Aluminium Complexes of *N,N'*-Ethylenebis(salicylideneimine)-(H_2salen). X-Ray Crystal Structures of [{Al(salen)}$_2$(μ-O)]·MeCN and [Al($OC_6H_2Me_3$-2,4,6)(salen)]†

Patrick L. Gurian,[a] Linda K. Cheatham,[a] Joseph W. Ziller[b] and Andrew R. Barron*[,a]

[a] *Department of Chemistry and Materials Research Laboratory, Harvard University, Cambridge, MA 02138, USA*

[b] *Department of Chemistry, University of California, Irvine, CA 94717, USA*

The reaction of $AlMe_3$ with H_2salen [*N,N'*-ethylenebis(salicylideneimine)] in MeCN gives the five-co-ordinate aluminium complex [AlMe(salen)] **1**. The interaction of **1** with H_2O, HOPh, $HOC_6H_4Bu^t$-4, $HOC_6H_2Me_3$-2,4,6, HO_2CMe, HO_2CPh, acetylacetone and 2-$HOC_6H_4C(O)Me$ has been studied, and the X-ray structures of two of the products [{Al(salen)}$_2$(μ-O)]·MeCN and [Al($OC_6H_2Me_3$-2,4,6)(salen)] have been determined. The proton and ^{27}Al-{^{1}H} NMR and IR spectra of the compounds have been recorded.

Group 13 (Ölander numbering) Schiff-base[1] complexes are surprisingly rare[2–6] when compared to the large number of trivalent transition-metal complexes that are known.[7] In the most extensive study to date Dzugan and Goedken[6] reported the reaction of $AlEt_3$ with a variety of tetradentate Schiff-base ligands. They showed that all the Schiff bases studied formed 1:1 adducts in which the aluminium had a five-co-ordinate square-based pyramidal geometry. Despite the possibility that the reactivity of these five-co-ordinate aluminium centres would be different from the more usual four-co-ordinate tetrahedral geometry, little attempt has been made to study their reaction chemistry. A report of the use of an aluminium complex of a chiral Schiff base as an initiator for the stereoselective oligomerization of methyloxirane[8] has prompted our investigation of the reactivity of methylaluminium Schiff-base complexes.

Results and Discussion

Interaction of $AlMe_3$ with 1 equivalent of *N,N'*-ethylenebis(salicylideneimine) (H_2salen) in MeCN allows the isolation of the pale yellow, air-sensitive [AlMe(salen)] **1** [equation (1)]. Compound **1** has been characterized by elemental analysis,

$$AlMe_3 + H_2salen \longrightarrow [AlMe(salen)] + 2CH_4 \quad (1)$$

IR and NMR spectroscopy (see Experimental section and Table 1). The ^{1}H NMR spectrum indicates both an inequivalence of the bridging methylene *endo* and *exo* protons, and a single vinylic resonance for the salen ligand, consistent with its tetradentate co-ordination about the aluminium in an analogous manner to that reported for the ethyl complex [AlEt(salen)].[6] The ^{27}Al-{^{1}H} NMR spectrum for **1** shows a broad resonance at δ 65 ($w_{\frac{1}{2}}$ = 1466 Hz), consistent with a five-co-ordinate aluminium centre.[9]

Several efforts were made to obtain crystals of compound **1** suitable for X-ray analysis. Although a set of crystals isolated from MeCN were most promising, the structure could be solved only by applying constraints on some of the atoms, and is of very poor quality.[10] The determination is sufficient, however, to demonstrate that the structure is essentially the same as that of the ethyl analogue;[6] the aluminium is five-co-ordinate in close to a square-faced pyramidal geometry.

Hydrolysis.—Hydrolysis of [AlEt(salen)] in moist solvents has been previously reported[6] to yield the hydroxy complex [Al(OH)(salen)], which in the presence of the parent alkyl complex reacts to give the μ-oxo species [equation (2)], R = Me or Et. The hydrolysis of **1** proceeds in an identical manner.

$$[AlR(salen)] \xrightarrow[-RH]{+H_2O} [Al(OH)(salen)] \xrightarrow[-RH]{+[AlR(salen)]} [\{Al(salen)\}_2(\mu\text{-}O)] \quad (2)$$

2

Crystals of [{Al(salen)}$_2$(μ-O)] **2** suitable for X-ray crystallography were obtained by the atmospheric hydrolysis of a concentrated MeCN solution of **1**. The structure of compound **2** is shown in Fig. 1; selected bond lengths and angles are given in Table 2. The crystallographic asymmetric unit contains, in addition to a molecule of **2**, a molecule of MeCN of solvation. Compound **2** consists of two Al(salen) moieties linked by a single oxygen atom bridge. Both aluminium atoms are five-co-ordinate. The co-ordination geometry around Al(2) is close to a square-based pyramid with the salen ligand occupying the basal sites, whilst the geometry around Al(1) is intermediate between square-based pyramidal and trigonal bipyramidal, where O(11) and N(21) occupy the pseudo-axial positions. The two salen ligands have the 'asymmetric umbrella' conformation, previously observed for other five-co-ordinate salen complexes.[7] In this arrangement, the ethylenediamine bridge is in a *gauche* conformation, and the two salicylaldimine groups of each ligand are both bent away from the bridging oxygen atom [O(1)]. A similar arrangement was observed in both the solvated[11,12] and unsolvated[13] structure of [{Fe(salen)}$_2$(μ-O)].

The Al(1)–O(1)–Al(2) angle [152.0(3)°] is larger than the range observed for the iron analogue [Fe–O–Fe' 139.1–144.6°],[11–13] consistent with the increased steric repulsion between the two salen ligands as a result of the decreased metal–oxygen distance in the aluminium *versus* the iron complex. The Al–O(1) distances [average = 1.705(5) Å] are comparable to the values reported for other oxo-bridged complexes containing

† μ-Oxo-bis{[*N,N'*-ethylenebis(salicylideniminato)-κ*N,N',O,O'*]-aluminium(III)}–acetonitrile (1/1) and [ethylenebis(salicylideneiminato)-κ*N,N',O,O'*](2,4,6-trimethylphenoxo)aluminium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Proton and ^{27}Al-{^1H} NMR data (298 K) for new complexes; J and $w_{\frac{1}{2}}$ values in Hz

Compound	^1H	Assignment	^{27}Al-{^1H}[a]
1 [AlMe(salen)]	8.40 (s)	2 H N=CH	65 (1460)
	7.52 [t, J(H–H) 8.6]	2 H	
	7.30 [d, J(H–H) 8.6]	2 H	
	7.26 [d, J(H–H) 8.6]	2 H	C_6H_4
	6.88 [t, J(H–H) 8.6]	2 H	
	4.14 (m)	2 H	
	3.87 (m)	2 H	C_2H_4
	−0.87 (s)	3 H Al–CH_3	
2 [{Al(salen)}$_2$(μ-O)]	7.97 (s)	4 H N=CH	*b*
	7.47 [t, J(H–H) 8.4]	4 H	
	7.05 (m)	8 H	C_6H_4
	6.82 [t, J(H–H) 8.4]	4 H	
	4.13 (m)	4 H	
	3.57 (m)	4 H	C_2H_4
3 [Al(OPh)(salen)]	8.44 (s)	2 H N=CH	29 (469)
	7.56 (m)	2 H	
	7.32 (m)	4 H	C_6H_4
	7.07 (m)	2 H	
	6.96 [d, J(H–H) 7.6]	2 H *m*-CH, Ph	
	6.74 [t, J(H–H) 7.6]	1 H *p*-CH, Ph	
	6.64 [d, J(H–H) 7.6]	2 H *o*-CH, Ph	
	4.14 (m)	2 H	C_2H_4
	3.83 (m)	2 H	
4 [Al($OC_6H_4Bu^t$-4)(salen)]	8.52 (s)	2 H N=CH	30 (463)
	7.58 [t, J(H–H) 8.2]	2 H	
	7.34 (m)	4 H	C_6H_4
	6.92 [t, J(H–H) 8.2]	2 H	
	7.09 (m)	2 H *o*-CH, Ph	
	6.58 (m)	2 H *m*-CH, Ph	
	4.24 (m)	2 H	C_2H_4
	3.89 (m)	2 H	
	1.33 (s)	9 H Bu^t	
5 [Al($OC_6H_2Me_3$-2,4,6)(salen)]	8.49 (s)	2 H N=CH	30 (470)
	7.56 [t, J(H–H) 8.2]	2 H	
	7.39 [d, J(H–H) 8.2]	2 H	C_6H_4
	7.23 [d, J(H–H) 8.2]	2 H	
	6.92 [t, J(H–H) 8.2]	2 H	
	6.70 (s)	2 H *m*-CH, $C_6H_2Me_3$	
	4.25 (m)	2 H	C_2H_4
	3.90 (m)	2 H	
	2.33 (s)	3 H *p*-CH_3, $C_6H_2Me_3$	
	2.00 (s)	6 H *o*-CH_3, $C_6H_2Me_3$	
6 [Al(O_2CMe)(salen)]	8.58 (s)	2 H N=CH	25 (651)
	7.61 [t, J(H–H) 7.1]	2 H	
	7.42 [d, J(H–H) 7.1]	2 H	
	7.30 [d, J(H–H) 7.1]	2 H	C_6H_4
	6.95 [t, J(H–H) 7.1]	2 H	
	4.48 (m)	2 H	
	3.98 (m)	2 H	C_2H_4
	2.08 (s)	3 H O_2CCH_3	
7 [Al(O_2CPh)(salen)]	8.59 (s)	2 H N=CH	28 (734)
	8.05 [d, J(H–H) 8.0]	2 H *o*-CH, Ph	
	7.62 (m)	2 H *p*-CH, Ph and C_6H, salen	
	7.44 (m)	4 H *m*-CH, Ph and C_6H, salen	
	7.29 [d, J(H–H) 8.0]	2 H	C_6H_2
	6.95 [t, J(H–H) 8.0]	2 H	
	4.55 (m)	2 H	
	4.01 (m)	2 H	C_2H_4
8 [Al(acac)(salen)]	8.37 (s)	2 H N=CH	2 (253)
	7.47 [t, J(H–H) 7.5]	2 H	
	7.36 [d, J(H–H) 7.5]	2 H	
	7.17 [d, J(H–H) 7.5]	2 H	C_6H_4
	6.80 [t, J(H–H) 7.5]	2 H	
	5.57 (s)	1 H CH, acac	
	4.25 (br s)	2 H	C_2H_4
	3.71 (br s)	2 H	
	2.01 (br s)	3 H	CH_3, acac
	1.86 (br s)	3 H	
9 [Al{2-$OC_6H_4C(O)Me$}(salen)]	8.37 (s)	2 H N=CH	9 (2720)
	7.29 [d, J(H–H) 6.8]	2 H	
	7.26 [t, J(H–H) 6.8]	2 H	C_6H_4
	6.72 [d, J(H–H) 6.8]	2 H	
	6.60 [t, J(H–H) 6.8]	2 H	

Table 1 (*continued*)

Compound	^{1}H	Assignment	^{27}Al-{^{1}H}[a]
9 [Al{2-OC$_6$H$_4$C(O)Me}(salen)]	7.24 [d, *J*(H–H) 8.0]	1 H	
	6.92 [t, *J*(H–H) 8.0]	1 H	
	6.62 [d, *J*(H–H) 8.0]	1 H } C$_4$H$_4$, Ph	
	6.28 [t, *J*H–H) 8.0]	1 H	
	3.83 (br s)	2 H } C$_2$H$_4$	
	3.75 (br s)	2 H	
	2.16 (s)	3 H Me, Ph	

[a] $w_{\frac{1}{2}}$ In parentheses. [b] Insufficiently soluble.

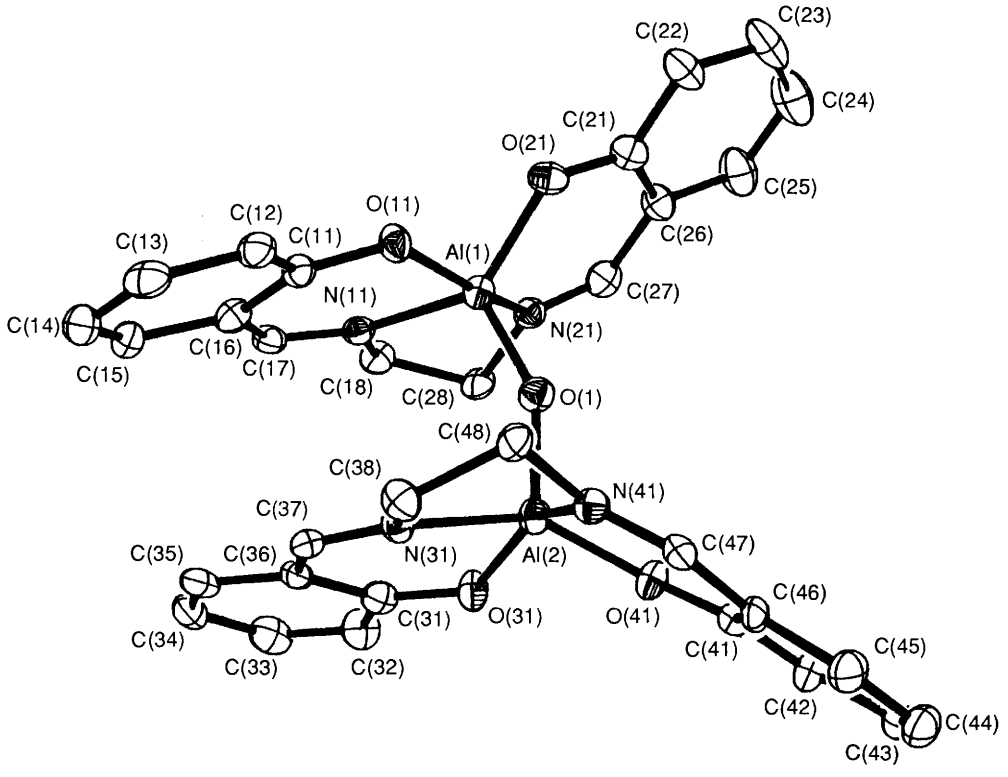


Fig. 1 The molecular structure of [{Al(salen)}$_2$(μ-O)] **2**. Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for [{Al(salen)}$_2$-(μ-O)]·MeCN **2**

Al(1)–O(11)	1.836(5)	Al(1)–O(21)	1.809(5)
Al(1)–N(11)	2.024(6)	Al(1)–N(21)	2.013(6)
Al(1)–O(1)	1.697(5)	Al(2)–O(1)	1.713(5)
Al(2)–O(31)	1.825(5)	Al(2)–O(41)	1.816(4)
Al(2)–N(31)	2.040(6)	Al(2)–N(41)	1.992(6)
O(11)–C(11)	1.320(8)	O(21)–C(21)	1.349(9)
N(11)–C(17)	1.306(9)	N(11)–C(18)	1.487(9)
N(21)–C(27)	1.288(10)	N(21)–C(28)	1.464(9)
O(31)–C(31)	1.328(9)	O(41)–C(41)	1.315(9)
N(31)–C(37)	1.281(9)	N(31)–C(38)	1.478(9)
N(41)–C(47)	1.290(10)	N(41)–N(48)	1.477(7)
O(11)–Al(1)–O(21)	89.0(2)	O(11)–Al(1)–N(11)	88.4(2)
O(11)–Al(1)–N(21)	159.3(3)	O(11)–Al(1)–O(1)	104.7(2)
O(21)–Al(1)–N(11)	131.9(3)	O(21)–Al(1)–N(21)	88.3(2)
O(21)–Al(1)–O(1)	116.5(2)	N(11)–Al(11)–N(21)	78.3(2)
N(11)–Al(1)–O(1)	110.6(2)	N(21)–Al(1)–O(1)	94.9(2)
O(31)–Al(2)–O(41)	86.9(2)	O(21)–Al(2)–N(41)	87.9(2)
O(31)–Al(2)–N(41)	147.4(3)	O(31)–Al(2)–O(1)	108.4(3)
O(41)–Al(2)–N(31)	145.3(3)	O(41)–Al(2)–O(41)	88.5(2)
O(41)–Al(2)–O(1)	110.4(2)	N(31)–Al(2)–N(41)	77.8(2)
N(31)–Al(2)–O(1)	103.9(2)	N(41)–Al(2)–O(1)	103.5(3)
Al(1)–O(1)–Al(2)	152.0(3)		

two five-co-ordinate aluminium atoms [1.679(2) and 1.68(1) Å] in which the Al–O–Al angle is 180°.[14,15]

Phenols.—Treatment of compound **1** with 1 equivalent of R′OH in MeCN results in *ca.* 80% yield of [Al(OR′)(salen)] (R′ = Ph **3**, C$_6$H$_4$Bu^t-4 **5** or C$_6$H$_2$Me$_3$-2,4,6 **6**) [equation (3)].

$$[AlMe(salen)] + R'OH \longrightarrow [Al(OR')(salen)] + CH_4 \quad (3)$$

No reaction is observed for the sterically hindered phenol HOC$_6$H$_2$Bu$^t_2$-2,6-Me-4. Compounds **3**–**5** have been characterized by IR and NMR spectroscopy (see Experimental section and Table 1). The ^{27}Al-{^{1}H} NMR spectrum for each compound consists of a broad peak centred between δ 29 and 30 indicative of a five-co-ordinate aluminium centre.[9] The peak positions for the phenoxide complexes are shifted approximately 35 ppm upfield of that found for the methyl derivative. This upfield shift of the ^{27}Al NMR signal with substitution of a methyl group by an aryl oxide is counter intuitive based on the relative electronegativity of these substituents. We have previously observed a similar but more pronounced trend in four-co-ordinate monomeric aluminium aryl oxide compounds,[16] which was found to be consistent with the presence of a degree of π donation of electron density from oxygen onto aluminium. It is possible, therefore, that a similar π donation is present in compounds **3**–**5**.

Table 3 Selected bond lengths (Å) and angles (°) for [Al($OC_6H_2Me_3$-2,4,6)(salen)] **5**

Molecule 1		Molecule 2	
Al(1)–O(1)	1.787(3)	Al(2)–O(4)	1.791(3)
Al(1)–O(2)	1.798(2)	Al(2)–O(5)	1.797(2)
Al(1)–O(3)	1.737(3)	Al(2)–O(6)	1.741(2)
Al(1)–N(1)	1.994(2)	Al(2)–N(3)	1.998(2)
Al(1)–N(2)	2.000(3)	Al(2)–N(4)	1.998(3)
O(1)–C(1)	1.332(4)	O(4)–C(26)	1.330(4)
O(2)–C(16)	1.323(3)	O(5)–C(41)	1.321(4)
O(3)–C(17)	1.358(3)	O(6)–C(42)	1.346(3)
N(1)–C(7)	1.288(5)	N(3)–C(32)	1.286(4)
N(1)–C(8)	1.468(5)	N(3)–C(33)	1.457(5)
N(2)–C(9)	1.480(3)	N(4)–C(34)	1.483(3)
N(2)–C(10)	1.292(4)	N(4)–C(35)	1.295(4)
O(1)–Al(1)–O(2)	89.1(1)	O(4)–Al(2)–O(5)	90.4(1)
O(1)–Al(1)–O(3)	113.1(1)	O(4)–Al(2)–O(6)	115.3(1)
O(1)–Al(1)–N(1)	89.5(5)	O(4)–Al(2)–N(3)	89.3(1)
O(1)–Al(1)–N(2)	136.5(1)	O(4)–Al(2)–N(4)	132.8(1)
O(2)–Al(1)–O(3)	105.1(1)	O(5)–Al(2)–O(6)	102.9(1)
O(2)–Al(1)–N(1)	161.5(1)	O(5)–Al(2)–N(3)	164.3(1)
O(2)–Al(1)–N(2)	89.6(1)	O(5)–Al(2)–N(4)	89.8(1)
O(3)–Al(1)–N(1)	92.4(1)	O(6)–Al(2)–N(3)	91.4(1)
O(3)–Al(1)–N(2)	109.2(1)	O(6)–Al(2)–N(4)	110.6(1)
N(1)–Al(1)–N(2)	78.8(1)	N(3)–Al(2)–N(4)	79.0(1)
Al(1)–O(3)–C(17)	134.5(2)	Al(2)–O(6)–C(42)	140.1(2)

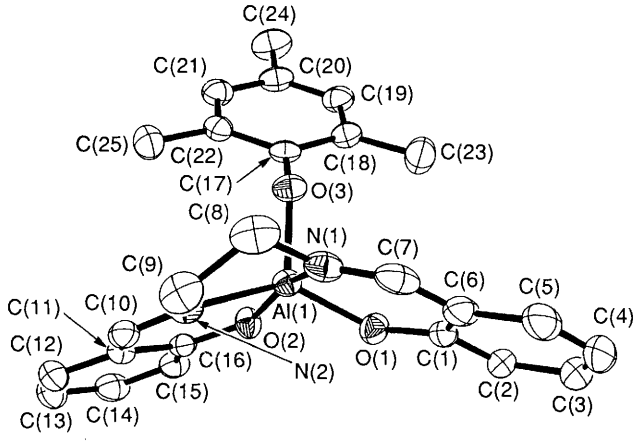


Fig. 2 The molecular structure of one of the two independent molecules of [Al($OC_6H_2Me_3$-2,4,6)(salen)] **5**. Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity

The molecular structure of compound **5** has been determined by X-ray crystallography. The two independent molecules present in the asymmetric units are shown in Fig. 2; selected bond lengths and angles are given in Table 3. As predicted by ^{27}Al-{^{1}H} NMR spectroscopy, compound **5** is monomeric with five-fold co-ordination around aluminium. The geometry around both aluminium atoms is intermediate between trigonal bipyramidal and square-based pyramidal, with pseudo-axial sites occupied by O(2) and N(1) on Al(1), and O(5) and N(3) on Al(2).

The Al–O distances associated with the salen ligands of compound **5** [1.787(3)–1.798(2) Å] are within experimental error of the values found in [AlEt(salen)] and **2** [1.800(5)–1.836(5) Å]. The aryl oxide alumimium distances are significantly shorter [Al(1)–O(3) 1.737(3), Al(2)–O(6) 1.741(2) Å], giving some support to the possibility of π donation from the aryl oxide to the aluminium centre.[16,17] It should be noted that the short Al–O distance reported for [(AlL)$_2$(μ-O)] (L = phthalocyaninate or 2-methylquinolin-8-olate) was proposed to be due to significant double-bond character achieved through p_π–d_π bonding.[14,15] As we have indicated previously,[18] the relatively high energy of the Al 3d orbitals would preclude their significant participation in π bonding. It is more likely, therefore, that if any π donation from oxygen to the five-co-ordinate aluminium centres is present in **2** and **5** it will involve the π-acceptor σ-antibonding orbitals on aluminium.[16,18]

Carboxylic Acids.—Compound **1** readily reacts with carboxylic acids to give the appropriate carboxylate complex [equation (4), R″ = Me or Ph]. The compounds [Al(O_2CMe)(salen)] **6** and [Al(O_2CPh)(salen)] **7** have been prepared in this manner. The ^{27}Al-{^{1}H} NMR spectra of **6** and **7** consist of broad single resonances at δ 25 and 28 respectively. The peak position and large linewidths (see Table 1) are indications of five-fold co-ordinations around aluminium, which in turn suggests the carboxylate ligands are unidentate. The latter is supported by the presence of absorption bands in the IR spectra at 1640 and 1570 cm^{-1} for **6** and 1680 and 1610 cm^{-1} for **7** diagnostic of unidentate co-ordination of a carboxylate group.[19–21]

$$[AlMe(salen)] + R''CO_2H \longrightarrow [Al(O_2CR'')(salen)] \quad (4)$$

Although suitable crystals of neither compound **6** nor **7** could be obtained for X-ray crystallography, the co-ordination around aluminium is undoubtedly similar to that found for **5**, while the carboxylate is most likely bound in an analogous manner to that in the crystallographically characterized complex [NMe_4][$AlMe_3(O_2CMe)$].[22]

Pentane-2,4-dione.—Reaction of compound **1** with 1 equivalent of pentane-2,4-dione (acetylacetone) (Hacac) in refluxing MeCN gives the acetylacetonate complex [Al(acac)(salen)] **8**, in moderate yield [equation (5)]. Unfortunately, we

$$[AlMe(salen)] + Hacac \longrightarrow \underset{\mathbf{8}}{[Al(acac)(salen)]} + CH_4 \quad (5)$$

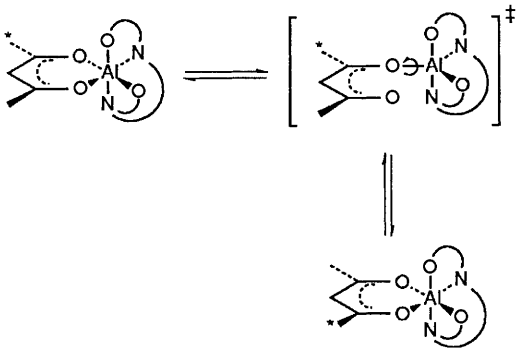
have been unable to obtain crystals of **8** suitable for X-ray diffraction, however the IR spectrum contains bands between 1520 and 1625 cm^{-1} indicative of a bidentate O,O′ co-ordination of the acac ligand to the aluminium centre.[23] The peak position (δ 2) and linewidth (253 Hz) of the single peak observed in the ^{27}Al-{^{1}H} NMR spectrum of compound **8** is almost identical to that observed for the aluminium atom in the most highly distorted octahedral site of the $[Al_3(H_{-1}cit)_3(OH)(H_2O)]^{4-}$ anion (H_3cit = citric acid).[24] The spectroscopic data are consistent, therefore, with a structure analogous to that found for [Co(acac)(salen)], in which the cobalt is in a distorted-octahedral environment and the acac group acts as a chelate ligand.[25] This geometry should give rise to inequivalent methyl groups on the acac ligand; one will be *cis* to a salen nitrogen, the other *trans* to the same nitrogen atom. This inequivalence is indeed observed in the room-temperature ^{1}H NMR spectrum of compound **8**, in which two broad peaks are present for the acac methyls. At temperatures above + 30 °C, however, only a single broad resonance is observed, indicating that the acac group is isomerizing.

The mechanism by which the acac ligand isomerizes most likely involves bond breaking. However, since the ethylene protons of the salen ligand remain essentially unchanged between 0 and 60 °C, a dissociative ion-pair mechanism can be ruled out. Saiko and Nagasawa[26] have proposed that one of the mechanisms for the ligand-substitution reaction of [Al(acac)$_3$] involves the breaking of a single Al–O bond, and the formation of an intermediate containing a unidentate acac ligand. We propose this to also be a plausible mechanism for the N-*cis*/N-*trans* isomerization shown in equation (6). Thus, at the high-

Table 4 Analytical data for aluminium complexes

Compound	M.p./°C	Analysis[a] (%) C	H	N
1 [AlMe(salen)]	228–230 (decomp.)	65.4 (66.2)	5.3 (5.5)	8.9 (9.1)
2 [{Al(salen)}$_2$(μ-O)]·CH_2Cl_2[b]	>250	57.3 (57.6)	4.3 (4.4)	8.1 (8.2)
3 [Al(OPh)(salen)]	164 (decomp.)	68.3 (68.4)	4.7 (4.9)	7.0 (7.3)
4 [Al($OC_6H_4Bu^t$-4)(salen)]	222 (decomp.)	70.9 (70.6)	6.2 (6.1)	6.3 (6.3)
5 [Al($OC_6H_2Me_3$-2,4,6)(salen)]	227 (decomp.)	70.1 (70.0)	5.8 (5.8)	6.5 (6.5)
6 [Al(O_2CMe)(salen)]	>250	61.4 (61.3)	4.8 (4.8)	7.8 (7.9)
7 [Al(O_2CPh)(salen)]	220 (decomp.)	66.1 (66.6)	4.6 (4.5)	6.7 (6.8)
8 [Al(acac)(salen)]	235–238 (decomp.)	64.5 (64.3)	5.3 (5.4)	6.9 (6.9)
9 [Al{2-$OC_6H_4C(O)Me$}(salen)]	>250	67.2 (67.3)	5.3 (4.9)	6.9 (6.5)

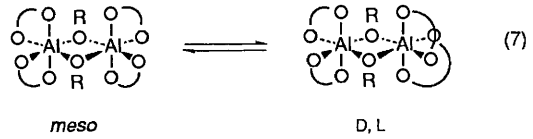
[a] Required values in parentheses. [b] CH_2Cl_2 of crystallization.



(6)

temperature limit, we propose that the acac ligand is rapidly interconverting through a transition state/intermediate in which one of the acac Al–O bonds is broken. This bond cleavage would be followed by either rotation about the remaining acac Al–O bond or a Berry pseudo-rotation, and finally by reformation of the Al–O bond, giving the other isomer.

It is interesting that the activation barrier for the acac isomerization in compound **8** (T_c = 303 K, $\Delta G^{\ddagger}$ = 58 kJ mol^{-1}) compares favourably to that reported by Wengrovious *et al.*[27] for the isomerization of the D,L and *meso* isomers of [$Al_2(OR)_2(acac)_4$] (T_c = 278 K, $\Delta G^{\ddagger}$ = 56 kJ mol^{-1}). These authors dismissed the possibility of rupture of one of the acac Al–O bonds, owing to the high temperatures (> 50 °C) required for isomerization to occur in [Al(acac)$_3$],[28] and proposed that it was one of the Al–O–Al bonds of the alkoxide bridge that was broken in the isomerization reaction [equation (7)].



meso D, L (7)

Given the similarity in activation parameters for the isomerization in compound **8** and [$Al_2(OR)_2(acac)_4$],[27] we propose that the cleavage of the acac Al–O bond is the preferred mechanism for both isomerization reactions.

2-Hydroxyacetophenone.—Treatment of compound **1** with 1 equivalent of 2-hydroxyacetophenone [2-$HOC_6H_4C(O)Me$], in refluxing MeCN, allows the isolation of [Al{2-OC_6H_4-C(O)Me}(salen)] **9** [equation (8)]. The ^{27}Al-{^{1}H} NMR

[AlMe(salen)] + 2-$HOC_6H_4C(O)Me$ ⟶ [Al{2-$OC_6H_4C(O)Me$}(salen)] + CH_4 (8)
9

spectrum of **9** consists of a broad single resonance at δ 9 consistent with a six-co-ordinate aluminium.[24] Unlike the acac derivative **8**, however, the linewidth of the resonance is very large ($w_{\frac{1}{2}}$ = 2720 Hz), suggesting that the aluminium atom is in an environment of low symmetry. If the acetylphenoxide is acting as a bidentate chelating ligand then compound **9** should be structurally similar to **8**. However, since only one set of salen ligand resonances are present in the ^{1}H NMR spectrum it is unlikely that **9** is conformationally rigid, suggesting, therefore, that **9** is fluxional in a similar manner to that observed for **8**. If, as we have proposed above, the N-*cis*/N-*trans* fluxionality involves Al–O bond breaking one would expect the activation barrier for isomerization in **9** to be significantly lower than in **8**, because of the lack of resonance stabilization in the acetylphenoxide as compared to acac. This is indeed observed since the ^{1}H NMR spectrum of **9** remains largely unchanged even at low temperatures.

Experimental

Microanalysis was performed by Oneida Research Services, Whitesboro, NY (Table 4). Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra (4000–700 cm^{-1}) were recorded on a Perkin-Elmer 598 spectrophotometer as Nujol mulls, NMR spectra in $CDCl_3$ on Bruker AM-250 (^{1}H) and AM-300 (^{27}Al-{^{1}H}) spectrometers {ppm relative to $SiMe_4$ (^{1}H) and external [$Al(H_2O)_6$]$^{3+}$ (^{27}Al)}. All manipulations were carried out under nitrogen. Solvents were dried, distilled and degassed before use.

N,N'-Ethylenebis(salicylideneimine) was prepared by condensing salicylaldehyde with ethylenediamine and recrystallizing from ethanol.[29] Trimethylaluminium (2.0 mol dm^{-3} solution in hexane) was used as supplied (Aldrich).

[*Ethylenebis*(*salicylideneiminato*)]*methylaluminium*(III) **1**.—Trimethylaluminium (10 cm^3, 20 mmol) was added to H_2salen (5.36 g, 20 mmol) in MeCN (30 cm^3). The reaction mixture was vented to allow the escape of the methane produced. The solution was refluxed for 3 h, cooled and the solvent removed under vacuum to give a yellow solid: yield *ca.* 98%. IR: 1650m, 1635m, 1610m, 1550m, 1400m, 1340m, 1240w, 1210m, 1190m, 1150m, 1130m, 1100w, 1080w, 1050m, 1030m, 910m, 810m and 770m cm^{-1}.

μ-*Oxo-bis*{[*ethylenebis*(*salicylideneiminato*)]*aluminium*(III)} **2**.—Atmospheric hydrolysis of compound **1** in CH_2Cl_2 or MeCN solution yielded pale yellow crystals. IR: 1620s, 1540s, 1330s, 1310s, 1260m, 1200m, 1140m, 1120m, 1090m, 1040m, 1020m, 960s, 900m, 850m, 800m, 750s and 740m cm^{-1}.

[*Ethylenebis*(*salicylideneiminato*)](*phenoxo*)*aluminium*(III) **3**.—To a MeCN (20 cm^3) solution of compound **1** (1.00 g, 3.25 mmol) was added HOPh (0.31 g, 3.25 mmol). The mixture was refluxed for 4 h, cooled and the solvent removed under vacuum to give a white powder, yield *ca.* 90%. IR: 1660s, 1640s, 1600s, 1590s, 1560s, 1540s, 1490s, 1470s, 1400s, 1350s, 1340s, 1330s, 1300s, 1270s, 1230m, 1200m, 1150m, 1130m, 1090m, 1050m, 1020m, 990m, 950w, 900m, 890m, 860s, 800s, 790m and 750s cm^{-1}.

(4-tert-*Butylphenoxo*)[*ethylenebis*(*salicylideneiminato*)]-*aluminium*(III) **4**.—This was prepared in an analogous manner to compound **3**, yield 80–90%. IR: 1660m, 1640s, 1550s,

1520m, 1490s, 1400m, 1350m, 1320m, 1280s, 1270m, 1210m, 1190m, 1150m, 1130m, 1120m, 1100m, 1060m, 1030m, 910m, 880m 850m, 760s and 720m cm^{-1}.

[*Ethylenebis(salicylideneiminato)*](2,4,6-*trimethylphenoxo*)-*aluminium*(III) **5**.—This was prepared in an anlogous manner to compound **3**, yield 85–90%. IR: 2260w, 1620s, 1550s, 1400(sh), 1350s, 1320s, 1270s, 1210s, 1160s, 1130s, 1100s, 1060s 1030s, 1000m, 990(sh), 910s, 860s, 820s, 770s and 740(sh) cm^{-1}.

Acetato[*ethylenebis(salicylideneiminato)*]*aluminium*(III) **6**.—To a MeCN (25 cm^3) solution of compound **1** (0.51 g, 1.65 mmol) was added $MeCO_2H$ (0.095 cm^3, 1.65 mmol). The mixture was stirred for 12 h, after which a pale yellow precipitate formed. The solution was filtered and the solid dried under vacuum. Yield: 60–65%. IR: 1640s, 1600m, 1570s, 1480s, 1390m, 1330s, 1310s, 1260m, 1240m, 1200s, 1140s, 1130s, 1080s, 1060s, 1030s, 980m, 900s, 850m, 800s, 765s and 730m cm^{-1}.

Benzoato[*ethylenebis(salicylideneiminato)*]*aluminium*(III) **7**.—This was prepared in an analogous manner to compound **6**, yield 70–75%. IR: 1680(sh), 1650s, 1610s, 1580w, 1540w, 1480s, 1410w, 1380s, 1370s, 1350s, 1330(sh), 1270m, 1240w, 1210w, 1170w, 1150m, 1130(sh), 1100m, 1070w, 1060m, 1030s, 960w, 940w, 910w, 900w, 860w, 840w, 810m, 790m, 770s and 720m cm^{-1}.

Acetylacetonato[*ethylenebis(salicyclideneiminato)*]-*aluminium*(III) **8**.—To a solution of compound **1** (100 g, 3.25 mmol) in MeCN (30 cm^3) at room temperature was added Hacac (0.33 cm^3, 3.25 mmol). The resulting solution was refluxed for 2 h, during which a pale yellow precipitate formed. Cooling, followed by filtration and drying under vacuum, gave a pale yellow powder, yield 55–60%. IR: 1625s, 1595s, 1520s, 1340s, 1310(sh), 1230w, 1210w, 1190w, 1140m, 1120w, 1020m, 970m, 920m, 895s, 850m, 800m, 750s and 730 cm^{-1}.

2-*Acetylphenoxo*[*ethylenebis(salicylideneiminato)*]-*aluminium*(III) **9**.—This was prepared in an analogous manner to compound **8**, yield 70–80%. IR: 1655w, 1640s, 1620s, 1600m, 1540s, 1480m, 1470s, 1400m, 1390m, 1360w, 1330m, 1305m, 1265m, 1240m, 1230w, 1205w, 1200m, 1165m, 1150m, 1145m, 1125m, 1095w, 1080w, 980m, 965m, 910m, 870m, 860m, 810s, 765s, 750w, 745m and 735w cm^{-1}.

X-Ray Crystallographic Study.—A crystal data summary is given in Table 5; fractional atomic coordinates are listed in Tables 6 and 7.

A crystal of compound **2** was mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[18] using a Nicolet R3m/v diffractometer operating in the θ–2θ scan mode. Data collection was controlled by using the Nicolet P3 program.[30] Empirical absorption corrections were applied to the data using the program PSICOR.[30] The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.000\,09\,(|F_o|)^2$. Further experimental data are given in Table 5.

The structure was solved using the direct methods program XS,[31] which revealed the position of most of the heavy atoms. Most but not all of the hydrogens were visible in the final

Table 5 Summary of X-ray diffraction data

Compound	[{Al(salen)}$_2$(μ-O)]·MeCN	[Al(OC$_6$H$_2$Me$_3$-2,4,6)-(salen)]
Formula	$C_{34}H_{31}Al_2N_5O_5$	$C_{25}H_{25}AlN_2O_3$
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*$\bar{1}$
a/Å	21.449(8)	11.833(1)
b/Å	14.144(6)	12.170(1)
c/Å	22.048(9)	17.835(2)
α/°	—	75.57(1)
β/°	107.26(3)	75.29(1)
γ/°	—	65.66(1)
U/Å^3	6387(4)	2233.3(5)
Z	8	4
D_c/g cm^{-3}	1.339	1.274
Crystal dimensions/mm	0.41 × 0.50 × 0.84	0.37 × 0.40 × 0.40
T/°C	−70	−90
Radiation	Mo-Kα (λ = 0.710 73 Å), graphite monochromator	
μ/cm^{-1}	1.35	0.114
2θ limits/°	4.0–50.0	4.0–45.0
No of data collected	10 592	6205
No unique	4208	5535
Observed data	2812 [$F > 4\sigma(F)$]	5425 [$F > 1\sigma(F)$]
R	0.076	0.061
R'	0.074	0.49
Final residual/e Å^{-3}	0.43	

Table 6 Fractional atomic coordinates (× 10^4) for [{Al(salen)}$_2$(μ-O)]·MeCN **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Al(1)	8 956(1)	1 278(2)	5 963(1)	N(31)	10 001(3)	2 718(4)	5 075(3)
O(11)	8 539(2)	1 296(3)	5 105(2)	C(31)	10 093(3)	3 927(5)	6 169(4)
N(11)	8 549(3)	2 550(4)	6 028(3)	C(32)	10 097(4)	4 583(5)	6 647(4)
C(11)	8 351(3)	2 012(5)	4 709(3)	C(33)	9 714(4)	5 390(6)	6 522(4)
C(12)	8 279(3)	1 873(5)	4 056(3)	C(34)	9318(4)	5 568(5)	5 900(4)
C(13)	8 078(4)	2 607(6)	3 625(3)	C(35)	9325(3)	4 951(5)	5 416(4)
C(14)	7 911(4)	3 498(6)	3 818(4)	C(36)	9709(3)	4 129(5)	5 543(3)
C(15)	7 962(3)	3 639(5)	4 452(3)	C(37)	9711(3)	3 519(5)	5 016(3)
C(16)	8 196(3)	2 905(5)	4 902(3)	C(38)	10 016(3)	2 217(5)	4 491(3)
C(17)	8 284(3)	3 120(5)	5 556(3)	O(41)	11 157(2)	1 701(3)	6 508(2)
C(18)	8 614(3)	2 893(5)	6 681(3)	N(41)	10 681(3)	1 222(4)	5 291(2)
O(21)	8 665(2)	83(3)	5 992(2)	C(41)	11 690(3)	1 254(5)	6 494(3)
N(21)	9 084(3)	1 374(4)	6 903(3)	C(42)	12 222(3)	1 180(5)	7 055(3)
C(21)	8 790(4)	−544(6)	6 474(4)	C(43)	12 802(4)	764(5)	7 064(4)
C(22)	8 653(4)	−1 497(6)	6 308(4)	C(44)	12 894(4)	413(5)	6 503(4)
C(23)	8 790(5)	−2 176(6)	6 789(5)	C(45)	12 377(4)	457(5)	5 946(4)
C(24)	9 055(5)	−1 932(7)	7 431(5)	C(46)	11 773(3)	845(5)	5 941(3)
C(25)	9 170(4)	−1 001(6)	7 583(4)	C(47)	11 240(4)	831(5)	5 353(4)
C(26)	9 051(4)	−291(5)	7 118(3)	C(48)	10 173(3)	1 178(5)	4 670(3)
C(27)	9 171(3)	694(6)	7 308(4)	O(1)	9 760(2)	1 401(3)	6 025(2)
C(28)	9 183(3)	2 354(5)	7 123(3)	N(1)	8 243(7)	6 617(10)	4 570(5)
Al(2)	10 402(1)	2 018(2)	5 909(1)	C(1)	8 115(6)	6 502(9)	4 056(7)
O(31)	10 459(2)	3 154(3)	6 314(2)	C(2)	7 938(5)	6 291(7)	3 372(6)

Table 7 Atomic coordinates ($\times 10^4$) for [Al($OC_6H_2Me_3$-2,4,6)(salen)] **5**

Molecule 1				Molecule 2			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Al(1)	9 049(1)	1 043(1)	6 720(1)	Al(2)	3 031(1)	3 885(1)	1 391(1)
O(1)	9 774(2)	1 906(2)	6 966(1)	O(4)	2 189(2)	3 196(2)	1 079(1)
O(2)	7 554(2)	1 992(2)	7 199(1)	O(5)	3 086(2)	2 853(2)	2 310(1)
O(3)	8 928(2)	1 368(2)	5 732(1)	O(6)	4 612(2)	3 490(2)	963(1)
N(1)	10 729(2)	−296(2)	6 543(1)	N(3)	2 525(2)	5 307(2)	531(1)
N(2)	8 622(2)	−431(2)	7 228(1)	N(4)	2 473(2)	5 282(2)	1 969(1)
C(1)	10 966(3)	1 801(3)	6 867(2)	C(26)	1 790(3)	3 382(3)	408(2)
C(2)	11 209(3)	2 758(3)	7 006(2)	C(27)	1 394(3)	2 521(3)	274(2)
C(3)	12 427(3)	2 673(4)	6 943(2)	C(28)	961(3)	2 691(3)	−416(2)
C(4)	13 429(3)	1 659(4)	6 733(2)	C(29)	897(3)	3 712(4)	−983(2)
C(5)	13 224(3)	696(4)	6 588(2)	C(30)	1 263(3)	4 568(3)	−857(2)
C(6)	11 998(3)	757(3)	6 647(2)	C(31)	1 724(3)	4 421(3)	−173(2)
C(7)	11 820(3)	−278(3)	6 516(2)	C(32)	2 047(3)	5 381(3)	−60(2)
C(8)	10 609(3)	−1 397(3)	6 434(2)	C(33)	2 710(3)	6 362(3)	645(2)
C(9)	9 632(3)	−1 632(3)	7 116(2)	C(34)	2 100(3)	6 522(2)	1 491(2)
C(10)	7 549(3)	−443(3)	7 627(2)	C(35)	2 455(2)	5 209(3)	2 709(2)
C(11)	6 479(3)	623(3)	7 814(2)	C(36)	2 776(2)	4 086(3)	3 356(2)
C(12)	5 355(3)	476(3)	8 239(2)	C(37)	2 771(3)	4 138(3)	4 034(2)
C(13)	4 322(3)	1 454(3)	8 459(2)	C(38)	3 060(3)	3 095(3)	4 587(2)
C(14)	4 375(3)	2 619(3)	8 262(2)	C(39)	3 362(3)	1 976(3)	4 366(2)
C(15)	5 457(3)	2 789(3)	7 838(2)	C(40)	3 374(3)	1 894(3)	3 602(2)
C(16)	6 526(2)	1 803(3)	7 600(1)	C(41)	3 078(3)	2 951(3)	3 032(2)
C(17)	8 142(3)	2 290(2)	5 280(1)	C(42)	5 740(3)	2 605(2)	1 059(2)
C(18)	8 462(3)	3 296(3)	4 884(2)	C(43)	6 230(3)	1 623(2)	642(2)
C(19)	7 663(3)	4 200(3)	4 398(2)	C(44)	7 438(3)	772(3)	700(2)
C(20)	6 578(3)	4 130(3)	4 289(2)	C(45)	8 195(3)	860(3)	1 150(2)
C(21)	6 305(3)	3 109(3)	4 671(2)	C(46)	7 681(3)	1 845(3)	1 552(2)
C(22)	7 072(3)	2 183(3)	5 163(2)	C(47)	6 474(3)	2 714(3)	1 522(2)
C(23)	9 667(3)	3 364(3)	4 962(2)	C(48)	5 477(3)	1 556(3)	99(2)
C(24)	5 714(3)	5 132(3)	3 760(2)	C(49)	9 507(3)	−70(3)	1 201(2)
C(25)	6 799(3)	1 044(3)	5 552(2)	C(50)	5 972(3)	3 792(3)	1 947(2)

difference map. Hydrogens were included as fixed atom contributors in the final cycles, d(C–H) = 0.96 Å. Details of the refinement are given in Table 5. Atomic scattering factors and anomalous scattering parameters were as given in ref. 32.

X-Ray data for compound **5** were collected on a Siemens P3 diffractometer equipped with a modified LT-2 low-temperature system. Laue symmetry determination, crystal class, unit-cell parameters and the crystal's orientation matrix were carried out by previously described techniques.[33]

All data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. There were no systematic absences nor any diffraction symmetry other than the Friedel conditions. The two possible triclinic space groups are $P1$ or $P\bar{1}$. The centrosymmetric space group $P\bar{1}$ was chosen and later proved to be correct by successful refinement of the model.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computer Package[34] or the SHELXTL-PLUS program set.[31] The analytical scattering factors for neutral atoms were used through the analysis;[32] the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included.[32] The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

The structure was solved by direct methods (MITHRIL)[35] and refined by full least-squares methods (SHELXTL-PLUS). Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 5).

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Financial support *via* an undergraduate fellowship (to P. L. G.) was provided by the Milton Foundation. Funds for the purchase of the Nicolet R3m/V diffractometer system were made available by the National Science Foundation under Grant CHE-85-14495. The assistance of Dr. A. W. Apblett and Mr. T. L. Feng with the ^{27}Al NMR measurements is gratefully acknowledged.

References

1 M. Calligaris and L. Randaccio, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1989, vol. 2, ch. 20.
2 K. S. Chong, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1977, **55**, 2540.
3 M. Agrawal, J. P. Tandon and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1405.
4 M. Agrawal, J. P. Tandon and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1070.
5 B. Szpoganicz and A. E. Martell, *Inorg. Chem.*, 1985, **24**, 2414.
6 S. J. Dzugan and V. L. Goedken, *Inorg. Chem.*, 1986, **25**, 2858.
7 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.*, 1972, 7, 385.
8 V. Vincens, A. Le Borgne and N. Spassky, *Makromol. Chem. Rapid Commun.*, 1989, **10**, 623.
9 A. R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A. J. Howes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 279.
10 A. R. Barron, unpublished work.
11 M. Gerloch, E. D. McKenzie and A. D. C. Towl, *J. Chem. Soc. A*, 1969, 2850.
12 P. Coggon, A. T. McPhail, F. E. Mabbs and V. N. McLachlen, *J. Chem. Soc. A*, 1971, 1014.
13 J. E. Davies and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1973, **29**, 1934.

14 Y. Kushi and Q. Fernando, *Chem. Commun.*, 1969, 555.
15 K. Y. Wynne, *Inorg. Chem.*, 1985, **24**, 1339.
16 M. D. Healy, J. W. Ziller and A. R. Barron, *J. Am. Chem. Soc.*, 1990, **112**, 2949.
17 M. D. Healy, J. W. Ziller and A. R. Barron, *Organometallics*, 1991, **10**, 597.
18 M. D. Healy, D. A. Wierda and A. R. Barron, *Organometallics*, 1988, **7**, 2543.
19 C. Oldham, *Prog. Inorg. Chem.*, 1968, **10**, 223.
20 C. D. Gamer and B. Hughes, *Adv. Inorg. Chem., Radiochem.*, 1975, **17**, 2.
21 J. Catterick and P. Thornton, *Adv. Inorg. Chem., Radiochem.*, 1977, **20**, 291.
22 J. L. Atwood, W. E. Hunter and K. D. Crissinger, *J. Organomet. Chem.*, 1977, **127**, 403.
23 D. A. Thornton, *Coord. Chem. Rev.*, 1990, **104**, 173.
24 T. L. Feng, P. L. Gurian, M. D. Healy and A. R. Barron, *Inorg. Chem.*, 1990, **29**, 408.
25 M. Calligaris, G. Nardin and L. Randaccio, *Chem. Commun.*, 1969, 1248.
26 K. Saito and A. Nagasawa, *Polyhedron*, 1990, **9**, 215 and refs. therein.
27 J. H. Wengrovius, M. F. Gavbauskas, E. A. Williams, R. C. Going, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 982.
28 N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, 1972, **14**, 391.
29 R. N. Prasad and J. P. Tandon, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1473.
30 *P3/R3 Data Collection Manual*, Nicolet Instrument Corp., Madison, WI, 1987.
31 G. M. Sheldrick, SHELXTL-PLUS, Nicolet Corporation, Madison, WI, 1986.
32 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
33 M. R. Churchill, R. A. Lashewycz and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 265.
34 UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981; C. Strouse, personal communication.
35 C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 4246.

Received 5th November 1990; *Paper* 0/04974C