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The First Structurally Characterized Salen–Indium Complexes

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In this manuscript are reported the synthesis and characterization of the first complexes of indium incorporating the acen and salen classes of ligands. This includes the compounds of formula LInMe (where L = acen (**1**) (*N*,*N*′-ethylenebis-(2-hydroxy-α-methylbenzylidenimine)), salen (**2**) (*N*,*N*′-ethylenebis(2-hydroxybenzylideneimine)), salophen (**3**) (*N*,*N*′-(1,2-phenylene)bis(2-hydroxybenzylidenimine)), salomphen (**4**) (*N*,*N*′-(4,5-dimethyl-1,2-phenylene)bis(2-hydroxybenzylidenimine)). Attempts to prepare the derivatives, [In(R)(salpen)] (salpen = *N*,*N*′-propylenebis(2-hydroxybenzylidenimine), R = Me, Et) led to the formation of the bimetallic complexes, [(InMe$_2$)$_2$(salpen)] (**5**) and [In(Et$_2$)$_2$(salpen)] (**6**). Dissolution of **5** and **6** in MeOH causes the formation of three unusual products. They are the ligand bridged compounds [{In(μ-OMe)(μ-salpen)}$_2$] (**7**), [{In(salpen)}$_2$(μ-salpen)] (**8**) and the methoxy-only bridged complex, [{In(salpen)(μ-OMe)}$_2$] (**9**). Compounds **7**—**9** are the first structurally characterized indium–salen complexes. For purposes of comparison, the structure of [{Al(salen)(μ-OMe)}$_2$] (**10**) will also be described.

Since their first preparation[1] in 1931 the salen class of ligands[2] have been of great historical utility.[3] They possess two imine and two oxide binding sites that are arranged in a planar array (Fig. 1). The relative size of the potentially tetradentate binding site can be manipulated by changing the type of alkyl or aryl that is used in the backbone. Additionally, the ligands are relatively easy to synthesize, deriving from the condensation of a diamine with salicylaldehyde. For these reasons, the chemistry of the salen ligands has been developed extensively for the transition metals, and continues to be a ligand of great interest. The chemistry of the structurally related acen ligands mirrors that of salen, and they are generally more soluble. Overall, the chemistry of the main group elements with these ligands has not been developed to an appreciable extent, although several compounds incorporating aluminum[4] and gallium[5] alkyls, aluminum alkoxides[6] and cations[7] have been reported.

In this manuscript the first complexes of indium incorporating the acen and salen classes of ligands is reported. This includes the compounds of formula [In(Me)(L)] (where L = acen (**1**) (*N*,*N*′-ethylenebis(2-hydroxy-α-methylbenzylidenime)), salen (**2**) (*N*,*N*′-ethylenebis(2-hydroxybenzylidenimine)), salophen (**3**) (*N*,*N*′-(1,2-phenylene)bis(2-hydroxybenzylidenimine)), salomphen (**4**) (*N*,*N*′-(4,5-dimethyl)(1, 2- phenylene)bis(2- hydroxybenzylidenimine)) and the bimetallic derivatives, [(InMe$_2$)$_2$(salpen)] (**5**) and [(InEt$_2$)$_2$(salpen)] (**6**) (salpen = *N*,*N*′- propylenebis(2- hydroxybenzylidenimine)). The dissolution of **5** and **6** in MeOH led to the formation of three unusual products. They are the ligand bridged compounds [{In(μ-OMe)(μ-salpen)$_2$] (**7**) and [{In(salpen)}$_2$(μ-salpen)] (**8**) and the methoxy-only bridged complex, [{In(salpen)(μ-OMe)}$_2$] (**9**).

Results and Discussion

Synthesis of the [In(Me)(salen)] Derivatives. The first structurally characterized group 13 complex incorporating a salen ligand was [Al(Et)(salen)].[4] It was prepared by the relatively straightforward reaction of AlEt$_3$ with salenH$_2$. This is also the method that was used to prepare the indium derivatives, **1**—**4**, which can be obtained in high yields (Scheme 1). The exception to this apparently simple preparation is the ligand salpenH$_2$ for which a 1 : 1 derivative ([In(R)(salpen)]) was not isolated (see following section). The acen derivative, **1**, had an InMe ^{1}H NMR resonance at $\delta = -0.34$. This resonance for **2**—**4** fell in the narrow range of $\delta = -0.19$ to -0.16. This slight difference may be attributed to the relatively electron releasing nature of the "extra" methyls on the acen ligand. The assumed 1 : 1 stoichiometry and closed structure of **1**—**4**, follows the precedent for group 13 salen complexes, in general.

Reactions Involving salpenH$_2$. When either Me$_3$In or Et$_3$In are combined with salpenH$_2$ a mixture of products result. There were no peaks in the ^{1}H NMR spectra of these reactions that matched those of the monometallic derivatives (**1**—**4**). Moreover, the integration corresponded to a complex having four times the expected number of Me or Et resonances. The NMR data for **5** and **6** prepared using two equivalents of the respective indium reagent with salpenH$_2$ matched the spectra for the products of the 1 : 1 reactions. This served to confirm that the products of the 1 : 1 reactions were the bimetallic derivatives, **5** and **6**. Using the spectrum of **6** as an example, it consisted, in part, of two peaks for the InEt groups and two for the propyl backbone. Thus, there was no evidence for the type of rigid solution state geometry observed for the 2 : 1[8] and 3 : 1 aluminum[9] and gallium[10]

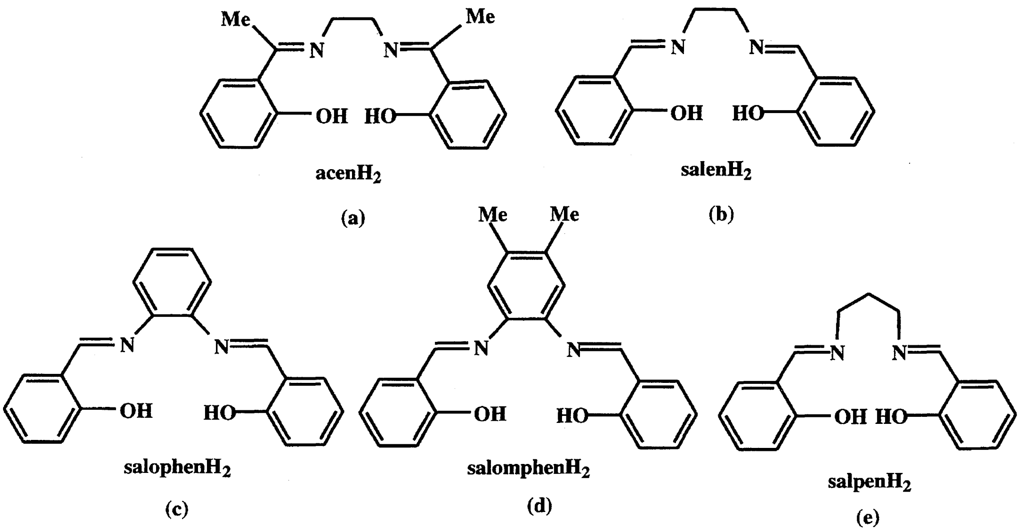
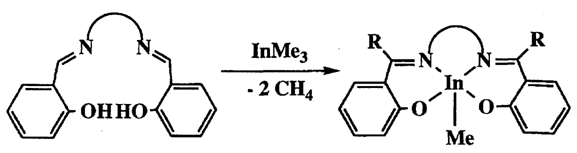


Fig. 1. The acen and salen ligands that are used in this study.



R	Ligand
Me	acen (1)
H	salen (2)
H	salophen (3)
H	salomphen (4)

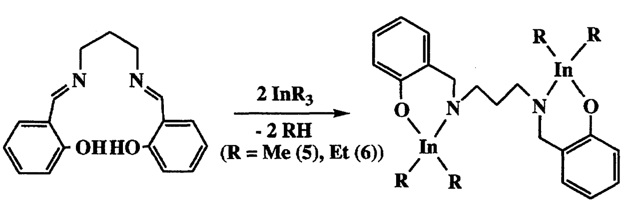
Scheme 1. Synthesis of the monometallic complexes having a “closed” structure.

complexes of the related salan ligands.

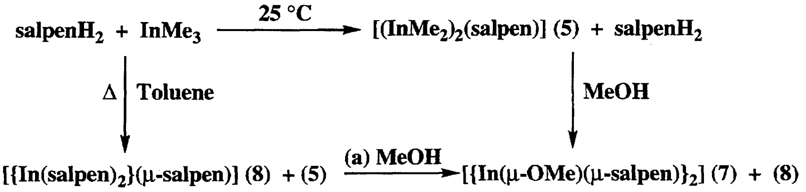
At this point it became apparent that the propyl backbone of the ligand favored open structures when combined with indium but not with aluminum.[4,7c)] This can be understood if the ionic radii of aluminum, gallium and indium are compared. For a five-coordinate atom they have values of 0.62, 0.69, and 0.85 Å, respectively. Thus, the great difference for indium implies that it will require a larger chelate to accommodate it in a square pyramidal or trigonal bipyramidal geometry. This would cause the propyl backbone to adopt a more linear conformation which could then induce either unfavorable eclipsing of the methylene hydrogens or an undesirably obtuse C–C–C bond angle. In order to avoid this situation the products that result take an open, bimetallic structure (Scheme 2). This is the first instance where the chemistry of indium has deviated from that of aluminum and gallium with regards to the salen ligands.

Bimetallic salen comples are actually very rare. The chelate effect is a strong inducement for the ligands to form monomeric complexes with whatever metal it is mixed with. To the best of our knowledge there are only two known bimetallic complexes that are structurally characterized. The first of these, salen$(GaMe_2)_2$, was reported by Storr in 1977.[5)] It was formed under forcing conditions using an excess of $GaMe_3$ and heating in a sealed tube. The second is the complex, acen$(BPh_2)_2$ which was the unusual product of the co-decomposition of BPh_4- and (acen) Al^+ in refluxing MeOH.[11)] Each of these complexes were demonstrated to adopt a *trans* conformation as is depicted for **5** and **6** in Scheme 2.

Reactions in Methanol. Compounds **7** and **8** were serendipitously discovered. They were initially isolated after the product of mixing Me_3In with salpenH_2 was extracted in MeOH (Scheme 3). On standing in air for several weeks two distinct crystalline compounds formed (**7** and **8**). The methoxy compound (**7**) can be formed separately by dissolving (salpen)$(InMe_2)_2$, prepared in situ, into methanol. The expected product was a methoxy-bridged species, following the precedent observed for [Al(R)(salen)] complexes reported previously, and for **10**.[7c)] However, it was surprising to observe a complex possessing both bridging methoxy groups and bridging ligand. This was the first of this type of structure to be observed for the group 13 elements. Compound **8** results when a 1 : 1 mixture of $InMe_3$ and ligand are



Scheme 2. Use of salpenH_2 leads to “open” bimetallic complexes.



Scheme 3. The reaction pathways involving $InMe_3$.

refluxed in toluene. It apparently results from the decomposition of one of the molecules as tentatively outlined in Scheme 3. It reflects the tendency for indium to adopt a six-coordinate geometry.

When **6** is extracted in MeOH, and left to stand in air for a few days, the expected product, **7**, crystallizes. However, the methoxy-only bridged species, **9**, is also isolated as crystals (Scheme 4). Thus, it would appear that there is not a significant difference, energetically, between compounds **7** and **9**. By comparison, when salenAlMe complexes are dissolved in MeOH only the methoxy-bridged analog to **9** (compound **10**) is obtained. Refluxing of a 1 : 1 mixture of $InEt_3$ and ligand for 57 h does not lead to **8**. Rather, unreacted starting materials is isolated from the reaction. This would imply that the ethyl group on indium is less prone to redistribution than methyl. The formation of **7**—**9** is probably due to the increased lability of the ligands on indium when compared to gallium and aluminum.

Structural Characterization of the Methoxy Derivatives. The molecular structures and atom numbering schemes for **7** and **9** and **10** are shown in Figs. 2, 3, and 4. Compounds **7** and **9** are two of the first structurally characterized salen-Indium complexes. Compound **7** also represents only the third[5,11)] instance where a salen-Group 13 complex has been demonstrated to adopt an "open" structure. Generally, each ligand binds a central metal through both sets of nitrogen and oxygens; the ancillary ligands provide the bridging moiety. This is the case, for example, in [{Al(acen)(μ-OMe)}$_2$][7c)] and compounds **9** and **10** (Tables 1, 2, and 3).

In **9** and **10** the bridging MeO groups adopt a *cis* orientation to one another and are directed to minimize contact with the ligand backbone. These two structures are nearly isomorphous to one another. They each feature the central metals in a distorted O_h geometry. The M–O–M′ angles are 104.1(2)° and 103.6(6)°, respectively. The primary difference between the two structures are the M–OMe bond distances which are naturally longer for **9** (2.152(6) Å) than for **10** (1.885(10) Å).

In compound **7** the methoxy groups are in the plane de-

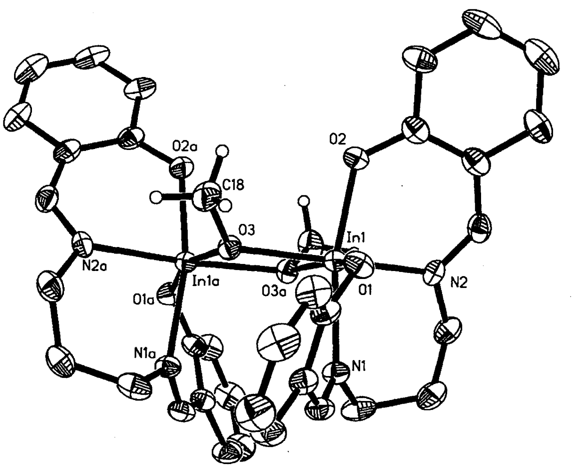


Fig. 2. Molecular structure and atom numbering scheme for [{In(salpen)(μ-OMe)}$_2$] (**9**).

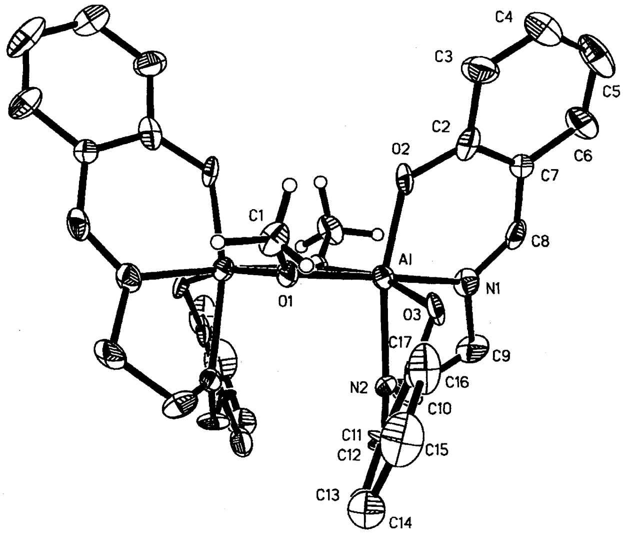
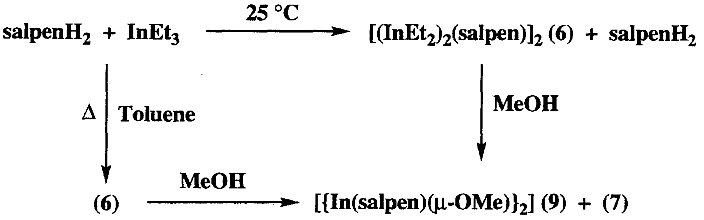


Fig. 3. Molecular structure and atom numbering scheme for [{Al(salen)(μ-OMe)}$_2$] (**10**).



Scheme 4. The reaction pathways involving $InEt_3$.

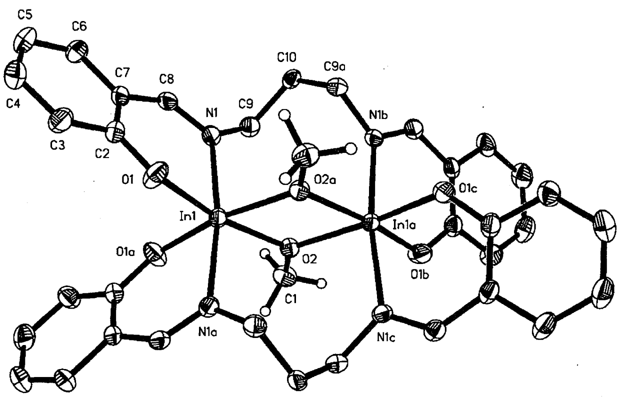


Fig. 4. Molecular structure and atom numbering scheme for [{In(μ-OMe)(μ-salpen)}$_2$] (**7**).

fined by the In and O atoms. The In–O distance to this group (2.145(3) Å) compares closely to that with the ligand oxygen (2.101(5) Å). These distances are fairly standard for both four-coordinate and six-coordinate indium complexes.12) The central In atom adopts a distorted O$_h$ geometry. The N(1)–In(1)–N(1A) angle is 171.4(2)° while the O–In(1)–O′ angles approximate 90°. The most narrow of these occurs for the O(2A)–In(1)–O(2) angle which is 73.8(2)°. Correspondingly, the In(1)–O(2)–In(1A) angle is 106.2(2)°. The lengthening of the In$_2$O$_2$ parallelogram along the In–In axis may be attributed to a tendency for the In atoms to repel one another. Thus, in group 13 complexes with bridging alkoxides the O–M–O′ angle generally decreases in the progression, Al > Ga > In. Although this observation has not been systematically established, it is partially bourne out in the representative series of dimeric complexes, [Me$_2$AlOSiMe$_2$Ph]$_2$,13) [Cp$_2$GaOEt]$_2$,14) and [^{t}Bu$_2$InOEt]$_2$15) which possess O–M–O′ angles of 83.7°, 79.5°, and 75.2°, respectively.

Structural Characterization of Compound 8. Compound **8** is an example of a bridged structure of a different type (Fig. 5). In this case it is bridged by only one ligand acting in a bidentate fashion to each of the two indium atoms. The indium atoms complete an O$_h$ geometry by further coordination to both N and O atoms of one ligand. Around In(1), the O(1) and O(3) atoms adopt a 167.4(2)° angle, while the other combinations of trans atoms maintain angles of 160.5(3)° (O(2)–In(1)–N(1)) and 163.8(2)° (N(2)–In(1)–N(3)). The In–O distances are approximately the same, with the bond to O(2) being the shortest (2.087(5) Å). Values lower than the ideal 90° for the atoms around In occurs for N–O pairs from the same ligand (O(1)–In(1)–N(1) = 81.3(2)° and O(3)–In(1)–N(3) = 83.1(2)°) while largest value occurs between a combination on different ligands (N(1)–In(1)–N-

Table 1. Bond Lengths (Å) for Compounds **7**—**10**

Bond lengths (Å)							
[{In(μ-OMe)(μ-salpen)}$_2$] (**7**)		[{In(salpen)}$_2$(μ-salpen)$_2$] (**8**)		[{In(salpen)(μ-OMe)}$_2$] (**9**)		[{Al(salen)(μ-OMe)}$_2$] (**10**)	
In(1)–O(1)	2.107(4)	In(1)–O(1)	2.114(5)	In(1)–O(1)	2.133(7)	Al–O(1)	1.887(9)
In(1)–O(2)	2.141(3)	In(1)–O(2)	2.088(5)	In(1)–O(2)	2.085(7)	Al–O(2)	1.826(12)
In(1)–N(1)	2.252(4)	In(1)–O(3)	2.122(5)	In(1)–O(3)	2.152(6)	Al–O(3)	1.871(13)
In(1)–O(1A)	2.107(4)	In(1)–N(1)	2.257(6)	In(1)–N(1)	2.222(8)	Al–N(1)	2.043(13)
In(1)–O(2A)	2.141(3)	In(1)–N(2)	2.258(7)	In(1)–N(2)	2.263(7)	Al–N(2)	2.045(14)
In(1)–N(1A)	2.252(4)	In(1)–N(3)	2.263(6)	In(1)–O(3A)	2.151(7)	Al–O(1A)	1.898(12)
O(1)–C(2)	1.305(7)	In(2)–O(4)	2.124(6)	O(1)–C(1)	1.334(9)	O(1)–C(1)	1.429(20)
O(2)–C(1)	1.393(10)	In(2)–O(5)	2.099(5)	O(2)–C(17)	1.304(10)	O(1)–AlA	1.898(12)
O(2)–In(1A)	2.141(3)	In(2)–O(6)	2.082(5)	O(3)–C(18)	1.418(10)	O(2)–C(2)	1.312(20)
N(1)–C(8)	1.285(7)	In(2)–N(4)	2.261(6)	O(3)–In(1A)	2.151(7)	O(3)–C(17)	1.329(23)
N(1)–C(9)	1.484(8)	In(2)–N(5)	2.231(7)	O(4)–C(19)	1.559(33)	N(1)–C(8)	1.296(23)
		In(2)–N(6)	2.265(6)	O(5)–C(20)	1.272(21)	N(1)–C(9)	1.486(24)
		O(1)–C(1)	1.312(8)	O(5)–C(20A)	1.272(21)	N(2)–C(10)	1.461(24)
		O(2)–C(17)	1.321(17)	N(1)–C(7)	1.268(10)	N(2)–C(11)	1.288(25)
		O(3)–C(18)	1.287(10)	N(1)–C(8)	1.493(10)		
		O(4)–C(34)	1.306(9)	N(2)–C(10)	1.494(11)		
		O(5)–C(35)	1.306(9)	N(2)–C(11)	1.294(11)		
		O(6)–C(51)	1.321(9)				
		O(7)–C(52)	1.704(30)				
		N(1)–C(7)	1.260(10)				
		N(1)–C(8)	1.469(10)				
		N(2)–C(10)	1.495(10)				
		N(2)–C(11)	1.281(12)				
		N(3)–C(24)	1.283(10)				
		N(3)–C(25)	1.485(8)				
		N(4)–C(27)	1.468(10)				
		N(4)–C(28)	1.278(9)				
		N(5)–C(41)	1.298(12)				
		N(5)–C(42)	1.451(12)				
		N(6)–C(44)	1.511(13)				
		N(6)–C(45)	1.279(10)				

Table 2. Bond Angles (deg) for Compounds **7**—**10**

Bond angles (deg)							
[{In(μ-OMe)(μ-salpen)}$_2$] (**7**)		[{In(salpen)}$_2$(μ-salpen)$_2$] (**8**)		[{In(salpen)(μ-OMe)}$_2$] (**9**)		[{Al(salen)(μ-OMe)}$_2$] (**10**)	
O(1)–In(1)–O(2)	167.8(2)	O(1)–In(1)–O(2)	88.4(2)	O(1)–In(1)–O(2)	91.4(2)	O(1)–Al–O(2)	94.5(5)
O(1)–In(1)–N(1)	85.8(2)	O(1)–In(1)–O(3)	167.2(2)	O(1)–In(1)–O(3)	89.2(2)	O(1)–Al–O(3)	92.9(5)
O(2)–In(1)–N(1)	92.3(1)	O(2)–In(1)–O(3)	102.7(2)	O(2)–In(1)–O(3)	94.8(2)	O(2)–Al–O(3)	92.7(6)
O(1)–In(1)–O(1A)	97.4(2)	O(1)–In(1)–N(1)	81.5(2)	O(1)–In(1)–N(1)	82.8(2)	O(1)–Al–N(1)	166.6(6)
O(2)–In(1)–O(1A)	94.5(2)	O(2)–In(1)–N(1)	160.6(3)	O(2)–In(1)–N(1)	167.3(2)	O(2)–Al–N(1)	89.3(6)
N(1)–In(1)–O(1A)	88.6(2)	O(3)–In(1)–N(1)	89.5(2)	O(3)–In(1)–N(1)	96.3(2)	O(3)–Al–N(1)	99.8(5)
O(1)–In(1)–O(2A)	94.5(2)	O(1)–In(1)–N(2)	104.2(2)	O(1)–In(1)–N(2)	103.7(2)	O(1)–Al–N(2)	99.8(5)
O(2)–In(1)–O(2A)	73.6(2)	O(2)–In(1)–N(2)	83.8(2)	O(2)–In(1)–N(2)	85.0(2)	O(2)–Al–N(2)	165.6(5)
N(1)–In(1)–O(2A)	94.5(1)	O(3)–In(1)–N(2)	83.4(3)	O(3)–In(1)–N(2)	167.0(2)	O(3)–Al–N(2)	85.1(6)
O(1A)–In(1)–O(2A)	167.8(2)	N(1)–In(1)–N(2)	82.7(2)	N(1)–In(1)–N(2)	85.5(2)	N(1)–Al–N(2)	77.1(6)
O(1)–In(1)–N(1A)	88.6(2)	O(1)–In(1)–N(3)	90.6(2)	O(1)–In(1)–O(3A)	162.2(2)	O(1)–Al–O(1A)	76.3(5)
O(2)–In(1)–N(1A)	94.5(1)	O(2)–In(1)–N(3)	90.7(2)	O(2)–In(1)–O(3A)	99.4(2)	O(2)–Al–O(1A)	98.8(6)
N(1)–In(1)–N(1A)	171.5(2)	O(3)–In(1)–N(3)	83.1(2)	O(3)–In(1)–O(3A)	75.8(2)	O(3)–Al–O(1A)	164.8(5)
O(1A)–In(1)–N(1A)	85.8(2)	N(1)–In(1)–N(3)	105.8(2)	N(1)–In(1)–O(3A)	89.1(2)	N(1)–Al–O(1A)	90.4(5)
O(2A)–In(1)–N(1A)	92.3(1)	N(2)–In(1)–N(3)	164.0(2)	N(2)–In(1)–O(3A)	91.4(2)	N(2)–Al–O(1A)	86.2(6)
In(1)–O(1)–C(2)	128.1(4)	O(4)–In(2)–O(5)	169.7(2)	In(1)–O(1)–C(1)	121.8(5)	Al–O(1)–C(1)	121.9(9)
In(1)–O(2)–C(1)	126.8(1)	O(4)–In(2)–O(6)	96.8(2)	In(1)–O(2)–C(17)	126.5(5)	Al–O(1)–AlA	103.6(5)
In(1)–O(2)–In(1A)	106.4(2)	O(5)–In(2)–O(6)	89.5(2)	In(1)–O(3)–C(18)	119.5(5)	C(1)–O(1)–AlA	126.1(9)
C(1)–O(2)–In(1A)	126.8(1)	O(4)–In(2)–N(4)	83.0(2)	In(1)–O(3)–In(1A)	104.1(2)	Al–O(2)–C(2)	129.8(11)
In(1)–N(1)–C(8)	120.8(4)	O(5)–In(2)–N(4)	88.2(2)	C(18)–O(3)–In(1A)	123.5(5)	Al–O(3)–C(17)	124.0(11)
In(1)–N(1)–C(9)	121.9(4)	O(6)–In(2)–N(4)	97.0(2)	C(20)–O(5)–C(20A)	93.7(20)	Al–N(1)–C(8)	125.6(13)
C(8)–N(1)–C(9)	116.3(5)	O(4)–In(2)–N(5)	92.0(2)	In(1)–N(1)–C(7)	124.1(5)	Al–N(1)–C(9)	115.7(11)
		O(5)–In(2)–N(5)	84.5(2)	In(1)–N(1)–C(8)	117.9(5)	C(8)–N(1)–C(9)	118.5(13)
		O(6)–In(2)–N(5)	160.6(2)	C(7)–N(1)–C(8)	117.9(6)	Al–N(2)–C(10)	113.1(11)
		N(4)–In(2)–N(5)	101.2(2)	In(1)–N(2)–C(10)	121.7(5)	Al–N(2)–C(11)	123.7(14)
		O(4)–In(2)–N(6)	85.7(2)	In(1)–N(2)–C(11)	121.7(5)	C(10)–N(2)–C(11)	121.7(15)
		O(5)–In(2)–N(6)	103.3(2)	C(10)–N(2)–C(11)	116.6(6)		
		O(6)–In(2)–N(6)	81.4(2)				
		N(4)–In(2)–N(6)	168.4(2)				
		N(5)–In(2)–N(6)	82.1(2)				
		In(1)–O(1)–C(1)	130.4(5)				
		In(1)–O(2)–C(17)	125.2(5)				
		In(1)–O(3)–C(18)	134.1(5)				
		In(2)–O(4)–C(34)	128.5(5)				
		In(2)–O(5)–C(35)	128.1(4)				
		In(2)–O(6)–C(51)	124.1(5)				
		In(1)–N(1)–C(7)	124.8(5)				
		In(1)–N(1)–C(8)	116.2(5)				
		C(7)–N(1)–C(8)	118.9(7)				
		In(1)–N(2)–C(10)	119.7(6)				
		In(1)–N(2)–C(11)	121.8(5)				
		C(10)–N(2)–C(11)	118.5(7)				
		In(1)–N(3)–C(24)	124.8(4)				
		In(1)–N(3)–C(25)	118.4(4)				
		C(24)–N(3)–C(25)	116.8(6)				
		In(2)–N(4)–C(27)	120.8(4)				
		In(2)–N(4)–C(28)	122.0(5)				
		C(27)–N(4)–C(28)	116.9(6)				
		In(2)–N(5)–C(41)	122.5(6)				
		In(2)–N(5)–C(42)	118.6(5)				
		C(41)–N(5)–C(42)	118.5(7)				
		In(2)–N(6)–C(44)	120.2(5)				
		In(2)–N(6)–C(45)	121.8(6)				
		C(44)–N(6)–C(45)	117.9(7)				
		O(1)–C(1)–C(2)	119.2(7)				
		O(1)–C(1)–C(6)	123.0(6)				

(3) = 106.0(3)°).

The type of bridging exhibited in **8** has been observed for bidentate alkyl amines such as TMEDA. The complex, $H_3Ga–N(Me)_2CH_2CH_2(Me)_2N–GaH_3$ also serves as a group 13 example.[16] It is, however, more well-known for transition metal complexes such as $[Co_2(3\text{-}MeO(salen))_3]$.[17]

Table 3. Crystal Data for Compounds **7**—**10**

Compound	**7**	**8**	**9**	**10**
Formula	$C_{10}H_{12}InNO_2$	$C_{52}H_{52}In_2N_6O_7$	$C_{20}H_{25}InN_2O_5$	$C_{17}H_{22}AlN_2O_5$
Formula weight	293.0	1102.6	488.2	361.3
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Fddd*	$P2_1/c$	$C2/c$	$C2/c$
a/Å	8.758(1)	10.854(3)	13.14(2)	12.665(4)
b/Å	24.704(4)	19.938(1)	16.55(3)	16.049(7)
c/Å	31.409(4)	23.515(1)	18.60(4)	17.665(4)
$\alpha/^\circ$	—	—	—	—
$\beta/^\circ$	—	102.70(1)	102.8(1)	100.38(2)
$\gamma/^\circ$	—	—	—	—
V/Å^3	6795(2)	4964(1)	3922(13)	3532(2)
Z	16	4	8	8
$D_{\mathrm{calcd}}/\mathrm{g\,cm^{-3}}$	1.142	1.475	1.654	1.360
Crystal size/mm	$0.5\times0.1\times0.1$	$1.0\times0.5\times0.2$	$0.8\times0.5\times0.3$	$0.4\times0.3\times0.3$
Temperature/K	298	298	298	298
2θ range/deg	7—45	3.5—45	3.4—45	3.5—45
Scan type	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
Scan speed/deg min^{-1}	8—60	14—60	8—60	6—60
Scan range/deg	0.48	0.35	0.60	0.60
Reflections collected	1444	8808	3037	2919
Indp reflections	1120	6460	2252	2307
Obsd reflections	858	4716	2278	698
$(F > X\sigma(F))$	4	4	4	4
No. of parameters	111	604	244	203
R	0.0309	0.0445	0.0446	0.0764
R_{w}	0.0339	0.0480	0.0485	0.0871
GOF	7.99	3.41	4.73	6.63
LarDiff. Peak/e Å^3	0.42	0.78	0.98	0.31

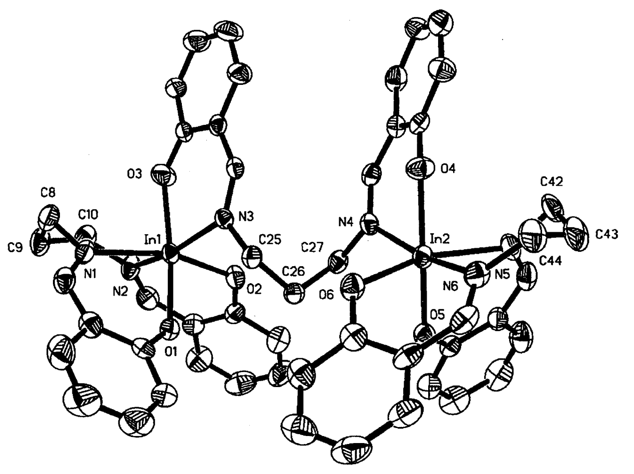


Fig. 5. Molecular structure and atom numbering scheme for [{In(salpen)}$_2$(μ-salpen)] (**8**).

Conclusions

This manuscript presented the first report of acen and salen complexes of indium. It was shown that an interesting range of mono- and bimetallic compounds form under various conditions. The confluence of several factors can be proposed to explain this diverse chemistry in comparison to the corresponding chemistry of aluminum and gallium: the relatively large size of indium, the lability of bonds to indium, and the tendency for indium to adopt to a six-coordinate geometry.

Experimental

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin–Elmer 2400 Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The synthesis of [salenAl(μ-OMe)]$_2$ was reported elsewhere.[7b)]

Synthesis of [In(Me)(acen)] (1). To a rapidly stirring suspension of acenH_2 (0.530 g, 1.79 mmol) in 15 mL of toluene was added trimethylindium (0.286 g, 1.79 mmol) neat at ambient temperature. The resulting mixture was allowed to stir at ambient temperature for one hour and then to reflux for one hour, never becoming clear in nature. The light yellow crystalline solid was isolated by filtration (0.462 g, 61%) and the supernatant was stored at 0 °C for a few days to yield light yellow microcrystals of **1** (Total yield: 0.512 g, 67%). Mp 199—204 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = -0.34$ (s, 3H, InC$\underline{H}_3$), 2.47 (s, 6H, C(C$\underline{H}_3$)), 3.71 (m, 2H, NC$\underline{H}_2$), 3.92 (m, 2H, NC$\underline{H}_2$), 6.62 (t, 2H, Ph$\underline{H}$), 7.07 (d, 2H, Ph$\underline{H}$), 7.22 (t, 2H, Ph$\underline{H}$), 7.38 (d, 2H, Ph$\underline{H}$); IR (KBr) 1597 vs, 1537 vs, 1470 s, 1435 vs, 1317 vs, 1221 s, 1163 s, 858 s, 756 s, 411 s cm^{-1}; MS [FAB] *m/z* 849 (DH)$^+$, 833 (D–CH_3) 425 (MH)$^+$, 409 (M$-CH_3$)$^+$. Analysis: Found: C, 54.21; H, 5.04%. Calcd for $C_{19}H_{21}N_2O_2In$: C, 53.80; H, 4.99%.

Synthesis of [In(Me)(salen)] (2). To a rapidly stirring solution of salenH_2 (0.500 g, 1.86 mmol) in 15 mL of toluene was added trimethylindium etherate (0.435 g, 1.86 mmol) in 10 mL of toluene at ambient temperature. The solution was clear and yellow in color. A yellow precipitate began to form immediately. The solution then was refluxed for 2 h and as the solution cooled to ambient temperature the precipitate reappeared. The precipitate was isolated to yield (0.457 g, 62%) of a yellow solid and the supernatant stored at −30 °C for one day to yield (0.111 g, 15%) of a yellow crystalline solid (0.568 g, 77% total). Mp 244—247 °C (decomp); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = -0.19$ (s, 3H, $\mathrm{InC\underline{H}_3}$), 3.67 (m, 2H, $\mathrm{NC\underline{H}_2}$), 3.94 (m, 2H, $\mathrm{NC\underline{H}_2}$), 6.60 (t, 2H, $\mathrm{Ph\underline{H}}$), 7.15 (m, 6H, $\mathrm{Ph\underline{H}}$), 8.22 (s, 2H, $\mathrm{PhC\underline{H}}$); IR (KBr) 3055 vwk, 2963 vwk, 1644 vs, 1538 vs, 1445 vs, 1300 s, 1150 s, 905 s, 760 vs cm^{-1}. Analysis: Found: C, 51.85; H, 4.39 %. Calcd for $\mathrm{C_{17}H_{17}N_2O_2In}$: C, 51.54, H, 4.33 %.

Synthesis of [In(Me)(salophen)] (3). To a stirring suspension of salophen$\mathrm{H_2}$ (0.839 g, 2.65 mmol) in 15 mL of toluene was added trimethylindium (0.424 g, 2.65 mmol) neat at ambient temperature. The mixture turned to a clear golden-brown colored solution. Then a precipitate formed, and the solution was allowed to stir at ambient temperature for 1/2 hour followed by reflux for one hour. As the solution cooled to ambient temperature the precipitate reformed and was isolated as a golden-brown solid (0.562 g, 48%). The filtrate was stored at 0 °C for one day in which golden colored crystals of **3** formed (Total yield: 0.765 g, 65%). Mp 236—239 °C (decomp); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = -0.16$ (s, 3H, $\mathrm{InC\underline{H}_3}$), 6.66 (t, 2H, $\mathrm{Ph\underline{H}}$), 7.04 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.21 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.36 (t, 2H, $\mathrm{Ph\underline{H}}$) 7.43 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.53 (t, 2H, $\mathrm{Ph\underline{H}}$), 8.51 (s, 2H, $\mathrm{PhC\underline{H}}$); IR (KBr) 3011 vwk, 1609 vs, 1586 vs, 1528 vs, 1460 vs, 1325 s, 1182 vs, 1150 vs, 918 s, 750 vs, 530 s cm^{-1}. Analysis: Found: C, 56.83; H, 3.87%. Calcd for $\mathrm{C_{21}H_{17}N_2O_2In}$: C, 56.78; H 3.86%.

Synthesis of [In(Me)(salomphen)] (4). To a rapidly stirring suspension of salomphen$\mathrm{H_2}$ (0.344 g, 1.0 mmol) in 20 mL of toluene was added trimethylindium (0.160 g, 1.0 mmol) neat at ambient temperature. Shortly after addition a bright yellow precipitate appeared. The mixture was allowed to stir at ambient temperature for 30 min then brought to reflux for one hour during which time the precipitate remained insoluble. It was isolated as a bright yellow powdery solid (0.265 g, 56%). Total yield: 0.367 g, 78%. Mp > 260 °C; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) $\delta = -0.19$ (s, 3H, $\mathrm{InC\underline{H}_3}$), 2.39 (s, 6H, $\mathrm{PhC\underline{H}_3}$), 6.60 (t, 2H, $\mathrm{Ph\underline{H}}$), 6.97 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.23 (m, 6H, $\mathrm{Ph\underline{H}}$), 8.45 (s, 2H, $\mathrm{PhC\underline{H}}$); IR (KBr) 3125 vwk, 2967 vwk, 1618 vs, 1530 vs, 1464 vs, 1385 s, 1177 s, 1146 s, 864 s, 760 s cm^{-1}; MS [FAB] *m/z* 473 $(\mathrm{MH})^+$, 457 $(\mathrm{M-CH_3})^+$. Analysis: Found: C, 58.23; H, 4.27%. Calcd for $\mathrm{C_{23}H_{21}N_2O_2In}$: C, 58.50, H, 4.48%.

Synthesis of [(InMe$_2$)$_2$(salphen)] (5). To a stirring solution of salphen$\mathrm{H_2}$ (0.353 g, 1.25 mmol) in 10 mL of toluene was added trimethylindium (0.200 g, 1.25 mmol), neat at ambient temperature. The exothermic reaction resulted in a clear, yellow colored solution. After 5 min. a precipitate appeared. The resultant mixture was allowed to stir at ambient temperature for 18 h whereupon the precipitate was isolated via filtration and solvent removal under vacuum. The resulting light yellow solid was washed once with $\mathrm{CH_2Cl_2}$ and dried under vacuum. (Yield = 0.322 g, 90%). Mp 176—181 °C (decomp); ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$), Peaks for the title compound only, $\delta = -0.07$ (s, 12H, $\mathrm{InC\underline{H}_3}$), 2.04 (m, 2H, $\mathrm{NCH_2(C\underline{H}_2)CH_2}$), 3.59 (t, 4H, $\mathrm{NC\underline{H}_2(CH_2)C\underline{H}_2}$), 6.53—7.32 (m, 8H, $\mathrm{Ph\underline{H}}$), 7.96 (s, 2H, $\mathrm{PhC\underline{H}}$); IR: 3050 wk, 2947 s, 2919 s, 2864 s, 1638 vs, 1597 vs, 1549 vs, 1472 vs, 1445 vs, 1410 vs, 1373 s, 1296 vs, 1186 vs, 1161 s, 1040 s, 903 s, 793 s, 752 vs, 525 s cm^{-1}. Analysis: Found: C, 44.42; H, 4.67%. Calcd for $\mathrm{C_{21}H_{28}N_2O_2In_2}$: C, 44.24; H, 4.92%.

Synthesis of [(InEt$_2$)$_2$(salpen)] (6). To a stirring solution of salpen$\mathrm{H_2}$ (0.612 g, 2.17 mmol) in 10 mL of toluene was added triethylindium (0.876 g, 4.34 mmol) in 10 mL of toluene at ambient temperature. Gas evolution was observed and a yellow precipitate formed immediately. The mixture was allowed to stir at 25 °C for 20 h before the precipitate was isolated by filtration. (yield 1.17 g, 86%). Mp 193—195 °C; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$), $\delta = 0.74$ (q, 8H, $\mathrm{InC\underline{H}_2CH_3}$), 1.20 (t, 12H, $\mathrm{InCH_2C\underline{H}_3}$), 2.09 (m, 2H, $\mathrm{NCH_2(C\underline{H}_2)CH_2}$), 3.60 (t, 4H, $\mathrm{NC\underline{H}_2(CH_2)C\underline{H}_2}$), 6.62 (t, 2H, $\mathrm{Ph\underline{H}}$), 6.81 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.01 (d, 2H, $\mathrm{Ph\underline{H}}$), 7.29 (t, 2H, $\mathrm{Ph\underline{H}}$), 8.03 (s, 2H, $\mathrm{PhC\underline{H}}$); IR 2905 vs (br), 2861 vs (br), 2816 s, 1632 vs, 1597 vs, 1547 vs, 1472 vs, 1443 vs, 1412 vs, 1291 vs, 1188 vs, 1159 vs, 1038 s, 903 s, 789 s, 748 s, 642 s, 596 s, 544 s, 502 s, 459 s cm^{-1}. Analysis: Found: C, 47.57; H, 5.51%. Calcd for $\mathrm{C_{25}H_{36}N_2O_2In_2}$: C, 47.95; H, 5.79%.

Synthesis of [{In(μ-OMe)(μ-salpen)}$_2$] (7) and [{In(salpen)}$_2$(μ-salpen)] (8). To a stirring suspension of salpen$\mathrm{H_2}$ (0.511 g, 1.81 mmol) in 15 mL of toluene was added trimethylindium (0.289 g, 1.81 mmol), neat at room temperature. After 5 min a precipitate appeared. The mixture was allowed to stir at room temperature for one half hour followed by vigorous reflux for one hour. This resulted in a clear, light yellow solution which was filtered, concentrated in vacuo, and stored at −30 °C for three days. During this time, an oily solid formed in the flask. The solution was filtered via cannula and the volatiles were removed under vacuum to leave behind an oily, light yellow solid (in quantitative yield based upon the formation of salpenInMe). This solid was extracted with dry methanol and filtered into a 25 mL erlenmeyer and the solution was allowed to stand undisturbed for one week at which point pale yellow needles of **7** and blocks of **8** formed (in 50% yield for each).

Characterization of (7): Mp > 260 °C; IR 3129 w, 2346 w, 1620 vs, 1539 s, 1472 s, 1452 s, 1404 vs, 1343 s, 1317 s, 1148 s, 966 w, 750 s cm^{-1}. Analysis: Found: C, 50.66; H, 4.12; N, 6.63%. Calcd for $\mathrm{C_{36}H_{38}In_2N_4O_6}$: C, 50.73; H, 4.49; N, 6.57%.

Characterization of (8): Mp 220—223 °C; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$, on powder) $\delta = 1.93$ (m, 2H, $\mathrm{CH_2(CH_2)CH_2}$, non-bridging), 2.52 (m, 2H, $\mathrm{CH_2(CH_2)CH_2}$, non-bridging), 2.67 (m, 2H, $\mathrm{CH_2(CH_2)CH_2}$, bridging), 3.55 (m, 8H, $\mathrm{NCH_2}$, non-bridging), 4.32 (m, 4H, $\mathrm{NCH_2}$, bridging), 6.49—7.29 (m, 24H, PhH), 7.96 (s, 2H, PhCH, bridging), 8.08 (s, 4H, PhCH, non-bridging); IR 3121 w, 2857 vw, 1620 vs, 1541 s, 1468 s, 1443 s, 1402 s, 1311 s (br), 1192 s, 1148 s, 1063 s, 1032 s, 762 s cm^{-1}. Analysis: Found: C, 57.10; H, 4.59; N, 7.76%. Calcd for $\mathrm{C_{51}H_{48}In_2N_6O_6}$: C, 57.21; H, 4.52; N, 7.62%.

Synthesis of [{In(μ-OMe)(μ-salpen)}$_2$] (7) and [{In(salpen)(μ-OMe)}$_2$] (9). salpen$\mathrm{H_2}$ (1.096 g, 3.88 mmol) was dissolved in 10 mL of toluene. Upon addition of triethylindium (0.785 g, 3.89 mmol) in 10 mL of toluene the solution turned from yellow to orange in color. After 2 min at ambient temperature slow gas evolution occurred and the solution became yellow again. After an additional 5 min a precipitate formed. The solution was brought to reflux whereupon the precipitate went back into solution and reflux was maintained for 57 h to yield a dark golden colored solution. The precipitate never reformed upon cooling to ambient temperature. The volatiles were removed in vacuo to yield 1.443 g, 88% (based upon the formulation, salpenInMe) of an oily golden colored solid.[18] (The oily solid gradually solidifies completely upon standing in the drybox). Of this oily solid, 0.320 g was extracted in 25 mL of dry methanol, filtered into a 50 mL Erlenmeyer flask and allowed to sit undisturbed for one day during which time yellow needles of (**7**) and yellow blocks of (**9**) grew in quantitative yield. After single crystal X-ray analysis showed (**9**) to be methoxy dimer a melting point was taken and was found to be > 260 °C. Then a pulverized sample of the title compounds was made and placed under vacuum for 5 min. Elemental analysis matched that for a methoxy dimer. Analysis: Found: C, 50.62; H, 4.59; N, 6.71%. Calcd for $C_{36}H_{38}N_4O_6$: C, 50.73; H, 4.49; N, 6.57%.

X-Ray Experimental. Crystals suitable for X-ray diffraction of **7** and **8** were isolated by the slow evaporation of a mixture of the two in MeOH. Compound **7** crystallizes as pale yellow thin needles, while **8** adopts a cubic morphology. Compounds **7** and **9** were isolated similarly from a parent reaction utilizing Et_3In. Compound **10** was crystallized as the single product from an evaporating MeOH solution. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 3. Complete data are deposited as Document No. 70014 at the Office of the Editor of Bull. Chem. Soc. Jpn. Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo $K\alpha$ (0.71073 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection for each compound and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. In order to obtain reasonable GOF values weighting schemes of 0.0002 for **7** and **8**, and 0.000325 for **10**.

There was solvent of crystallization in compounds **8** (MeOH), **9** (MeOH), and **10** (H_2O). There were hydrogen bonding contacts in **8** and **10**. In **8**, the contact occurs between the MeOH and O(7) at a distance of 2.9 Å. In **10** there were two contacts; one between the water and O(3) (2.9 Å) and the other between the water and the aromatic hydrogen H16A (2.4 Å). These types of contacts are fairly routine in salen and Salan main group complexes. In one series of $SalanH_2Zn$ complexes the solvent contacts were shown to have no detectable effect on the bond distance and angles within the chelate.[19]

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