **I** comprises three, very similar molecules of the penta-coordinated metal complex and three CH₂Cl₂ molecules. The crystallographically independent molecules of both the metal complex and solvent are related approximately by a pseudotranslation along the longest *b* axis. The deviations from a translational relationship are visualized in Figure 2a. An implication of the pseudotranslation along the *b* axis is the presence of the pseudo 2₁ axes parallel to *a* and parallel to *c*. The crystal packing (Figure 3a) can be described as composed of polar zigzag chains that extend along the *a* axis and are formed by the complex molecules related by the exact and pseudo 2₁ axes, each parallel to *a*. Adjacent molecules on the chain are associated through the C–H···Cl interactions which involve the chlor-

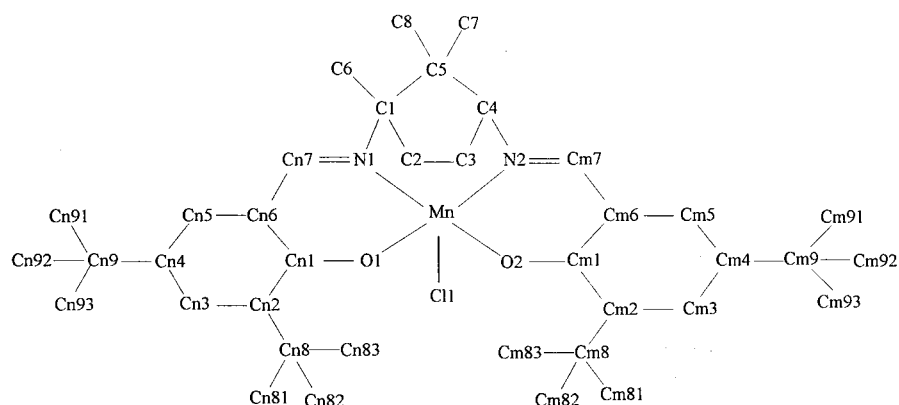


Figure 1. The numbering scheme adopted for the three independent complex molecules in **I** ($n = 1, m = 2$ for A, $n = 3, m = 4$ for B and $n = 5, m = 6$ for C) and for one complex molecule in **II** ($n = 1, m = 2$).

ide ligand (Table II). The chains of the same polarity (determined by the Mn–Cl bond vectors) form layers in the *ab* planes and each layer of one polarity is surrounded by two layers of the opposite polarity. Each CH₂Cl₂ molecule is connected with the chloride ligand of the complex by the C–H···Cl interaction (Table II) and sits in a cavity formed by three successive complex molecules within a chain. The cavity is enclosed with the *t*-butyl groups from adjacent chains so that the guest molecules are completely locked in their cavities. There are no intermolecular distances shorter than van der Waals radii apart from those mentioned above, which involve the chloride ligand and operate within the chains. This unusual packing may be rationalised, at least partially, when the three independent chains are compared to each other. Figure 2b presents a superposition of the three solvate moieties obtained by fitting the Mn positions of the three independent chains. From this picture it is obvious that the arrangements of the complex molecules within each of the chains are nearly the same and that the solvent molecules take essentially similar positions with respect to the chains. Thus, the different packing of the whole zigzag chains is responsible for the deviation from the translational relationship, discussed above. It may infer that the solvate moieties exist in solution and during crystallization these moieties arrange themselves around the CH₂Cl₂ molecules.

The removal of the CH₂Cl₂ molecules from the crystal gave structure **II** with the same space group type but with the *b* parameter reduced by a factor *ca.* 3 and with one complex molecule in the asymmetric unit. This implies that the chains along *a* become translationally equivalent; the pseudo 2₁ axis is replaced by the exact 2₁ axis and that both orientational and translational movements of the complex molecules have to occur during crystal transformation. Comparison of the molecular packing for **I** and **II** (Figure 3) indicates large-scale displacements of the atoms on transformation and a new arrangement of the complex molecules within chains. The largest atomic shifts of *ca.* 8 Å were detected for the atoms of *t*-butyl groups

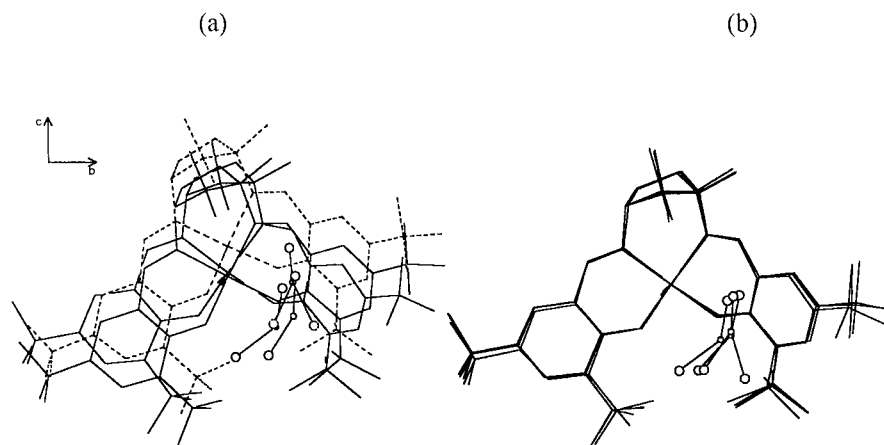


Figure 2. Superposition of the three symmetry independent complexes and solvent molecules in **I** viewed along the *a* axis (H atoms are omitted): by their translation along the *b* axis so that the MnA, MnB and MnC atoms have the same *y* coordinate (a), and by fitting the Mn positions of the three independent chains (b).

Table II. Geometry of C–H···Cl interactions in **I** and **II**

	Distances (Å)			Angles (°)
	C–H	H···Cl	C···Cl	C–H···Cl
I				
C(9A)–H(9A)···Cl(1A)	0.99	2.53	3.427(11)	151
C(9B)–H(91B)*···Cl(1B)	0.99	2.65	3.444(12)	136
C(9B)–H(91)**···Cl(1B)	0.99	2.53	3.446(12)	158
C(47)–H(47)···Cl(1A) ⁱ	0.95	2.77	3.246(8)	112
C(4B)–H(4B)···Cl(1A) ⁱ	1.00	2.84	3.543(9)	128
C(27)–H(27)···Cl(1B) ⁱ	0.95	2.82	3.358(8)	117
C(4A)–H(4A)···Cl(1B) ⁱ	1.00	2.74	3.506(8)	134
C(67)–H(67)···Cl(1C) ⁱⁱ	0.95	2.77	3.311(8)	117
C(4C)–H(4C)···Cl(1C) ⁱⁱ	1.00	2.76	3.525(8)	134
II				
C(2)–H(2)···Cl	0.99	2.69	3.473(15)	136
C(27)–H(27)···Cl ⁱ	0.95	3.03	3.442(10)	108
C(8)–H(82)···Cl ⁱ	0.98	2.88	3.710(12)	144

* Occupancy 0.66(2), ** occupancy 0.34(2), symmetry codes: ⁱ $-1/2 + x, 1/2 - y, 1 - z$; ⁱⁱ $-1/2 + x, 3/2 - y, 1 - z$.

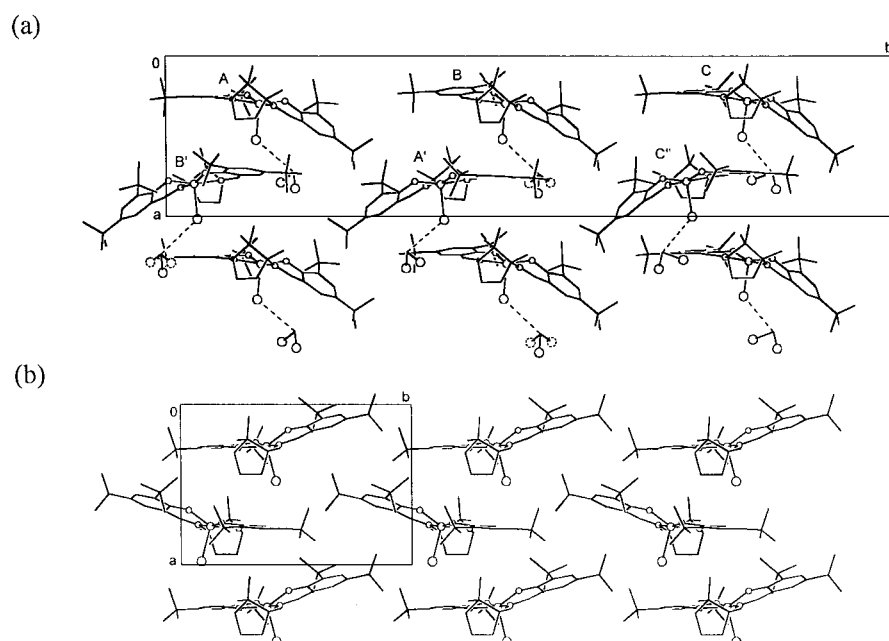


Figure 3. Projection of the crystal structures of **I** and **II** along the *c* axis: $(tBuSalcam)MnCl \cdot CH_2Cl_2$ (a) and the solvent free complex (b), showing the section around $z = 1/2$. H atoms are omitted. The letters A, B and C mark three symmetry independent complex molecules. The molecules within pairs: A–B' and B–A', are related by pseudo 2_1 axes along *a* and those within a pair C–C'' are related by an exact 2_1 axis. Symmetry codes; ' $1/2 + x, 1/2 - y, 1 - z$, '' $1/2 + x, 3/2 - y, 1 - z$.

at C(n9). These shifts are associated with a drastic conformational change of the Schiff base ligand as well as with a rotation of the whole complex molecules around the direction of the *c* axis by a mean of 20° . The effect of all structural changes is a shortening of separations between the Mn atoms: by *ca.* 0.5 \AA within each chain along *a* and by *ca.* 1 \AA between the adjacent chains in the *ab* plane which result in an anisotropic reduction of the lattice parameters, going from **I** to **II** (see Table I). There are no distinct channels or sizeable voids in the crystal structure of **II**. Apart from the C–H \cdots Cl contacts within chains (Table II) some short intermolecular C \cdots C distances in the range of $3.28\text{--}3.44 \text{ \AA}$ were found between the aromatic rings C(11)–C(16) and C(21)–C(26) and the methyl groups C(8) and C(193) from the adjacent chains in the *ab* plane. These presumably attractive interactions seem to be responsible for the lattice reduction as well as for a new crystal order on transformation.

A difference in a conformation of the Schiff base ligand and a different distortion of the manganese coordination polyhedron are the most pronounced geometrical differences between the three complex molecules in **I** and that in **II** (Figure 4). The coordination geometry around the Mn ion in the three molecules

of **I** is tetragonal pyramidal and both roughly planar salicylideneiminato 'wings' are bent along the O...N line, the dihedral angle between their mean planes being in the range 37–42°, but the bending along O(1)...N(1) is considerably larger than that along O(2)...N(2). In **II**, the basal N₂O₂ set shows a rather large distortion towards tetrahedral (the dihedral angle between the MnO(1)N(1) and MnO(2)N(2) planes is about 32°) and two salicylideneiminato 'wings' are twisted one to other by an angle of *ca.* 19°, consistent with the tetrahedral twist of the basal coordination plane. Generally, both the O...N bendings in **II** are smaller than those in **I**, thus relevant chelate rings are more planar in the former. The situation of the bridging cyclopentane ring with respect to the coordination polyhedron, is only slightly different in both compounds. It is important to note that in each case the C(8) methyl group blocks the sixth coordination site around manganese, *trans* to the Cl ion, which seemed to be responsible for an unexpectedly low catalytic activity in epoxidation found for this complex [5]. The Mn–O and Mn–N distances as well as the distances of the Cl atoms from the mean N₂O₂ plane (2.62–2.75 Å) are as observed in other similar Mn(III) complexes [9–13]. Steric effects of the presence of the C(6) methyl group seem to be responsible for a small elongation of the Mn–N(1) and N(1)–C(1) bond lengths in comparison to the Mn–N(2) and N(2)–C(4) bond lengths and the different bending of the two salicylideneiminato 'wings' in the three molecules of **I** causes some differences between the two halves of the Schiff base ligand, namely, these in the angles around the O and N atoms (Table III).

It is obvious that a conformational flexibility of the Schiff base is responsible for the observed transformation of the crystal. The conformation of the ligand in **I** seems to be more strained than that in **II** and the large bending of one of the salicylideneiminato 'wings' may be considered as being exerted by packing forces. Hence, the complex molecules at a surface of the crystal should exhibit a lesser bending than that found and/or their conformations should be easily deformable by motions of the CH₂Cl₂ molecules that might initiate an escape of solvent. The conformational changes of the complex molecules at the crystal surface would proceed far inside along the *a* direction, following solvent removal, but they should occur in the opposite directions for adjacent *ab* layers. However, no feasible pathway of the solvent escape can be given. Instead, from both structures presented it is obvious that unpacking of the starting crystal **I** and repacking into the daughter crystal **II** must take place.

In order to examine any specific interaction of the (^{*t*}BuSalcam)MnCl complex with dichloromethane in solution we have studied mixed-solvent solutions by UV-Vis, CD, and ¹H NMR spectral methods. The examination of the electronic spectra showed that; (i) the CT absorption band (Mn^{III} → N(azomethine)) centred at 418.4 nm (in toluene) shifted slightly to 414.0 nm (in CH₂Cl₂), (ii) the negative CD band shifted from 440.3 nm (in toluene) to 433.3 nm (in CH₂Cl₂), whereas the intraligand bands remain unshifted upon solvent change, (iii) an isosbestic point at about 510 nm was present for CD spectra in mixed toluene-CH₂Cl₂ solvents.

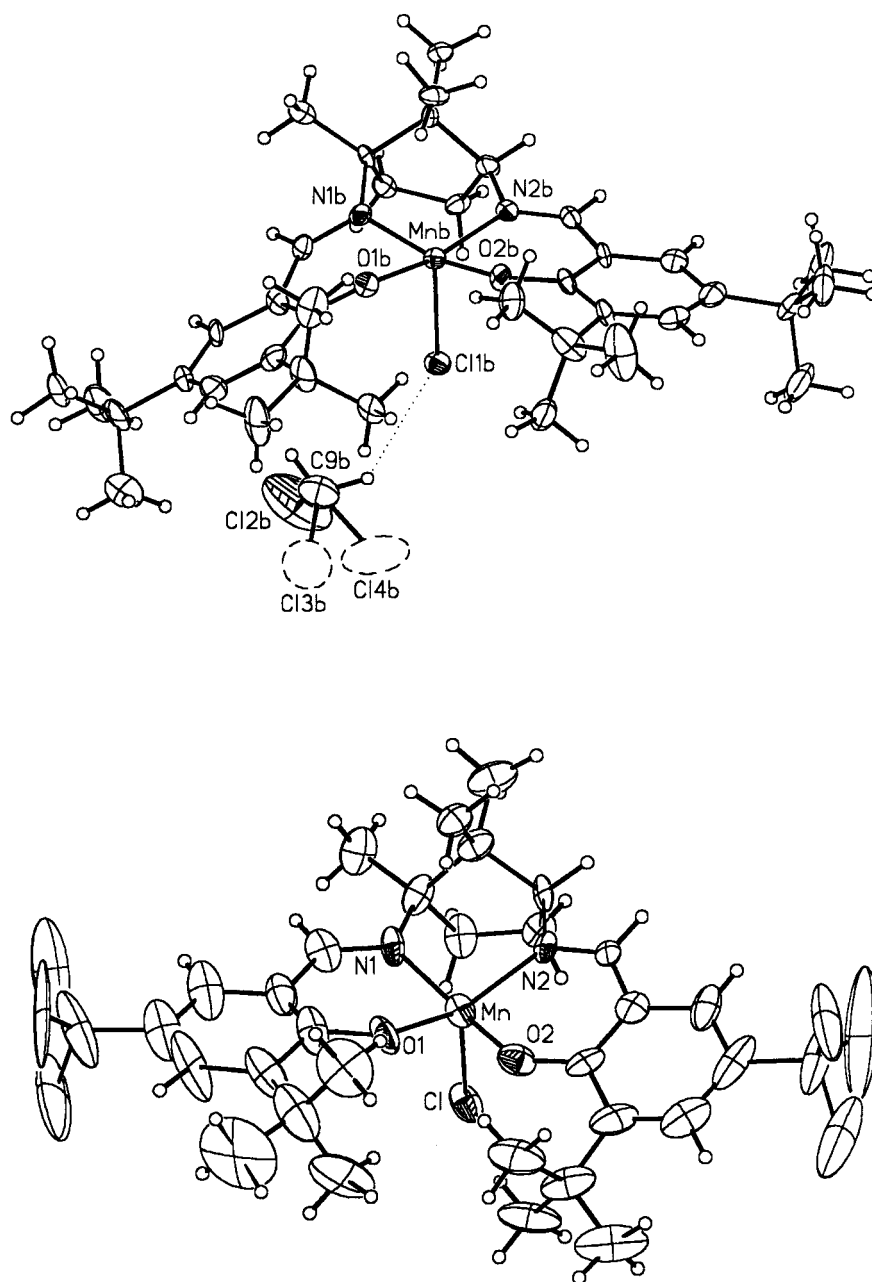


Figure 4. The displacement ellipsoids (50% probability) at 120 K for one of the three independent solvate units in **I** (top) and for the solvent-free metal complex in **II** (bottom).

Table III. Selected bond lengths (Å) and angles (°) for I and II

	Compound I			Compound II
	Molecule A	Molecule B	Molecule C	
	n = 1 m = 2	n = 3 m = 4	n = 5 m = 6	n = 1 m = 2
Mn–O(2)	1.887(6)	1.907(6)	1.898(6)	1.882(8)
Mn–O(1)	1.907(5)	1.891(5)	1.898(5)	1.895(7)
Mn–N(2)	2.002(7)	2.001(7)	1.987(7)	2.015(8)
Mn–N(1)	2.046(6)	2.056(7)	2.069(6)	2.062(9)
Mn–Cl(1)	2.376(3)	2.379(3)	2.380(3)	2.377(7)
N(1)–C(n7)	1.304(10)	1.299(10)	1.274(10)	1.309(10)
N(1)–C(1)	1.515(10)	1.514(10)	1.509(10)	1.480(12)
N(2)–C(m7)	1.304(10)	1.272(10)	1.284(10)	1.301(9)
N(2)–C(4)	1.440(10)	1.472(10)	1.473(11)	1.455(11)
O(1)–C(n1)	1.331(9)	1.347(9)	1.310(9)	1.357(12)
O(2)–C(m1)	1.314(9)	1.305(9)	1.312(10)	1.301(10)
O(2)–Mn–O(1)	88.3(3)	88.5(3)	89.7(3)	83.7(4)
O(2)–Mn–N(2)	89.2(3)	88.9(3)	88.9(3)	89.1(3)
O(1)–Mn–N(2)	165.8(3)	166.8(3)	166.0(3)	148.8(3)
O(2)–Mn–N(1)	165.5(3)	164.8(3)	166.8(3)	169.9(3)
O(1)–Mn–N(1)	88.3(3)	88.2(3)	87.4(3)	90.3(4)
N(2)–Mn–N(1)	90.6(3)	91.0(3)	90.8(3)	91.9(3)
O(2)–Mn–Cl(1)	98.8(2)	99.4(2)	97.8(2)	94.5(2)
O(1)–Mn–Cl(1)	97.4(2)	96.4(2)	97.9(2)	107.0(3)
N(2)–Mn–Cl(1)	96.8(2)	96.9(2)	96.1(2)	103.8(2)
N(1)–Mn–Cl(1)	95.7(2)	95.7(2)	95.4(2)	95.0(2)
C(n7)–N(1)–C(1)	114.3(6)	114.1(7)	117.1(7)	116.0(8)
C(n7)–N(1)–Mn	115.5(6)	116.9(6)	115.0(6)	120.9(7)
C(1)–N(1)–Mn	129.2(6)	128.4(5)	127.0(5)	123.1(5)
C(m7)–N(2)–C(4)	116.8(7)	116.0(7)	115.8(7)	114.0(6)
C(m7)–N(2)–Mn	123.0(6)	124.2(6)	124.1(6)	124.0(6)
C(4)–N(2)–Mn	120.2(5)	119.7(5)	120.1(5)	121.9(5)
C(n1)–O(1)–Mn	123.7(5)	124.0(5)	125.0(5)	130.5(8)
C(m1)–O(2)–Mn	130.7(5)	130.8(5)	129.4(5)	133.9(6)

These results can be attributed to an association of the complex with dichloromethane in solution. The hypsochromic shift of the CT band (both in absorption and CD spectra) upon change of solvent from toluene to CH_2Cl_2 suggests that some changes in the coordination sphere of the central metal ion take place. Further evidence for this association have come from ^1H NMR spectra of the ($^t\text{BuSalcam}$)MnCl complex in mixed deuterated solvents; toluene- d_8 /CD $_2$ Cl $_2$. The resonance of one of the salicylic aromatic resonances shifts about 11 ppm upfield, whereas the corresponding resonance of the second salicylic substituent shifts only 3 ppm upfield on going from toluene- d_8 into CD $_2$ Cl $_2$. Corresponding changes in the position of the broad azomethine proton resonances (bandwidth 5300 Hz) are very large; in toluene- d_8 both resonances overlap at -200 ppm, whereas in CD $_2$ Cl $_2$ the resonances shift upfield to -210 and -250 ppm. The observed solvent-induced shifts of the proton resonances must be due to a specific interaction of the metal complex with solvent molecules. Moreover, the different shifts of the two salicylic rings and azomethine protons suggest a significant conformational change of the ligand within the complex, presumably similar to those found in the solid state. Finally, using the ^1H NMR spectra in mixed solvents the formation constant of ($^t\text{BuSalcam}$)MnCl· n CD $_2$ Cl $_2$ was estimated to be equal to 0.32 ± 0.01 (with $n = 1$). For comparison, a similar procedure was applied to the Jacobsen's catalyst [3]; ($^t\text{BuSalchl}$)MnCl (where $^t\text{BuSalchlH}_2$ ligand is derived from 3,5-di-*t*-butyl salicyl aldehyde and cyclohexane-1,2-diamine). Also in this case a hypsochromic shift in UV-Vis and CD spectra was observed upon change of solvent from toluene to CH_2Cl_2 . However, all four aromatic proton resonances shifted about 5 ppm upfield in the ^1H NMR spectrum of ($^t\text{BuSalchl}$)MnCl in CD $_2$ Cl $_2$ compared with that in toluene- d_8 (the azomethine proton resonances in CD $_2$ Cl $_2$ solvent were not detected). The spectral observations in the case of Jacobsen's catalyst can also be interpreted in terms of the formation of solvated species in dichloromethane solution, which eventually seems to be a general property of salenMnCl-type complexes.

Acknowledgements

The authors thank the Polish Committee for Scientific Research for financial support (KBN Grant No 3-T09A-028-12) and Professor Z. Galdecki (Technical University of Łódź, Poland) for allowing the use of the Siemens SHELXTL/PC program in his laboratory.

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