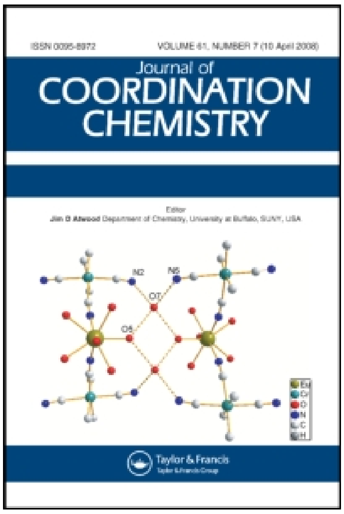

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SYNTHESIS, STRUCTURE AND REACTIVITY OF SalanH$_2$-METAL COMPLEXES

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SYNTHESIS, STRUCTURE AND REACTIVITY OF SalanH$_2$-METAL COMPLEXES

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The present work is an exploration into synthesis of complexes of general formula LH$_2$M (where M = Mn, Fe, Cu, and Al). The results obtained for L = Salophan (M = Fe (**1**), Cu (**2**)); Salomphan (M = Mn (**3**), Fe(**4**), Cu(**5**); Salpan (M = Fe(**6**), Cu(**7**)) and L = Salean (M = AlCl) (**8**) are reported. When **8** is dissolved in MeOH, [SaleanH$_2$AlOMe]$_2$ (**9**) is formed. In MeOH, and in the presence of air, **1** and **4** undergo oxidation of both the ligand and metal (Fe(II) to Fe(III) to form the "half" Schiff base complexes, [SalophanHFeOMe]$_2$ (**10**) and [SalomphanHFeOMe]$_2$ (**11**). Compounds **9–11** were structurally characterized. Crystal Data: (**9**) $C_{36}H_{46}Al_2N_4O_7$, Space Group P-1 (no. 2) with a = 7.536(1) Å, b = 10.513(2)Å, c = 11.997(2) Å, α = 97.72(1), β = 94.040(10)°, γ = 102.73(1), V = 914.8(3) Å^3 and Z = 2. With 226 parameters refined on 1226 reflections having F>6.0σ(F), the final R values were R = 0.0540 and R$_w$ = 0.0565; (**10**), $C_{46}H_{46}Fe_2N_4O_8$, Space Group P-1 (no. 2) with a = 9.400(2) Å, b = 10.718(4) Å, c = 12.354(3) Å, α = 76.28(3), β = 67.89(2)°, γ = 86.63(3), V = 1119.7(7) Å^3 and Z = 2. With 289 parameters refined on 1327 reflections having F>6.0σ(F), the final R values were R = 0.0672 and R$_w$ = 0.0749; (**11**), $C_{48}H_{54}Fe_2N_4O_8$, Space Group P-1 (no. 2) with a = 9.047(2) Å, b = 11.723(2) Å, c = 12.419(3) Å, α = 80.14(2), β = 68.68(3)°, γ = 85.88(2), V = 1208.8(4) Å^3 and Z = 2. With 307 parameters refined on 2171 reflections having F>4.0σ(F), the final R values were R = 0.0546 and R$_w$ = 0.0573.

KEYWORDS: SalanH$_4$, SalenH$_2$, iron, aluminium, X-ray structure

INTRODUCTION

Tetradentate Schiff base (Figure 1a) ligands were first studied systematically in 1931[1] and since that time have been used extensively in the complexation of transition metals and to a lesser extent the main group elements.[2] Complexes of this class of ligand have been used in the reversible binding of oxygen[3], the expoxidation of olefins,[4] as enzyme models[5] and, more recently, as Lewis acid catalysts.[6]

Considering the widespread use and prevalence of the Schiff base complexes, it is surprising that the hydrogenated derivatives (Figure 1b) have not been systematically explored. These may be anticipated to have similar uses as the Schiff base analogues, although the presence of an amine rather than imine functionality will have some effect on the electronic and structural properties of the system. These differences could conceivably improve the properties of a catalyst created with this

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ligand. For instance, the amine hydrogens may act to direct a coordinating substrate, either through hydrogen bonding or through a mild steric effect. Additionally, the ligand may be modified as needed by changing the constituents at R^1, R^2 and R^3. A brief listing of some ligand permutations, along with the corresponding nomenclature is shown in Figure 1.

Compared to the analogous $SalenH_2$ ligands, structurally characterized metal complexes derived from the $SalanH_4$ ligands are rare. Some examples include the complexes: $Salean(Bu^t)H_2Mo(O)_2$,[7] $(SalophanH)_2Mo$,[8] $[SaleanH_2FeOH]_2$,[9] $(Salean(Me, Bu^t)H_2FeOMe]_2$,[10] and $Salean(Me, Bu^t)H_2Ni$.[11] Main group element combinations are limited to complexes of Zn,[12] Sn,[13] Al[14-17] and Ga.[16,17] Considering the potential advantages of such a ligand system, the need for a systematic exploration of the chemistry of these ligands with transition and main group elements is clearly evident.

The present work is an exploration into the synthesis of complexes of general formula LH_2M (where M = Mn, Fe, Cu, and Al). The results obtained for L = Salophan (M = Fe(**1**), Cu(**2**)); Salomphan (M = Mn(**3**), Fe(**4**), Cu(**5**); Salpan (M = Fe(**6**), Cu(**7**)) and L = Salean (M = AlCl (**8**) are reported. Where **8** is dissolved in MeOH, $[SaleanH_2AlOMe]_2$ (**9**) forms. In MeOH, and in the presence of air, **1** and **4** undergo oxidation of both the ligand and Fe(II) to form the "half" Schiff base complexes, $[SalophanHFeOMe]_2$ (**10**) and $[SalomphanHFeOMe]_2$ (**11**).

RESULTS AND DISCUSSION

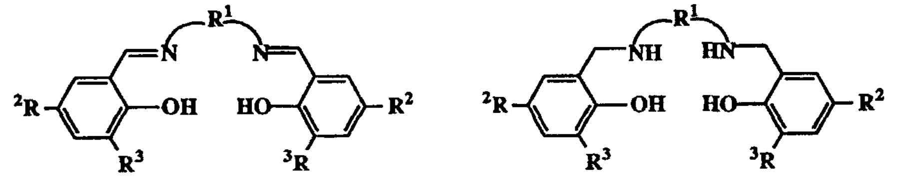
Compounds **1**–**7** are prepared by reaction of the respective metal chloride with LH_4 and NEt_3 in anhydrous MeOH. After cooling to −30°C, colored solids for each of the compounds precipitate. The presence of NH stretches in the IR for all of the compounds (except **2**, **5** and **7**) in the range 3263–3236 cm^{-1}) indicate that the metals are bound to the ligand through the oxygen atoms. Additionally, the O-H stretches for the parent ligands (3600–3400 cm^{-1}) are absent. Although the NH stretch for the Cu derivatives (**2**, **5** ands **7**) is not observed, the absence of an O-H resonance for these molecules provides indirect evidence for such bonding. Solution data on **1**–**7** was not available due to the insolubility of the complexes.

$$LH_4 \xrightarrow[MeOH]{2NEt_3} \xrightarrow[-2[HNEt_3]Cl]{MCl_2} LH_2M \tag{1}$$

L = Salophan; M = Fe (**1**), Cu (**2**)
Salomphan; Mn (**3**), Fe (**4**), Cu (**5**)
Salpan; Fe (**6**), Cu (**7**)

$$2\ SaleanH_4 \xrightarrow[Tol,\ -2\ CH_4]{[Me_2AlCl]_2} 2\ SaleanH_2AlCl\ (\mathbf{8}) \xrightarrow[-2\ HCl]{MeOH} [SaleanH_2AlOMe]_2\ (\mathbf{9}) \tag{2}$$

The $SalanH_2AlCl$ complexes are extremely hard to make. Attempts to prepare the $SalpanH_2$-, $SalophanH_2$– and $SalomphanH_2$– analogues were unsuccessful. Formation of these complexes is complicated by the fact that HCl elimination occurs concurrently with methane elimination during the synthetic procedure. In general, this leads to a mixture of the desired chloride and at least one other product that



SalenH$_2$ Ligand (a)	R^1	R^2	R^3	SalanH$_4$ Ligand (b)
1. SalenH$_2$	Et	H	H	SaleanH$_4$
2. SalophenH$_2$	Ph	H	H	SalophanH$_4$
3. SalomphenH$_2$	3,4-Me$_2$Ph	H	H	SalomphanH$_4$
4. Salen(t-Bu)H$_2$	Et	H	t-Bu	Salean(t-Bu)H$_4$
5. Salen(Me,t-Bu)H$_2$	Et	Me	t-Bu	Salean(Me,t-Bu)H$_4$

Figure 1 The SalenH$_2$ and SalanH$_4$ ligands described in the text (4 and 5) and used in this study (1–3)

is tentatively identified as [SalanHAl]$_2$.[18] Separation of the products of this reaction have been unsuccessful to date. However, by slowly adding Me$_2$AlCl (cooled to -30°C) to a stirring solution of the SaleanH$_4$ ligand in toluene, the SaleanH$_2$-derivative, **8**, can be isolated in high yield with good purity. Dissolution of this compound and stirring of 1h results in formation of [SaleanH$_2$AlOMe]$_2$ (**9**). The IR data for these compounds are very similar to that displayed by the transition metal derivatives with N-H stretches of 3219 and 3221 cm^{-1}, respectively.

An X-ray crystallographic study of (**9**) indicates that the molecule is a methoxy-bridged dimer. The molecular structure and atom numbering scheme are shown in Figure 2; selected bond distances and angles are located in Table 1. The Al$_2$O$_2$ four-membered ring is planar with somewhat widened Al-O-Al' angles (103.3(2)°) and, consequently, narrowed O-Al-O' angles (76.7(2)°). The disparity in these angles reflects the steric effect of two SalanH$_2$-ligands. It should be noted that these angles (and the distances, as well) are very similar to those seen for the Schiff base analogue, [AcenAlOMe]$_2$ (Acen = N, N'-ethylenebis(2-hydroxyphenylene(methyl)-imine).[19]

Surprisingly, the oxygen atoms display a planar three-coordinate geometry. This implies the presence of an Al-O π interaction within the four-membered ring with shorter Al-O bond lengths. This is, however, not the case; with distances of 1.864(5) Å which compares closely to the distance in [AcenAlOMe]$_2$ (Al-O(ave) = 1.90 Å) where the bridging methoxy group adopts a non-planar, distorted tetrahedral, geometry. In systems where a significant degree of π bonding occurs, the Al-O distances are generally on the order of 1.70–1.74 Å.[20] The presence of a planar, bridging, methoxy group is not unique to this aluminium complex but is also found in the structures of the iron derivatives, **10** and **11** (see below).

The compounds which incorporate aryl-based ligands, SalophanH$_2$ and SalomphanH$_2$ (**1–5**) demonstrate varying degrees of oxygen sensitivity while the SalphanH$_2$ complexes (**6** and **7**) are not oxygen sensitive. Preliminary results indicated that **1–5** undergo ligand dehydrogenation to the corresponding Schiff base derivative as demonstrated generally in Scheme 1c. The Schiff base complexes are insoluble and analyze with varying degrees of solvent (DMF and MeOH) and

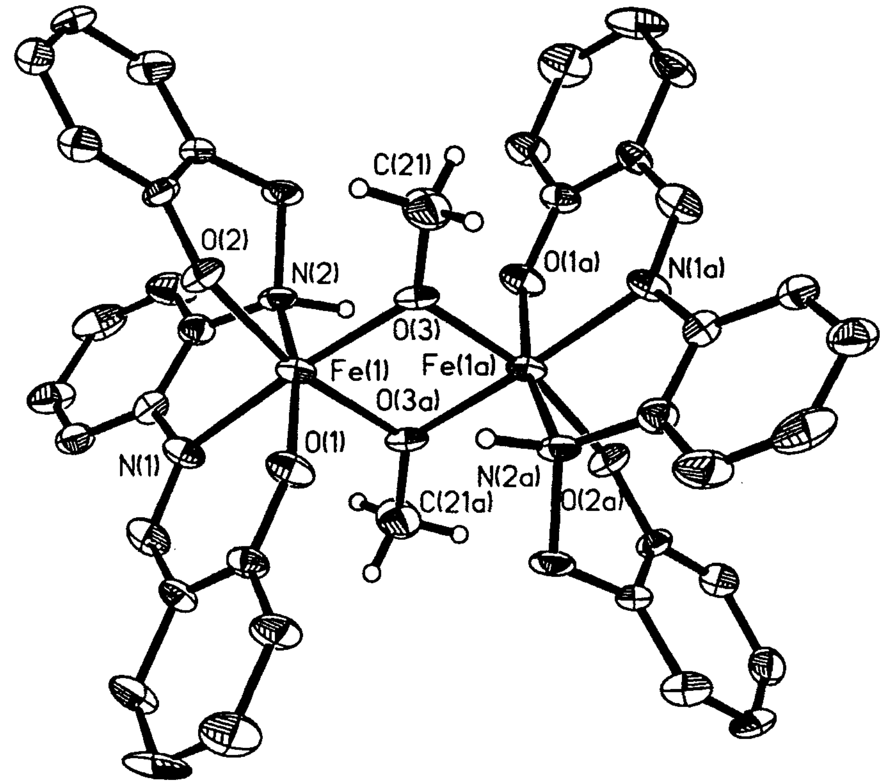
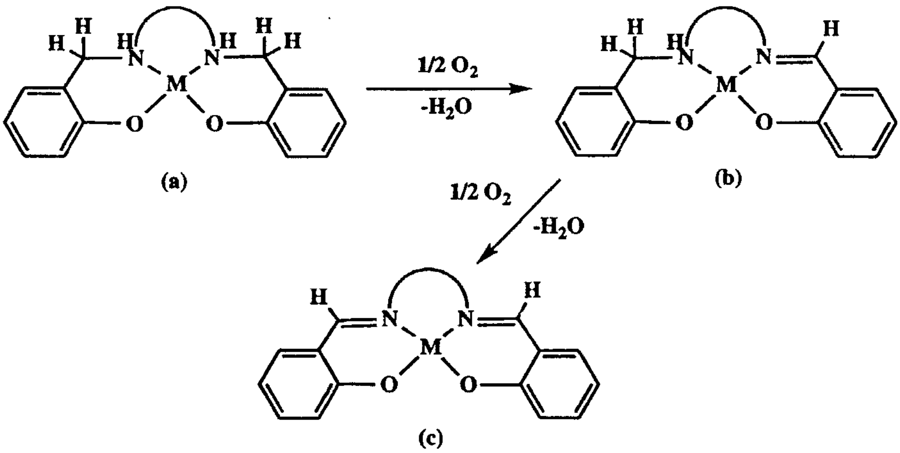


Figure 2 Molecular structure and atom numbering scheme for [SaleanH$_2$AlOMe]$_2$ (**9**)



Scheme 1 General depiction of the transformation of SalanH$_2$M (a) to the "half" Schiff base, SalanHM (b) and the "full" Schiff base, SalenM (c).

Table 1 Selected bond distances (Å) and angles (deg) for [SaleanH$_2$AlOMe]$_2$ (**9**), [SalophanHFeOMe]$_2$·2MeOH (**10**) and [SalomphanHFeOMe]$_2$·2MeOH (**11**).

(9)		**(10)**		**(11)**	
Al-O(1)	1.828(5)	Fe(1)-O(1)	1.928(8)	Fe(1)-O(1)	1.919(4)
Al-O(2)	1.832(5)	Fe(1)-O(2)	1.941(10)	Fe(1)-O(2)	1.951(5)
Al-O(3)	1.864(5)	Fe(1)-O(3)	1.968(9)	Fe(1)-O(3)	2.029(5)
Al-N(1)	2.073(6)	Fe(1)-N(1)	2.138(11)	Fe(1)-N(1)	2.153(5)
Al-N(2)	2.103(6)	Fe(1)-N(2)	2.169(10)	Fe(1)-N(2)	2.168(5)
Al-O(3A)	1.911(5)	Fe(1)-O(3A)	2.029(11)	Fe(1)-O(3A)	1.979(4)
O(1)-C(1)	1.339(7)	O(1)-C(1)	1.315(15)	O(1)-C(1)	1.299(7)
O(2)-C(16)	1.345(9)	O(2)-C(20)	1.346(13)	O(2)-C(22)	1.335(6)
O(3)-C(17)	1.425(8)	O(3)-C(21)	1.418(19)	O(3)-C(23)	1.400(9)
O(3)-A1A	1.911(5)	N(1)-C(7)	1.302(16)	N(1)-C(7)	1.278(8)
N(1)-C(7)	1.487(9)	N(1)-C(8)	1.439(15)	N(1)-C(8)	1.429(7)
N(1)-C(8)	1.482(9)	N(2)-C(13)	1.443(18)	N(2)-C(15)	1.454(8)
N(2)-C(9)	1.499(10)	N(2)-C(14)	1.520(15)	N(2)-C(16)	1.484(9)
N(2)-C(10)	1.489(8)				
O(1)-Al-O(2)	91.8(2)				
O(1)-Al-O(3)	94.3(2)	O(1)-Fe(1)-O(2)	96.0(4)	O(1)-Fe(1)-O(2)	96.5(2)
O(2)-Al-O(3)	97.8(2)	O(1)-Fe(1)-O(3)	98.0(4)	O(1)-Fe(1)-O(3)	93.1(2)
O(1)-Al-N(1)	92.4(2)	O(2)-Fe(1)-O(3)	94.0(4)	O(2)-Fe(1)-O(3)	167.8(2)
O(2)-Al-N(1)	91.9(2)	O(1)-Fe(1)-N(1)	87.7(4)	O(1)-Fe(1)-N(1)	86.7(2)
O(3)-Al-N(1)	168.0(2)	O(2)-Fe(1)-N(1)	93.9(4)	O(2)-Fe(1)-N(1)	83.3(2)
O(1)-Al-N(2)	174.3(2)	O(3)-Fe(1)-N(1)	169.8(5)	O(3)-Fe(1)-N(1)	94.9(2)
O(2)-Al-N(2)	89.7(2)	O(1)-Fe(1)-N(2)	164.5(4)	O(1)-Fe(1)-N(2)	164.3(2)
O(3)-Al-N(2)	90.9(2)	O(2)-Fe(1)-N(2)	88.1(4)	O(2)-Fe(1)-N(2)	87.7(2)
N(1)-Al-N(2)	82.1(2)	O(3)-Fe(1)-N(2)	96.6(4)	O(3)-Fe(1)-N(2)	85.2(2)
O(1)-Al-O(3A)	93.4(2)	N(1)-Fe(1)-N(2)	77.2(4)	N(1)-Fe(1)-N(2)	77.9(2)
O(2)-Al-O(3A)	172.7(2)	O(1)-Fe(1)-O(3A)	93.1(4)	O(1)-Fe(1)-O(3A)	98.3(2)
O(3)-Al-O(3A)	76.7(2)	O(2)-Fe(1)-O(3A)	167.1(4)	O(2)-Fe(1)-O(3A)	94.4(2)
N(1)-Al-O(3A)	92.9(2)	O(3)-Fe(1)-O(3A)	75.7(4)	O(3)-Fe(1)-O(3A)	76.6(2)
N(2)-Al-O(3A)	85.6(2)	N(1)-Fe(1)-O(3A)	95.6(4)	N(1)-Fe(1)-O(3A)	170.3(2)
		N(2)-Fe(1)-O(3A)	85.5(4)	N(2)-Fe(1)-O(3A)	96.4(2)
		Fe(1)-O(3)-C(21)	128.6(10)	Fe(1)-O(3)-C(23)	127.0(4)
		Fe(1)-O(3)-Fe(1A)	104.3(4)	Fe(1)-O(3)-Fe(1A)	103.4(2)

oxygen incorporation. For example, there is evidence for complexes of formula SalenM·O_2, (SalenMO)n and (SalenM)O (where M = transition metal). These compounds have precedent in the literature; Salen-transition metal complexes are known to be oxygen sensitive.[2] Additionally, these observations follow previous reports of ligand dehydrogenation in other SalanH$_2$-transition metal complexes.[10,11,21] In one rare example a "half" Schiff base complex (Salean(tBu$_2$)$_2$H)Ni formed.[21] In this complex only one arm of the ligand is dehydrogenated (Scheme 1b). Work is currently underway to achieve a systematic understanding of the reaction shown in Scheme 1.

The formation of a "half" Schiff base complex is observed for the Fe derivatives, **10** and **11**. Thus, the combination of LH$_4$ and FeCl$_2$ in MeOH (where L = Salophan and Salomphan), followed by exposure to air leads to both oxidation of the metal (from Fe(II) to Fe(III) and the ligand. This oxidation does not proceed to the full Schiff base (Scheme 1c), but stops at the "half" Schiff base stage (Scheme 1b). This was found for both of the Fe complexes (**10** and **11**) resulting in complexes of formula [SalophanHFeOMe]$_2$ (**10**) and [SalomphanHFeOMe]$_2$ (**11**). This is the first instance where a SalanH$_2$Fe complex has demonstrated such oxygen activity.

Indeed, the iron complexes, in general, are not air sensitive as demonstrated for [SaleanH$_2$FeX]$_2$ (where X = OH[9] and OMe[10]) and SalphanH$_2$Fe (6). The increased oxygen sensitivity of the Salophan and Salomphan ligands may be attributed to the electronic effect of the aryl ring which places more electron density on the NH-CH$_2$ group and makes it more susceptible to electrophilic attack of the O$_2$ molecule. Why the ligands in **10** and **11** only dehyrogenate one time is not immediately clear. However, the reasons for this behaviour will be directly relevant to the mechanism of oxygen coordination in these complexes.

A crystallographic study of **10** and **11** was undertaken to explore a structure-dehydrogenation relationship. The structures of the two compounds were nearly identical, including the presence of two hydrogen-bonded MeOH molecules. The molecular structure and atom-numbering scheme for **10** is representative of the two compounds and is shown in Figure 3. A view accentuating the presence of the hydrogen-bonded MeOH molecules is shown in Figure 4. Important bond distances and angles are located in Table 1. Each structure consists of two LHFeOMe units, with bridging methoxy groups. This gives the Fe atom a distorted octahedral geometry. The most significant distortion from ideal geometry occurs for the angle formed by the axial atoms, (O(1)-Fe(1)-N(2), for **10** (164.5(4) and **11** (164.3(2)°). The equatorial positions are occupied by O(3), O(3a), N(1) and O(2) which are planar (max dev. 0.027 Å). In each structure the Fe-O bond distances for the ligand (ave. 1.935 Å) are somewhat shorter than those for the bridging methoxy group

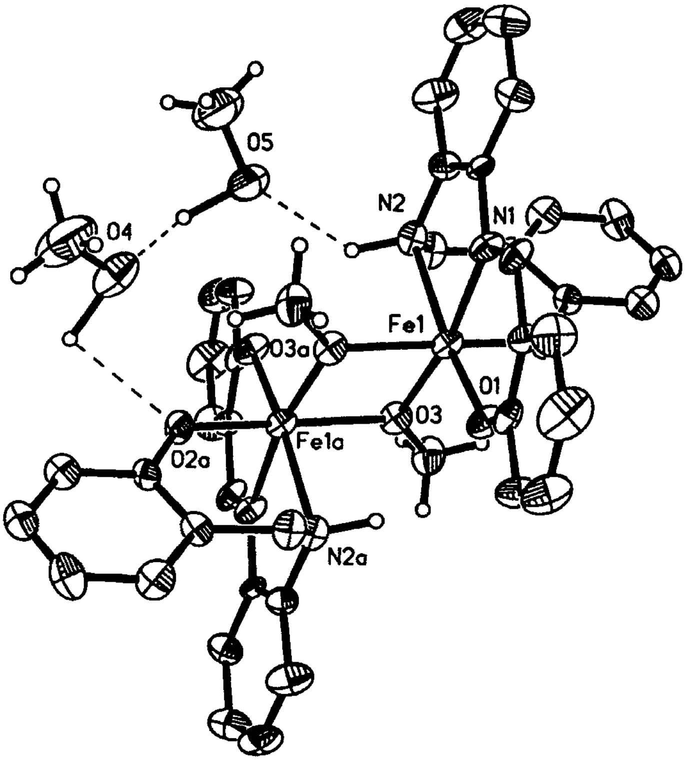


Figure 3 Molecular structure and atom numbering scheme for [SalophanHFeOMe]$_2$ (**10**)

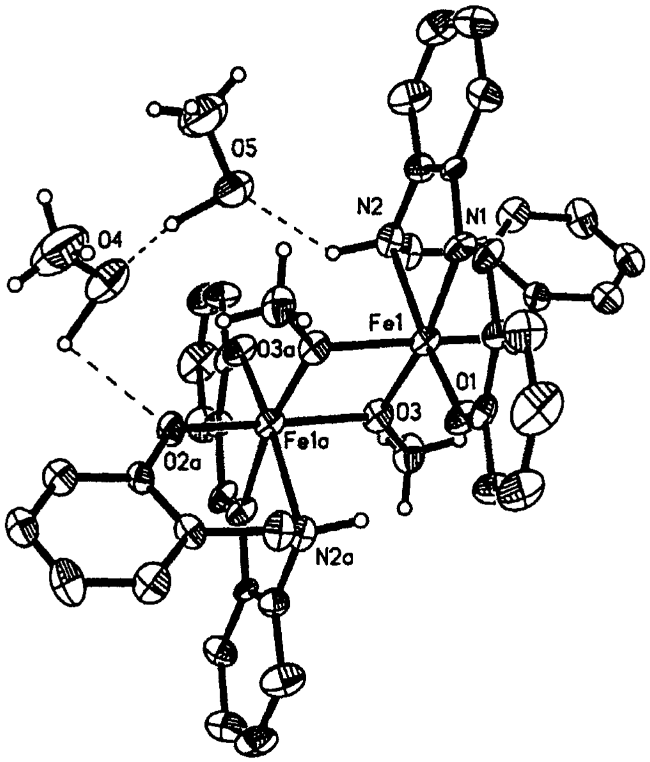


Figure 4 Hydrogen bonding in [SalophanHFeOMe]$_2$·2MeOH (**10**).

(ave. 2.00 Å). The Fe-N distances are marginally longer (ave. 2.155 Å) but do not differ significantly for the N = C group compared to the HN-CH$_2$ group. Additionally, all of the Fe-O and Fe-N distances are marginally longer than found for the Al-O and Al-N bond distances in keeping with the ionic radii of six-coordinate Al^{3+} (0.675 Å) and high spin Fe^{3+} (0.785 Å).[22]

Similar ligand arrangements, bond distances and angles are observed in the structures of [SaleanH$_2$FeX]$_2$ (where X = OH[9], OMe[10]) and for **9** for which there are no N = CH bonds. Surprisingly, this implies that there is little structural change around the central metal on going from a complex with an amine bond, NH-CH$_2$, to one with one imine bond, N = CH as for **10** and **11**.

Another interesting feature of these molecules is that the NH groups participate in hydrogen bonding. Both **10** and **11** exhibit such bonding to a MeOH molecule (which is further hydrogen-bonded to a second methanol). A molecular structure emphasizing the hydrogen-bonded groups for **10** is shown in Figure 4. Compound **11** is isostructural. In each structure the hydrogen bond between the N-H and O is 2.1 Å. There is a secondary contact between the second MeOH group and O(2) at appx. 2.7 Å. It was noted in the introduction that the use of the SalanH$_4$ ligands may lead to interesting structures due to the presence of the amine hydrogen. The structures of **10** and **11** confirm this and also represent a new feature for these molecules that is not present for the Schiff base analogues.

It appears that oxidation of SalanH$_2$M(II) complexes is very dependent on the nature of the Salan ligand. For those which are composed of an aryl group (SalophanH$_4$ and SalomphanH$_4$), the oxidations occur very readily. For those that are not (SalphanH$_2$M; where M = Fe and Cu), the conversion does not occur. In the case of the partially dehydrogenated complexes (**10** and **11**) the reaction may be limited by the ability of the metal to coordinate oxygen, which is apparently the first step in the process.

EXPERIMENTAL PROCEDURE

General Considerations

All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. The ligands SaleanH$_2$, SalpanH$_2$, SalophanH$_2$ and SalomphanH$_2$ were synthesized as previously described.[12] 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 Mattson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

Preparation of SalophanH$_2$Fe (1)

To a solution of SalophanH$_4$ (6.24 mmol, 2.0 g) in MeOH (40 mL) was added two equivalents of NEt$_3$ (12.48 mmol, 1.73 mL). The solution was stirred for 15 min after which a solution of one equivalent of the metal halide FeCl$_2$ (6.24 mmol, 0.79 g) in MeOH (50 mL) was added. The solution was stirred and refluxed for 1 h and then cooled to -30°C for 12h resulting in a red precipitate. The solution was then filtered and the solid pumped to dryness to yield 1.13 g (48.3%) of **1**: Mp 206–208°C. IR (KBr, cm^{-1}): 3283 (s), 3254 (s), 3152 (m, br) 3063 (m), 3030 (m), 2936 (m, Br), 2878 (m), 2606 (w, br), 2498 (w), 1595 (s), 1566 (m), 1480 (s), 1452 (s), 1399 (m), 1265 (s, br), 1111 (s), 1038 (s), 928 (m), 864 (s) 752 (s), 629 (w), 590 (m), 521 (m). Calcd. (SalophanH$_2$Fe·MeOH + ,): C, 59.73; H, 5.25. Found: C, 59.69; H, 5.05.

Preparation of SalophanH$_2$Cu(2)

The preparation was as described for **1** using SalophanH$_4$ (6.24 mmol, 2.0 g), MeOH (40 mL), NEt$_3$ (12.48 mmol, 1.73 mL) and CuCl$_2$ (6.24 mmol, 0.84 g) in MeOH (40 mL). Yield of **1**: 1.05 g (44.1 %): Mp 131–133°C (dec). IR (KBr, cm^{-1}): 3011 (m, br), 2770 (w, br), 2627 (m, br), 2498 (w), 1595 (m), 1549 (w), 1481 (s), 1452 (s), 1398 (w), 1275 (s), 1235 (m), 1113 (m), 1026 (m), 889 (m), 856 (w), 829 (w), 829 (w), 785 (w), 739 (s), 610 (w), 544 (w), 486 (s). Anal. Calcd. (+ MeOH): C, 60.93; H, 5.36. Found: C, 60.65; H, 5.49.

Preparation of SalomphanH$_2$Mn (3)

The preparation was as described for **1** using SalomphanH$_4$ (5.74 mmol, 2.0 g) in

MeOH (60 mL), NEt_3 (11.48 mmol, 1.60 mL), and $MnCl_2$ (5.74 mmol, 0.72 g) in MeOH (60 mL). Yield, 1.45 g (63.0%) of **3**: Mp >260°C. IR (KBr, cm^{-1}): 3237 (m), 3067 (br, w), 2917 (br, m), 2863 (m), 1595 (s), 1510 (s), 1481 (s), 1451 (s), 1321 (s), 1269 (s), 1194 (w), 1113 (m), 1092 (m), 1053 (m), 866 (s), 801 (m), 756 (s), 637 (w), 585 (w), 502 (w), 485 (w). Anal. Calcd. C, 65.84; H, 5.52. Found: C, 65.71; H, 5.62.

Preparation of SalomphanH$_2$Fe (4)

The preparation was as described for **1** using SalomphanH$_4$ (5.74 mmol, 2.0 g), MeOH (60 mL), NEt_3 (11.48 mmol, 1.60 mL) and $FeCl_2$ (5.74 mmol, 0.73 g) in MeOH (60 mL). Yield of pale red **4**: 1.43 g (61.9%): Mp 155–7°C (dec). IR (KBr, cm^{-1}): 3248 (m), 3142 (br, m), 3055 (m), 3027 (m), 2920 (m), 2879 (m), 2607 (m), 1595 (s), 1566 (w), 1508 (m), 1480 (s), 1451 (s), 1400 (m), 1279 (br, s), 1196 (w), 1111 (w), 1040 (s), 928 (m), 880 (s), 851 (w), 754 (s), 729 (w), 623 (w), 606 (w), 525 (w), 500 (m), 478 (s). Anal. Calcd. (+MeOH): C, 63.61; H, 6.03. Found: C, 63.37; H, 6.05.

Preparation of SalomphanH$_2$Cu (5)

The preparation was as described for **1** using SalomphanH$_4$ (5.74 mmol, 2.0 g), MeOH (60 mL), NEt_3 (11.48 mmol, 1.60 mL) and $CuCl_2$ (5.74 mmol, 0.77 g) in MeOH (40 mL). Yield of green **5**: 1.55 g (65.9%): Mp 162–4°C (dec). IR (KBr, cm^{-1}): 3063 (m), 3007 (m), 2967 (m), 2924 (m), 2841 (br, s), 2498 (m), 2284 (br, w), 1595 (s), 1570 (w), 1508 (m), 1480 (s), 1452 (s), 1400 (w), 1285 (s), 1229 (m), 1200 (w), 1150 (m), 1113 (m), 1094 (w), 1038 (w), 1005 (w), 926 (w), 883 (m), 847 (w), 799 (m), 752 (s), 729 (m), 631 (w), 577 (m), 548 (w), 486 (m). Anal. Calcd. (+MeOH): C, 62.50; H, 5.93. Found: C, 62.71; H, 6.21.

Preparation of SalpanH$_2$Fe (6)

The preparation was as described for **1** using SalpanH$_4$ (6.94 mmol, 2.0 g), MeOH (125 mL), NEt_3 (13.87 mmol, 1.93 mL) and $FeCl_2$ (6.94 mmol, 0.88 g) in MeOH (50 mL). Yield of **5**: 1.32 g (55.4%): Mp 210–212°C (dec). IR (KBr, cm^{-1}): 3369 (w, br), 3263 (m), 3177 (s, br), 3059 (m), 3005 (m), 2916 (s), 2866 (s), 2809 (s), 2591 (w), 1593 (s), 1566 (s), 1480 (s), 1451 (s), 1364 (w), 1287 (s, br), 1150 (m), 1111 (m), 1044 (s), 909 (s), 880 (s), 824 (w), 756 (s), 729 (s), 665 (w), 615 (m), 590 (m), 569 (w), 507 (s), 459 (s), 428 (m). Anal. Calcd (+MeOH): C, 58.08; H, 6.49. Found: C, 58.10; H, 6.38.

Preparation of SalpanH$_2$Cu (7)

The preparation was as described for **1** using SalpanH$_4$ (6.94 mmol, 2.0 g), MeOH (125 mL), NEt_3 (13.87 mmol, 1.93 mL) and $CuCl_2$ (6.94 mmol, 0.93 g) in MeOH (50 mL). Yield of **7**: 1.54 g (63.8%): Mp 240-242°C (dec). IR (KBr, cm^{-1}): 3160 (s), 3061 (s), 2901 (s), 2863 (s), 2604 (w, br), 1593 (s), 1564 (s), 1478 (s), 1447 (s), 1283 (s, br), 1192 (w), 1146 (w), 1111 (m), 1076 (s), 1036 (s), 1013 (s), 988 (m), 918 (s), 874 (s), 812 (w), 758 (s), 733 (s), 583 (m), 561 (w), 521 (w), 480 (m) 436 (w). Anal. Calcd: C, 58.69; H, 5.79. Found: C, 58.71; H, 5.86.

Preparation of SaleanH$_2$AlCl (8)

To a suspension of SaleanH$_4$ (3.00 g, 11.02 mmol) in toluene (50 mL) at 25°C was added a solution of Me$_2$AlCl (1.328 g, 11.02 mmol), cooled to −30°C, in toluene (40 mL). The dimethlyaluminium chloride solution was added slowly over a period of several min. A white precipitate formed and a gas evolved upon addition. The mixture was stirred at 25°C for 2 h, filtered and the solid dried in *vacuo* yielding (**8**) as a white powder (3.186 g, 87%). mp >260°C. IR (KBr) 3219 m, 3032 m, 2939 m, 2860 m, 1601 s, 1487 s, 1456 s, 1292 s(br), 1031 m, 885 s, 756 s, 638 m. Anal. Calcd: C 57.75; H 5.45. Found, C 57.75, H 5.86.

Preparation of [SaleanH$_2$AlOMe]$_2$·2MeOH (9)

To (**8**) (2.00 g, 6.01 mmol) at 25°C was added MeOH (50 mL). The resulting white suspension was stirred for 3h. The mixture was filtered and the solid dried *in vacuo* yielding (**9**) as a white powder (1.11 g, 51%). Crystals of (**9**) were obtained by slow concentration of the filtrate at 25°C mp >260°C. IR (KBr) 3396 br, 3221 s, 2945 m, 2906 m, 2831 m, 1601 s, 1485 s, 1454 s, 1402 m, 1300 s, 1076 s, 901 m, 756 s, 638 s. Anal. Calcd: C, 60.00; H, 6.94; Found: C, 59.90; H, 6.94.

Preparation of [SalophanHFe(OMe)]$_2$·2MeOH (10)

A sample of **1** was dissolved in MeOH and then stirred in air, resulting in an immediate color change from red to brown. The conversion of **1** to **10** was quantitative. Mp 181-183°C (dec). IR (KBr, cm^{-1}): 3461 (s, br), 3117 (s, br), 2912 (w, br), 2818 (w), 1611 (s), 1539 (s), 1460 (s, br), 1387 (m), 1317 (m), 1275 (s), 1204 (w), 1152 (w), 1128 (w), 1045 (m), 980 (w), 922 (w), 878 (m), 752 (s), 608 (w), 482 (s). Anal. Calcd: C, 60.43; H, 5.76. Found: C, 59.89; H, 5.55.

Preparation of [SalomphanHFe(OMe)]$_2$·2MeOH (11)

A sample of **4** (0.1 g, 0.25 mmol) was dissolved in MeOH (20mL) and then stirred in air, resulting in an immediate color change from red to brown. The conversion of **4** to **11** was quantitative. Mp 130–132°C (dec). IR (KBr, cm^{-1}): 3434 (w, br), 3125 (w, br), 2917 (m, br), 2812 (w), 2625 (w, br), 2498 (w), 1615 (s), 1599 (s), 1537 (s), 1507 (w), 1478 (s), 1443 (s), 1381 (m), 1321 (m), 1290 (s, br), 1211 (w), 1181 (w), 1148 (m), 1040 (m), 918 (w), 880 (m), 752 (m), 604 (w), 498 (m). Anal. Calcd: C, 62.21; H, 5.87. Found: C, 62.43; H, 5.83.

X-Ray Experimental

For **9**, **10** and **11** crystals suitable for X-ray analysis were grown from the filtrate over several weeks at −30°C. There was one molecule of MeOH as solvent of crystallization for **9**. For **10** and **11** there were two MeOH molecules that were hydrogen bonded to the complex. Each structure was collected in the centrosymmetric space group P-1. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 2. Atomic coordinates for complexes (**9**), (**10**) and (**11**) are found in Tables 3, 4, and 5. Data were collected on a Siemens P4 diffractometer using graphite monochromated MoK$_\alpha$ (0.71073 Å)

Table 2 Crystal data for [SaleanAlOMe]$_2$ (**9**), [SalophanHFeOMe]$_2$·2MeOH (**10**) and [SalomphanHFeOMe]$_2$·2MeOH (*11*)

Compound	**9**	**10**	**11**
Formula	$C_{36}H_{46}Al_2N_4O_7$	$C_{46}H_{46}Fe_2N_4O_8$	$C_{48}H_{54}Fe_2N_4O_8$
Formula weight	700.7	894.6	926.7
Crystal System	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a (Å)	7.536(1)	9.400(2)	9.047(2)
b (Å)	10.513(2)	10.718(4)	11.723(2)
c (Å)	11.997(2)	12.354(3)	12.419(3)
α(°)	97.72(1)	76.28(3)	80.14(2)
β(°)	93.45(1)	67.89(2)	68.68(3)
γ(°)	102.73(1)	86.63(3)	85.88(2)
V(Å^3)	914.8(3)	1119.7(7)	1208.8(4)
Z	2	2	2
D_{calc} (Mg/cm^3)	1.272	1.386	1.317
Crystal size (mm)	$(0.4)^3$	$(0.3)^3$	0.4 × 0.2 × 0.2
Temperature (K)	298	298	298
2θ range(deg)	3.5–45	2.0–45	2.0–45
Scan type	2θ–θ	2θ–θ	2θ–θ
Scan speed (deg/min)	8–60	8–60	8–60
Scan range (deg)	0.60	0.73	0.60
Reflections collected	3038	3566	3877
Indp Reflections	2387	2920	3161
Obsd Reflections	1226	1327	2171
(F > X σ (F))	6	6	4
No parameters	226	289	307
R	0.0540	0.0672	0.0546
R_w	0.0565	0.0749	0.0573
GOF	1.07	2.28	1.38
LarDiff.Peak (e/Å^3)	0.32	0.72	0.40

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (× 10^3) for [SaleanH$_2$AOMe]$_2$ (**9**)

Atom	x/a	y/b	z/c	U(eq)
Al	4575(3)	9592(2)	1106(2)	39(1)
O(1)	4199(6)	11185(4)	1727(4)	49(2)
O(2)	2571(6)	8698(4)	1701(4)	48(2)
O(3)	3444(6)	9627(4)	-312(3)	42(2)
O(4)	467(8)	320(8)	3084(6)	104(3)
N(1)	6294(7)	9505(5)	2495(4)	41(2)
N(2)	5221(8)	7788(5)	517(4)	45(2)
C(1)	5033(9)	12008(7)	2652(6)	44(3)
C(2)	5044(10)	13351(7)	2727(6)	54(3)
C(3)	5806(11)	14227(8)	3682(7)	66(4)
C(4)	6632(11)	13808(8)	4575(8)	69(4)
C(5)	6644(10)	12483(8)	4512(6)	59(3)
C(6)	5838(10)	11575(7)	3565(6)	45(3)
C(7)	5732(10)	10128(7)	3563(5)	50(3)
C(8)	6317(9)	8105(6)	2529(6)	47(3)
C(9)	6584(10)	7483(7)	1343(6)	55(3)
C(10)	3593(11)	6679(7)	162(6)	59(3)
C(11)	2390(10)	6398(7)	1086(6)	53(3)
C(12)	1691(12)	5093(9)	1241(8)	77(4)
C(13)	570(14)	4810(10)	2077(10)	97(5)
C(14)	143(11)	5811(10)	2774(9)	83(5)
C(15)	806(9)	7106(8)	2645(7)	61(3)
C(16)	1937(9)	7423(8)	1802(6)	48(3)
C(17)	1578(10)	9064(8)	-706(7)	70(4)
C(18)	1029(13)	1404(11)	3887(10)	122(6)

Table 4 Atomic coordinates (× 10^5) and equivalent isotropic displacement coefficients (× 10^4) for $[\mathrm{SalophanHFeOMe}]_2 \cdot 2\mathrm{MeOH}$ (**10**)

Atom	x/a	y/b	z/c	U(eq)
Fe(1)	341(2)	1377(2)	116(2)	35(1)
O(1)	- 865(10)	1136(9)	1809(8)	48(4)
O(2)	2140(9)	2133(9)	159(8)	46(4)
O(3)	1188(9)	- 350(9)	157(8)	42(4)
O(4)	- 1870(15)	- 1106(15)	7419(11)	92(7)
O(5)	136(14)	1097(12)	6595(10)	84(7)
N(1)	- 731(12)	3178(11)	- 150(10)	40(5)
N(2)	1285(11)	2070(12)	- 1821(9)	39(5)
C(1)	- 2065(14)	1721(14)	2416(11)	39(6)
C(2)	- 2864(15)	1136(14)	3620(11)	52(7)
C(3)	- 4102(19)	1711(18)	4328(13)	73(9)
C(4)	- 4599(17)	2883(20)	3848(14)	81(9)
C(5)	- 3823(16)	3465(15)	2652(13)	63(8)
C(6)	- 2557(14)	2887(12)	1928(10)	37(6)
C(7)	- 1840(15)	3585(14)	686(11)	47(7)
C(8)	- 122(14)	3950(13)	- 1360(11)	33(6)
C(9)	- 489(15)	5220(14)	- 1685(13)	50(7)
C(10)	101(16)	5913(16)	- 2844(15)	63(8)
C(11)	1166(18)	5308(19)	- 3682(13)	73(9)
C(12)	1569(17)	4048(18)	- 3386(13)	66(8)
C(13)	946(15)	3397(14)	- 2197(11)	41(6)
C(14)	2986(13)	1795(14)	- 2295(11)	45(6)
C(15)	3921(14)	2572(12)	- 1924(12)	39(6)
C(16)	5316(16)	3162(15)	- 2740(13)	58(7)
C(17)	6257(16)	3808(15)	- 2417(15)	62(8)
C(18)	5806(16)	3893(13)	- 1232(14)	53(8)
C(19)	4423(15)	3331(14)	- 401(13)	50(7)
C(20)	3463(14)	2676(13)	- 702(12)	37(6)
C(21)	2564(16)	- 790(15)	316(15)	63(8)
C(22)	- 3266(27)	- 897(27)	7329(20)	163(18)
C(23)	- 258(25)	1743(23)	5663(18)	125(15)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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. Hydrogen atoms involved in hydrogen bonding were found from difference Fourier maps and refined as free atoms.

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Table 5 Atomic coordinates (× 10^5) and equivalent isotropic displacement coefficients (× 10^4) for [SalomphanFeOMe]$_2$·2MeOH (**11**)

Atom	x/a	y/b	z/c	U(eq)
Fe(1)	362(1)	1217(1)	215(1)	36(1)
O(1)	-930(5)	1055(4)	1846(4)	49(2)
O(2)	2216(5)	1838(3)	355(3)	43(2)
O(3)	-1217(5)	384(3)	-182(4)	44(2)
O(4)	265(9)	1019(5)	6604(5)	99(4)
O(5)	-1948(8)	-803(5)	7340(5)	98(4)
N(1)	-729(6)	2897(4)	36(4)	37(2)
N(2)	1395(6)	1802(4)	-1654(4)	37(2)
C(1)	-2139(8)	1623(6)	2463(6)	46(3)
C(2)	-2995(9)	1139(7)	3627(6)	63(3)
C(3)	-4248(11)	1718(8)	4295(7)	84(4)
C(4)	-4723(12)	2792(9)	2890(8)	107(5)
C(5)	-3905(10)	3279(8)	2764(7)	80(4)
C(6)	-2627(8)	2719(6)	2036(6)	47(3)
C(7)	-1852(8)	3307(5)	850(6)	48(3)
C(8)	-86(7)	3564(5)	-1104(5)	38(3)
C(9)	-489(8)	4709(5)	-1406(6)	42(3)
C(10)	94(8)	5282(5)	-2553(6)	49(3)
C(11)	-450(9)	6505(6)	-2839(7)	62(3)
C(12)	1164(9)	4717(6)	-3407(6)	52(3)
C(13)	1880(12)	5313(7)	-4661(7)	90(4)
C(14)	1591(9)	3580(6)	-3106(6)	57(3)
C(15)	968(7)	2998*5)	-1970(5)	40(3)
C(16)	3132(9)	1580(6)	-2054(6)	46(3)
C(17)	3972(8)	2357(5)	-1629(6)	44(3)
C(18)	5264(9)	2985(6)	-2407(6)	57(3)
C919)	6048(9)	3704(7)	-2018(8)	71(4)
C(20)	5544(9)	3799(6)	-857(8)	62(4)
C(21)	4248(8)	3183(6)	-65(7)	53(3)
C(22)	3452(7)	2433(5)	-438(6)	42(3)
C(23)	-2600(8)	850(6)	-351(7)	58(3)
C(24)	-239(16)	1635(9)	5745(10)	134(8)
C(25)	-3399(13)	-627(11)	7285(11)	140(8)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

SUPPLEMENTARY MATERIAL

Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, observed and calculated structure factors and unit cell views are available upon request.

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