selenides and their sulfide and oxide derivatives.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-8701007).

Registry No. $[(CH_3)_2(CH_3(CH_2)_7)Si]_2Se$, 109528-33-8; $(CH_3)_2(CH_3(CH_2)_7)SiCl$, 18162-84-0; Li_2Se, 12136-60-6; $[NH_4]_2[WSe_4]$, 22474-80-2; $[NH_4]_2[WO_4]$, 15855-70-6; $[NEt_4]_2[MoSe_4]$, 114956-91-1; Na_2MoO_4, 7631-95-0; $[AsPh_4]_2[WSe(Se_4)_2]$, 114956-93-3; Se_8, 12597-33-0; $[NEt_4]_2[MoSe(Se_4)_2]$, 114956-94-4; $[AsPh_4]_2[WS(Se_4)_2]$, 113584-94-4; SeS_2, 7488-56-4; $[NEt_4]_2[MoS(Se_4)_2]$, 114956-96-6; $[AsPh_4]_2[WO(Se_4)_2]$, 114956-98-8; $Se_4(N(C_5H_{10}))_2$, 66168-04-5; $[NEt_4]_2[MoO(Se_4)_2]$, 114957-00-5; ^{77}Se, 14681-72-2.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positions, and additional distances and angles for $[NEt_4]_2[MoO(Se_4)_2]$ and $[AsPh_4]_2[WS(Se_4)_2]$ (Tables IS–IIIS and VS–VIIS) (11 pages); listings of $10|F_o|$ vs $10|F_c|$ (Tables IVS and VIIIS) for both complexes (61 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Monash University, Clayton, Victoria, Australia 3168

Synthesis and Magnetic Properties of μ-Organoimido-Bridged Iron(III) Salicylaldimine Compounds. Structure of (μ-*p*-Tolylimido)bis[(*N*,*N*′-ethane-1,2-diylbis(salicylaldiminato))iron(III)] ([Fe(salen)]$_2$N(Tol))

Peter J. Nichols, Gary D. Fallon, Keith S. Murray, and Bruce O. West*

Received December 29, 1987

The reaction of tetradentate or bidentate Fe(II) salicylaldimine compounds with aryl azides in methylene chloride results in elimination of nitrogen and formation of Fe(III) μ-organoimido-bridged complexes [Fe(Lig)]$_2$NR. Studies of the magnetic susceptibilities of the compounds to 4.2 K show that they possess antiferromagnetic coupling similar to that of the analogous μ-oxo compounds. Mössbauer spectra indicate Fe(III) centers with $S = {}^5/_2$ spin. Crystal data for (μ-*p*-tolylimido)bis[(*N*,*N*′-ethane-1,2-diylbis(salicylaldiminato))iron(III)] ([Fe(salen)]$_2$N(Tol)) ($C_{39}H_{35}Fe_2N_5O_4$): triclinic, $P\bar{1}$, $a = 13.331$ (4) Å, $b = 12.123$ (5) Å, $c = 11.002$ (5) Å, $\alpha = 101.88$ (2)°, $\beta = 96.64$ (3)°, $\gamma = 97.53$ (4)°, $V = 1706$ (1) Å^3, $Z = 2$. The Fe–(μ-N)–Fe angle is 129.6 (6)°.

Introduction

Organoimido complexes of the transition metals are of considerable present interest.[1] Such compounds have been implicated in industrial catalytic processes[2] and enzymatic functions,[3] while other studies have explored their potential for use as reagents or catalysts in the stereospecific transfer of organoimido groups to organic substrates.[4]

The present known range of metal–imido compounds contains relatively few examples from the first transition series, i.e. those elements filling 3d orbitals compared to the heavier 4d and 5d series. Further, there are still few examples known of compounds having chelating ligands attached to the metal in addition to the organoimido group. Dithiocarbamato[5] and porphyrinato[6] ligands have been successfully involved in a variety of such complexes, while Re(V) derivatives containing a variety of salicylaldimines[7] have been reported.

We have previously described[8] the reactions of aryl azides with a Cr(II) porphyrin (Cr(P)) and Fe(II) salicylaldimines (Fe(salR)), which result in the formation of organoimido complexes Cr(NR)(P) and [Fe(salR)]$_2$NR, and in this paper report more fully on the synthesis and properties of the Fe derivatives.

Experimental Section

Materials and Techniques. All manipulations were carried out in dry solvents under purified nitrogen as previously described. Spectra were recorded as follows: infrared, PE 180; mass, PE-RMU-6E. Microanalyses were carried out by the Australian Microanalytical Service and the Australian National University.

The equipment and procedures for magnetic susceptibility and Mössbauer spectral measurements have also been described.[9]

Aryl Azides.[10] Phenyl azide, *p*-tolyl azide, and *p*-chlorophenyl azide were prepared by reaction of the corresponding arenediazonium sulfate with NaN_3 in a two-phase diethyl ether–water mixture and were purified by distillation under pressure or by chromatography on Florisil (60–100 mesh) with ether as eluent. Cyclohexyl azide[11] was prepared from bromocyclohexane. Trimethylsilyl azide was obtained from Aldrich. *Caution!* The aryl azides as a class are reported to detonate if heated to temperatures above 100 °C, while organic azides in general should be treated as potentially liable to detonate, particularly in the presence of heavy metals or acids.

The azides in this work were never subjected to temperatures in excess of 80 °C under any experimental conditions. No instances of explosion were encountered in any aspect of the work.

Fe(III) Complexes. Fe^{II}(salen)py, Fe^{II}(salphen), and Fe^{II}(salmah) (abbreviations for ligands and imido groups used are displayed in Figure 1) were prepared[12] under nitrogen, by reaction between the appropriate, preformed Schiff base and [Fe(py)$_4$(SCN)$_2$] in ethanol. The pyridine solvate of Fe(salen) was isolated from the reaction mixture. However, there was no microanalytical or mass spectral evidence for the incorporation of pyridine in the preparation of Fe(salphen) and Fe(salmah). The bidentate complex Fe(saltol)$_2$ was similarly prepared but with anhydrous

---

(1) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
(2) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Row, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251.
(3) Prough, R. A.; Freeman, P. C.; Hines, R. N. *J. Biol. Chem.* **1981**, *256*, 4178.
(4) (a) Chang, A. O.; Oshino, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.
(5) Mo: Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063. Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409. Nb, Ta: Tan, L. S.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 1744. Fe: Mahy, J.-P.; Battioni, P.; Mansuy, D.; Fisher, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699.
(6) V: Buchler, J. W.; Pfeifer, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1362. Mn: Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 3073.
(7) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Polizzotti, G. *Inorg. Chim. Acta* **1984**, *90*, 121.
(8) Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191.
(9) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1561.
(10) *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 736.
(11) Knouzi, N.; Vaultier, M.; Carrie, R. *Bull. Soc. Chim. Fr.* **1985**, 815.
(12) Elliott, R. L.; Nichols, P. J.; West, B. O. *Aust. J. Chem.* **1986**, *39*, 975.

0020-1669/88/1327-2795$01.50/0

Table I. Microanalytical and Magnetic Moment Data

complex	color	anal.,[a] % C	H	N	magnetic moment (300 K), μ_B/molecule
$[Fe(salen)]_2N(Tol)\cdot CH_2Cl_2$[b]	black	57.9 (57.6)	4.8 (4.5)	8.8 (8.4)	2.8
$[Fe(salphen)]_2N(Tol)\cdot CH_2Cl_2$[b]	brown	60.5 (62.0)	3.5 (4.0)	7.5 (7.5)	
$[Fe(salen)]_2N(Tol)$	tan	62.1 (62.5)	4.6 (4.7)	9.1 (9.4)	2.7
$[Fe(salen)]_2N(Ph)$	tan	61.7 (62.1)	4.0 (4.5)	10.0 (9.5)	2.8
$[Fe(salen)]_2N(ClPh)$[b]	tan	59.5 (59.3)	4.2 (4.2)	9.0 (9.1)	3.2
$[Fe(salphen)]_2N(Ph)$	tan	66.5 (66.4)	4.2 (4.0)	8.1 (8.4)	
$[Fe(salphen)]_2N(ClPh)$[b]	tan	64.0 (63.8)	3.8 (3.7)	8.0 (8.1)	
$[Fe(saltol)_2]_2N(Tol)$	brown	71.2 (71.5)	4.9 (5.2)	6.3 (6.6)	2.7
$[Fe(saltol)_2]_2N(Ph)$	brown	71.5 (71.3)	5.4 (5.1)	6.1 (6.7)	
$[Fe(saltol)_2]_2N(ClPh)$[b]	brown	69.4 (69.1)	5.0 (4.9)	6.2 (6.5)	2.6

[a] Calculated values in parentheses. [b] Microprobe indicated the presence of Fe and Cl in the appropriate ratios.

$Fe^{II}(CH_3COO)_2$ being used[13] instead of the thiocyanate complex. $Fe(Et_2dtc)_2$ was prepared from $Fe(SO_4)\cdot 7H_2O$ and sodium diethyldithiocarbamate,[14] and $Fe(TPP)(pip)_2$, from Fe(TPP)Cl and piperidine[15] (TPP is the dianion of 5,10,15,20-tetraphenylporphyrin).

Synthesis of μ-Arylimido-Iron(III) Salicylaldimine Complexes. The following description is typical of the reactions carried out:

(μ-*p*-Tolylimido)bis[(*N*,*N'*-ethane-1,2-diylbis(salicylaldiminato))iron(III)] ([Fe(salen)]₂N(Tol)). A dry, deoxygenated solution of *p*-tolyl azide (0.24 g, 1.8 mmol) in toluene (60 mL) was added to Fe(salen)py (1.2 g, 3.0 mmol). The red-brown suspension was stirred at room temperature for 3 h. The resulting brown-orange suspension was filtered, and the tan product was washed with hexane and dried under vacuum at 10^{-3} Torr (yield ca. 95%). IR (Nujol), cm^{-1}: 1638 vs, 1619 vs, 1599 vs, 1537 vs, 1325 vs, 1310 vs, 1240 m, 1218 s, 1198 vs, 1170 m, 1147 vs, 1128 s, 1092 s, 1048 s, 1031 s, 982 m, 958 m, 908 vs, 853 s, 830 s, 799 s, 757 vs, 742 s, 699 m. Mass spectrum: *m/e* 105 (*p*-tol-N), 106 (*p*-tol-NH), 107 (*p*-tol-NH_2), 322 (Fe(salen)).

The following compounds were prepared in high yields (ca. 95%) by an analogous procedure with toluene suspensions of the appropriate Fe(II) complex reacting with an aryl azide: $[Fe(salen)]_2N(Ph)$, $[Fe(salen)]_2N(ClPh)$, $[Fe(salphen)]_2N(Ph)$, $[Fe(salphen)]_2N(ClPh)$. The mass spectra of the complexes included peaks for the aromatic amines RNH_2^+, RNH^+, and RN^+ together with the appropriate metal complex ions $Fe(salen)^+$ or $Fe(salphen)^+$.

The preparations of $[Fe(salen)]_2N(Tol)$ and $[Fe(salphen)]_2N(Tol)$ were also carried out successfully in CH_2Cl_2. The reagents dissolved readily in the solvent on the scale employed, e.g. *p*-tolyl azide (0.2 g, 1.5 mmol), Fe(salen)py (1 g, 2.5 mmol), and CH_2Cl_2 (40 mL). Nitrogen was evolved over 10 min, and the initial red-brown color of the solution lightened to orange-brown. Stirring was continued for 1 h, the solution evaporated to half-volume, and dry hexane (40 mL) added. The mixture was cooled to 0 °C for 1 h and then filtered and the recovered black solid washed with hexane and dried at 10^{-3} Torr (yield 0.7 g, 70%). The products thus prepared contained 1 mol of CH_2Cl_2, confirmed by microprobe and mass spectral analysis.

The bis-bidentate $Fe^{II}(saltol)_2$ dissolved in toluene and reacted readily in this solvent with *p*-chlorophenyl azide. The green-red initial color of the solution changed to brown-orange over 3 h as N_2 was evolved (scale: Fe(II) complex, 1 g, 2 mmol; azide, 0.2 g, 1.3 mmol; toluene, 50 mL). The solution volume was reduced, hexane was added (50 mL), and the mixture was cooled to 0 °C for 1 h. The brown solid was then filtered out, washed with hexane, and dried in vacuo (0.6 g, 60%). IR (Nujol), cm^{-1}: 1617 vs, 1601 vs, 1545 s, 1507 s, 1345 s, 1324 vs, 1310 s, 1220 m, 1191 vs, 1153 vs, 1128 m, 1038 m, 1025 m, 990 m, 931 m, 871 s, 841 vs, 832 sh, 806 s, 773 s, 759 vs, 747 s, 695 m. Mass spectrum: *m/e* 125 (ClC_6H_4N), 126 (ClC_6H_4NH), 127 ($ClC_6H_4NH_2$), 211 (saltolH), 476 ($Fe(saltol)_2$).

The *p*-tolyl- and phenylimido derivatives of $Fe(saltol)_2$ were prepared similarly. Analytical data for the complexes are collected in Table I.

Isotopically Labeled Compounds. Phenyl azide isotopically labeled with nitrogen-15 in the α-position ($Ph^{15}NNN$) was prepared[16] by diazotization of $Ph^{15}NH_2$ (Cambridge Isotope Laboratories; 99% ^{15}N) and used in the synthesis of $[Fe(salen)]_2{}^{15}N(Ph)$.

^{18}O-labeled $[Fe(salen)]_2{}^{18}O$ was prepared by reacting $[Fe(salen)]_2N(Tol)$ with $H_2{}^{18}O$ water (61.3% ^{18}O enrichment; Yeda Research and Development) in toluene. IR (Nujol) spectra showed bands at 825 cm^{-1} vs (Fe-^{16}O-F) and 783 cm^{-1} vs (Fe-^{18}O-Fe), the 783-cm^{-1} band being absent in the spectrum of "unlabeled" $[Fe(salen)]_2O$.

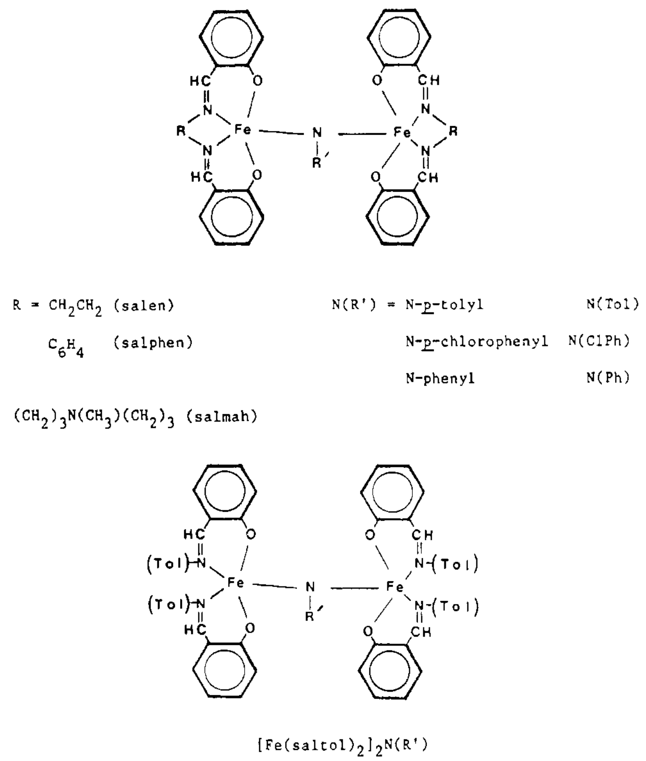

Figure 1. Bond diagrams and abbreviations for Fe(III) μ-organoimido complexes.

Crystallographic Study of [Fe(salen)]₂N(Tol). Crystals of $[Fe(salen)]_2N(Tol)$ were prepared according to the following procedure. A solution of *p*-tolyl azide (0.4 g) in toluene (50 mL) was layered onto a solution of Fe(salen)py (0.8 g) in CH_2Cl_2 (40 mL). After the layered solutions were allowed to stand at room temperature for 24 h, black-red crystals were deposited at the solvent interface. The crystals were collected, washed with hexane, and dried under a flow of nitrogen. Some of these crystals were found to contain CH_2Cl_2 by electron microprobe examination, while others were unsolvated. The crystals decomposed significantly if left unprotected in the X-ray beam. The successful analysis was on a crystal protected from the atmosphere by a coating of Araldite resin.

Intensity measurements were made at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation. Cell parameters were determined from 24 accurately centered reflections and calculated by the standard Philips program. The data collection and crystal parameters are listed in Table II. Three standard reflections monitored every 4 h showed at 30% decrease in intensity over the data collection period. Intensity data were processed as described previously,[17] an allowance being made for the decomposition. A numerical absorption

---

[13] Calderazzo, F.; Floriani, C.; Henzi, R.; L'Eplattenier, F. *J. Chem. Soc. A* **1969**, 1378.

[14] Pignolet, L. H.; Lewis, R. A.; Holm, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 360.

[15] Epstein, L. M.; Straub, D. K.; Maricondi, C. *Inorg. Chem.* **1967**, *6*, 1720.

[16] Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025.

[17] Fallon, G. D.; Gatehouse, B. M. *J. Solid State Chem.* **1980**, *34*, 193.

[18] Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table II. Crystallographic Data for [Fe(salen)]$_2$N(Tol)

mol formula; mol wt	$C_{39}H_{35}Fe_2N_5O_4$; 749.4
cryst system; space group	triclinic; $P\bar{1}$ (by successful refinement)
temp, °C	20 (1)
cell dimens	a = 13.331 (4) Å, b = 12.123 (5) Å, c = 11.002 (5) Å, α = 101.88 (2)°, β = 96.64 (3)°, γ = 97.53 (4)°
Z	2
V, Å^3	1706 (1)
d, g·cm^{-3}: obsd; calcd	1.45 (1); 1.46
F(000)	776
μ, cm^{-1}	9.0
λ(Mo Kα), Å	0.71073
cryst dimens, mm	0.19 × 0.18 × 0.12
scan speed, deg/s	0.08
2θ limits, deg	$6 \leqslant 2\theta \leqslant 60$
scan range, deg	$\pm(0.75 \pm 0.3 \tan \theta)$
no. of data collcd	8261 ($\pm h,+k,\pm l$)
R_{int} for redundant data	0.081
no. of unique data [$I \geqslant 3\sigma(I)$]	1552
goodness of fit	2.23
final agreement factors	R = 0.074; R_w = 0.064

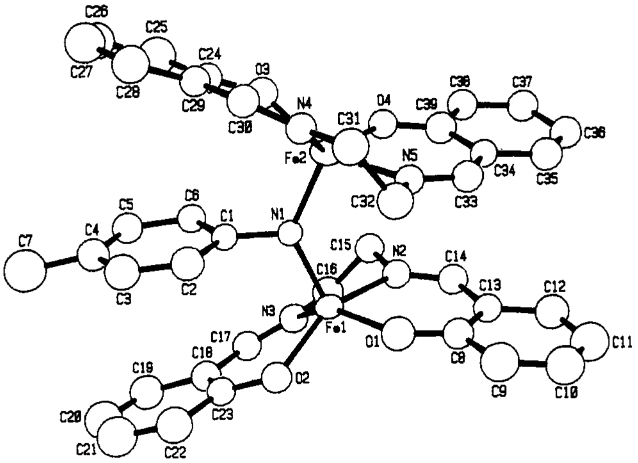

Figure 2. ORTEP drawing of [Fe(salen)]$_2$N(Tol) giving the atom-labeling scheme. Atoms are represented by 50% probability ellipsoids.

correction was applied,[19] the maximum and minimum transmission factors being 0.904 and 0.806, respectively. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion.[18] All calculations were performed on a VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick.[19]

The structure was solved by direct methods. Full-matrix least-squares refinement employing anisotropic thermal parameters for Fe and isotropic thermal for all other atoms (a single isotropic thermal parameter for hydrogen—which refined to 0.077 (9)—positioned in geometrically idealized positions: C–H = 0.97 Å) reduced R to 0.074 and R_w to 0.064, respectively, at convergence, where $R_w = \sum_w{}^{1/2}(||F_o| - |F_c||)/\sum_w{}^{1/2}|F_o|$ and $w = [\sigma^2(F_o)]^{-1}$. The highest peak in the difference Fourier synthesis was 0.50 e Å^{-3}. Atomic parameters are given in Table III, and selected bond lengths and angles, in Table IV.

Results and Discussion

Synthesis of Fe–N(R)–Fe Salicylaldimine Complexes. The iron(II) complexes Fe(salen)py, Fe(salphen), and Fe(saltol)$_2$ reacted readily with aryl azides in toluene or CH_2Cl_2 to produce complexes that are dimeric, arylimido-bridged iron(III) salicylaldimine complexes (Table I, Figures 1 and 2). CH_2Cl_2 was found to be strongly retained by the compounds, as has also been found for oxo-bridged complexes such as [Fe(salen)]$_2$O.[20,21] Reactions also could be carried out in THF. However, there were significant problems arising from hydrolysis in this solvent. Fe(salen) did not react with p-tolyl azide in pyridine probably because pyridine, weakly coordinating to the complex, can block initial coordination of the azide.

Table III. Atomic Parameters for [Fe(salen)]$_2$N(Tol)

atom	x	y	z	U(iso), Å^2
Fe(1)	0.0152 (2)	0.6898 (2)	0.3650 (2)	a
Fe(2)	−0.0041 (2)	0.8319 (2)	0.1294 (2)	a
C(1)	−0.1619 (12)	0.7108 (13)	0.2213 (14)	0.032 (4)
C(2)	−0.2266 (13)	0.7678 (15)	0.2957 (15)	0.051 (5)
C(3)	−0.3286 (14)	0.7265 (15)	0.2834 (16)	0.056 (5)
C(4)	−0.3727 (13)	0.6271 (15)	0.1983 (16)	0.049 (5)
C(5)	−0.3151 (12)	0.5725 (14)	0.1222 (15)	0.046 (5)
C(6)	−0.2096 (12)	0.6120 (13)	0.1305 (14)	0.039 (5)
C(7)	−0.4822 (14)	0.5760 (17)	0.1958 (19)	0.083 (7)
C(8)	0.2117 (13)	0.8320 (14)	0.5002 (15)	0.045 (5)
C(9)	0.2606 (14)	0.9248 (16)	0.6001 (17)	0.067 (6)
C(10)	0.3650 (14)	0.9477 (16)	0.6267 (17)	0.067 (6)
C(11)	0.4258 (16)	0.8866 (16)	0.5616 (17)	0.071 (6)
C(12)	0.3843 (13)	0.8008 (15)	0.4598 (16)	0.056 (5)
C(13)	0.2769 (12)	0.7712 (14)	0.4293 (14)	0.040 (5)
C(14)	0.2370 (13)	0.6750 (14)	0.3229 (15)	0.046 (5)
C(15)	0.1116 (12)	0.5367 (13)	0.1807 (14)	0.046 (5)
C(16)	0.0457 (12)	0.4504 (14)	0.2279 (15)	0.052 (5)
C(17)	−0.1021 (12)	0.4506 (14)	0.3274 (14)	0.045 (5)
C(18)	−0.1775 (13)	0.4933 (15)	0.4002 (16)	0.047 (5)
C(19)	−0.2761 (14)	0.4227 (16)	0.3937 (16)	0.059 (6)
C(20)	−0.3502 (16)	0.4597 (17)	0.4572 (18)	0.073 (7)
C(21)	−0.3310 (15)	0.5661 (17)	0.5332 (18)	0.076 (6)
C(22)	−0.2403 (14)	0.6355 (16)	0.5479 (16)	0.061 (6)
C(23)	−0.1603 (13)	0.6059 (14)	0.4793 (14)	0.039 (5)
C(24)	−0.1957 (13)	0.8142 (14)	−0.0405 (15)	0.040 (5)
C(25)	−0.2730 (15)	0.7415 (16)	−0.1315 (16)	0.067 (6)
C(26)	−0.3714 (14)	0.7662 (16)	−0.1516 (16)	0.059 (5)
C(27)	−0.3910 (15)	0.8686 (16)	−0.0858 (17)	0.068 (6)
C(28)	−0.3226 (14)	0.9396 (16)	0.0013 (17)	0.058 (6)
C(29)	−0.2229 (13)	0.9179 (14)	0.0257 (15)	0.040 (5)
C(30)	−0.1547 (13)	0.9979 (14)	0.1138 (15)	0.045 (5)
C(31)	0.0006 (13)	1.0836 (14)	0.2557 (15)	0.054 (5)
C(32)	0.0763 (12)	1.0369 (14)	0.3358 (15)	0.054 (5)
C(33)	0.2124 (13)	0.9497 (14)	0.2528 (15)	0.045 (5)
C(34)	0.2583 (12)	0.8731 (13)	0.1694 (14)	0.036 (4)
C(35)	0.3659 (13)	0.8825 (15)	0.1824 (16)	0.050 (5)
C(36)	0.4187 (13)	0.8205 (14)	0.1073 (15)	0.050 (5)
C(37)	0.3619 (13)	0.7416 (14)	0.0032 (15)	0.050 (5)
C(38)	0.2554 (13)	0.7235 (14)	−0.0151 (15)	0.048 (5)
C(39)	0.2020 (14)	0.7876 (15)	0.0665 (16)	0.049 (5)
N(1)	−0.0553 (8)	0.7454 (10)	0.2390 (10)	0.030 (3)
N(2)	0.1424 (10)	0.6381 (11)	0.2859 (12)	0.042 (4)
N(3)	−0.0242 (10)	0.5081 (11)	0.3029 (12)	0.044 (4)
N(4)	−0.0636 (10)	0.9887 (11)	0.1651 (12)	0.041 (4)
N(5)	0.1152 (10)	0.9488 (11)	0.2526 (11)	0.039 (4)
O(1)	0.1134 (9)	0.8094 (9)	0.4808 (10)	0.053 (3)
O(2)	−0.0738 (8)	0.6745 (9)	0.4894 (10)	0.046 (3)
O(3)	−0.1040 (8)	0.7888 (9)	−0.0199 (9)	0.048 (3)
O(4)	0.1034 (8)	0.7713 (9)	0.0440 (9)	0.041 (3)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.043 (2)	0.039 (2)	0.028 (2)	0.002 (2)	0.002 (2)	0.007 (2)
Fe(2)	0.048 (2)	0.031 (2)	0.030 (2)	0.008 (2)	0.012 (2)	0.007 (1)

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$.

There may be some analogy between these types of reactions and those of Fe(II) complexes with molecular oxygen,[22] where $Fe^{IV}{=}O$ species are proposed to form and react with further Fe(II) complex to form μ-oxo species. Thus, if the first step in the azide reactions results in formation of $Fe^{IV}{=}NR$ complex just as $(\eta^5\text{-}C_5Me_5)V^{II}$ reacts with N_3Ar to give $(\eta^5\text{-}C_5Me_5)_2V^{IV}{=}NAr$,[23a] then the further reaction

$$(L)Fe^{IV}{=}NR + Fe^{II}L \rightarrow (L)Fe^{II}\text{–}N(Ar)\text{–}Fe^{III}(L)$$

could produce the bridged imido species observed. The exact form of the initial reactions of azide and Fe(II) is unclear at present although some evidence for the existence of an unstable orga-

---

(19) Sheldrick, G. M. "SHELX-76: A Program for Crystal Structure Determination"; Cambridge University: Cambridge, England, 1975.

(20) Lewis, J.; Mabbs, F. E.; Richards, A. *J. Chem. Soc. A* **1967**, 1014.

(21) Coggin, P.; McPhail, A. T.; Mabbs, F. E.; McLachlan, V. N. *J. Chem. Soc. A* **1971**, 1014.

(22) Chin, D.-H.; LaMar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344.

(23) (a) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945. (b) Osborne, J. H.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3098.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[Fe(salen)]_2N(Tol)$

Fe(1)-N(1)	1.87 (1)	Fe(2)-N(1)	1.88 (1)
Fe(1)-O(1)	1.95 (1)	Fe(2)-O(3)	1.92 (1)
Fe(1)-O(2)	1.93 (1)	Fe(2)-O(4)	1.94 (1)
Fe(1)-N(2)	2.10 (1)	Fe(2)-N(4)	2.14 (1)
Fe(1)-N(3)	2.14 (1)	Fe(2)-N(5)	2.12 (1)
	Fe···Fe	3.399 (3)	
O(1)-C(8)	1.29 (2)	O(3)-C(24)	1.31 (2)
O(2)-C(23)	1.31 (2)	O(4)-C(39)	1.29 (2)
N(2)-C(14)	1.27 (2)	N(4)-C(30)	1.31 (2)
N(3)-C(17)	1.26 (2)	N(5)-C(33)	1.29 (2)
C(13)-C(14)	1.46 (2)	C(29)-C(30)	1.37 (2)
C(15)-C(16)	1.49 (2)	C(31)-C(32)	1.51 (3)
C(17)-C(18)	1.44 (2)	C(33)-C(34)	1.42 (2)
N(2)-C(15)	1.48 (2)	N(4)-C(31)	1.46 (2)
N(3)-C(16)	1.47 (2)	N(5)-C(32)	1.45 (2)
N(1)-C(1)	1.41 (2)	C(4)-C(7)	1.50 (2)
N(1)-Fe(1)-O(1)	112.1 (5)	N(1)-Fe(2)-O(3)	104.7 (5)
N(1)-Fe(1)-O(2)	107.8 (5)	N(1)-Fe(2)-O(4)	114.3 (5)
N(1)-Fe(1)-N(2)	103.5 (5)	N(1)-Fe(2)-N(4)	106.8 (5)
N(1)-Fe(1)-N(3)	103.8 (5)	N(1)-Fe(2)-N(5)	101.1 (5)
O(1)-Fe(1)-O(2)	93.2 (4)	O(3)-Fe(2)-O(4)	93.6 (4)
O(1)-Fe(1)-N(2)	85.9 (5)	O(3)-Fe(2)-N(4)	85.9 (5)
O(1)-Fe(1)-N(3)	142.5 (5)	O(3)-Fe(2)-N(5)	151.7 (5)
O(2)-Fe(1)-N(2)	146.4 (5)	O(4)-Fe(2)-N(4)	137.5 (5)
O(2)-Fe(1)-N(3)	85.5 (5)	O(4)-Fe(2)-N(5)	86.1 (5)
N(2)-Fe(1)-N(3)	75.5 (5)	N(4)-Fe(2)-N(5)	75.6 (5)
Fe(1)-N(1)-C(1)	113.6 (10)	Fe(2)-N(1)-C(1)	116.7 (10)
C(2)-C(1)-C(6)	115.9 (14)	C(3)-C(4)-C(5)	119.0 (16)
N(1)-C(1)-C(6)	121.2 (14)	C(3)-C(4)-C(7)	121.0 (16)
N(1)-C(1)-C(2)	122.8 (12)	C(5)-C(4)-C(7)	119.9 (14)
	Fe(1)-N(1)-Fe(2)	129.6 (6)	

noazide-V(η^5-C_5Me_5) adduct has been presented[24] and $N_2{}^{15}NC_6H_5$ has been found to give $(\eta^5\text{-}C_5Me_5)_2V^{15}NC_6H_5$,[23a] indicating a possible site for attack by Fe(II).

Several other Fe(II) complexes were reacted with aryl azides, but imido complexes could not be isolated. Thus, the five-coordinate Fe(II) complex Fe(salmah) did not react with *p*-tolyl azide under conditions similar to those found successful for other Fe(II) complexes. This is comparable with the generally decreased activity of the complex toward oxygen[25] and Lewis bases compared to that of the other species examined. Fe(salmah) does form an oxo-bridged derivative, although rather slowly, but reacts readily with the strong oxidizer $Cr^{IV}O(TPP)$ to give Cr^{III}–O–Fe^{III} compounds.[12]

$Fe^{II}(Et_2dtc)_2$ did react with *p*-tolyl azide in CH_2Cl_2, and N_2 was evolved. The major Fe-containing product isolated, however, was $Fe^{III}(Et_2dtc)_3$. The fate of the organoimide group has not been determined so far. Possibly the lability of the dithiocarbamate groups may provide a route for decomposition of a reactive Fe^{IV}–NR species or even the anticipated bridged product. It is noteworthy that no authentic μ-oxo Fe(III) dithiocarbamato complex has been reported, while oxygen reacting with $Fe(Et_2dtc)_2$ also yields $Fe(Et_2dtc)_3$.[14]

The arylimido Fe(III) complexes are stable in the solid state for hours if exposed to the atmosphere and are stable for many weeks if kept under a dry atmosphere. The bis-bidentate complexes $[Fe(saltol)_2]_2N(R)$ are more reactive in the solid state, and a change to the red-orange color of the μ-oxo complex[26] is noticed soon after the dry complexes are exposed to moist air. The addition of water to solutions of the complexes in solvents such as toluene, THF, or CH_2Cl_2 results in rapid color changes with the appropriate oxo-bridged compound and primary amine being isolated from the solutions. There was no evidence for the intervention of dioxygen in the hydrolysis since reaction with $H_2{}^{18}O$ in toluene gave $[Fe(salen)]_2{}^{18}O$, as evidenced by the Fe–^{18}O–Fe IR frequency observed at 783 cm^{-1} (cf. Fe–^{16}O–Fe at 825 cm^{-1}). Thus

$$[Fe(salen)]_2N(Tol) + H_2O \rightarrow [Fe(salen)]_2O + p\text{-tol-}NH_2$$

Ph_3P did not abstract the *p*-tolylimido group from $[Fe(salen)]_2N(Tol)$ although this reaction does take place with the porphyrinato complex (TPP)Cr=N(Tol),[8] Ph_3P=N(Tol) being formed. No exchange of the *p*-tolylimido group for oxygen from Ph_3PO could be detected from solutions of the latter reagent with $[Fe(salen)]_2N(Tol)$. This lack of reactivity may be due to steric hindrance to attack on the μ-*p*-tolylimido–iron bond or, in the case of the Ph_3P reaction, be due to the difficulty in reducing Fe^{III}(salen) to Fe^{II}(salen).

Infrared Spectra. The complexes have spectra that are very similar to those of the analogous μ-oxo with the notable absence of the strong bands in the 800-cm^{-1} region due to asymmetric stretching frequencies of the Fe–O–Fe system.

The *p*-tolyl and *p*-chlorophenyl derivatives (but not the phenyl) however each show a strong band at 820 cm^{-1} due to C–H out-of-plane vibrations of para-disubstituted benzene rings. The bands remain at this frequency when observed in either Nujol mulls or CH_2Cl_2 solution whereas the Fe–O–Fe band in $[Fe(salen)]_2O$ moves from 825 cm^{-1} in Nujol to 800 cm^{-1} in CH_2Cl_2.[27] An absorption at 700 cm^{-1} observed in each of the azides (PhN_3, *p*-$TolN_3$, *p*-$ClPhN_3$) is also retained in the spectra of the metal–imido complexes.

Metal–imido stretching frequencies are still somewhat uncertainly defined in general.[1] An exception appears to be V=N(R) stretching frequencies,[23b] which have been allocated values in the range 920–970 cm^{-1} on the basis of ^{15}N isotopic labeling in $(C_5Me_5)_2V$=N(R) derivatives. There is as yet no clear-cut evidence for the frequencies found for imido-bridged systems because of the complications due to other ligand vibrations as well as likely strongly coupled M–N and N–R vibrations. It has not been possible to identify any frequencies above 700 cm^{-1} that can be ascribed to Fe–N(R)–Fe vibrations. The ^{15}N-labeled complex $[Fe(salen)]_2{}^{15}NPh$ was prepared as part of the present study, but its spectrum was found to be virtually identical with that of the unlabeled complex above 700 cm^{-1}.

Mass Spectra. The complexes fail to show molecular ions under the conditions of measurement used, but fragments corresponding to the monomeric iron complexes and ions derived from the organoimido group are readily observed. Thus, $[Fe(salen)]_2N(Tol)$ displays $[Fe(salen)]^+$ fragments and $[p\text{-}CH_3C_6H_4N]^+$, $[p\text{-}CH_3C_6H_4NH]^+$, and $[p\text{-}CH_3C_6H_4NH_2]^+$.

Other Reactions. Fe(salen) and $Fe^{II}(saltol)_2$ react readily with Me_3SiN_3, but the products are the monomeric azide derivatives $[Fe(Lig)]N_3$ identified by the strong azide absorptions at 2100 cm^{-1}, their high magnetic moments (5.3 μ_B), and microanalytical data. The reaction of several trisubstituted silyl azides[23a] with $(\eta^5\text{-}C_5Me_5)_2V$ has also yielded the azides $(\eta^5\text{-}C_5Me_5)_2VN_3$ whereas aryl azides gave the imido complexes $(\eta^5\text{-}C_5Me_5)_2V$=NR. This difference was suggested to be due to steric hindrance to the attack of V on the α-nitrogen compared with an easier approach to the γ-N. Cyclohexyl azide appeared not to react at all with Fe(salen)

---

(24) Gambarrotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49.

(25) Niswander, R. H.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 1511.

(26) van den Bergen, A.; Murray, K. S.; O'Connor, M. J.; Rehak, N.; West, B. O. *Aust. J. Chem.* **1968**, *21*, 1505.

(27) It has been noted that the infrared spectra of unsolvated $[Fe(salen)]_2O$ and its CH_2Cl_2 solvate differ markedly in the 800–900-cm^{-1} region. This has no doubt led to the confusion over the assignment of the μ-oxo stretching frequencies for these complexes.[13,21] Isotopic labeling studies have confirmed the assignment of the μ-oxo band in the unsolvated species (825 cm^{-1}, Fe–^{16}O–Fe; 783 cm^{-1}, Fe–^{18}O–Fe). A similar (43 cm^{-1}) shift has been found for ^{18}O and ^{16}O $[Fe(TPP)]_2O$.[28] The CH_2Cl_2 $[Fe(salen)]_2O$ solvate does not have a band at 825 cm^{-1}, but there is a notable increase in the intensity of bands around the 800-cm^{-1} region. This group of absorptions generally decreases in intensity upon ^{18}O substitution. The presence of strong ligand peaks around 800 and 760 cm^{-1} prevents the accurate assignment of μ-oxo stretching frequencies for this compound. The difference in μ-oxo stretching frequencies between the unsolvated and solvated species is no doubt due to strong hydrogen bonding between CH_2Cl_2 and the oxygen atom in the μ-oxo bond in the solvated complex, as is apparent from the crystal structure of that complex.[21]

(28) Saxton, R. J.; Olson, L. W.; Wilson, L. J. *J. Chem. Soc., Chem. Commun.* **1982**, 984.

Table V. Structural Data for [Fe(salen)]$_2$X Bridged Complexes

compd	Fe–X,[a] Å	X–Fe–X, deg	d,[b] Å	α,[c] deg	β,[c] deg	γ,[d] deg	ref
[Fe(salen)]$_2$N(Tol)	1.87 (1)	129.6 (6)	0.594 (3)	29.4	6.8	25.5	this work
			0.589 (3)	19.6	7.7	21.4	
[Fe(salen)]$_2$O	1.78 (1)	144.6 (6)	0.581	4.5	14.3	10.7	30
			0.572	2.5	15.0	16.2	
[Fe(salen)]$_2$O·2py	1.797 (16)	139.1 (9)	0.570	19.7	21.4	41.0	36
			0.549	9.9	15.8	24.1	
[Fe(salen)]$_2$O·CH$_2$Cl$_2$	1.794 (9)	142.2 (5)	0.570	11.3	23.6	34.3	21
			0.550	11.9	14.7	26.4	
[Fe(salen)]$_2$S	2.170 (2)	121.8 (1)	0.591	12.0	17.4	29.4	31
			0.625	11.5	17.2	26.6	

[a] Mean value. [b] Displacement of Fe from N_2O_2 least-squares plane. [c] Dihedral angle between N_2O_2 coordination plane and least-squares planes of salicylaldiminato group. [d] Dihedral angle between salicylaldiminato group planes.

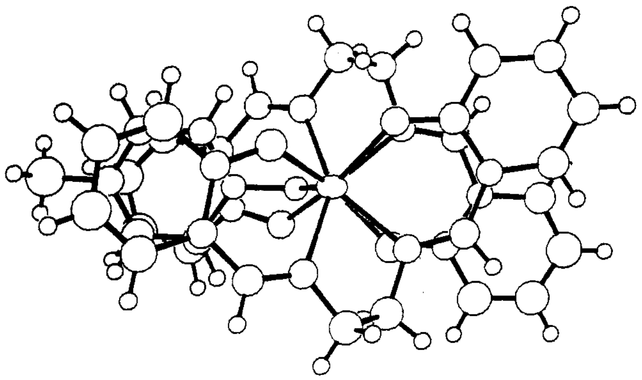

Figure 3. ORTEP drawing of [Fe(salen)]$_2$N(Tol) viewed down the Fe···Fe axis.

Table VI. Mössbauer Spectral Parameters for μ-Organoimido Fe(III) Complexes with Comparison Data

complex	T, K	δ,[a] mm/s	ΔE_Q, mm/s	Γ,[b] mm/s
[Fe(salen)]$_2$N(Tol)	77	0.43	0.77	0.12
[Fe(salphen)]$_2$N(Tol)[c]	77	0.43	0.75	0.11
[Fe(saltol)$_2$]$_2$N(Tol)	77	0.48	1.41	0.21
[Fe(saltol)$_2$]$_2$N(ClPh)	77	0.45	1.35	0.21
[Fe(salen)]$_2$O[37]	77	0.46	0.78	
[Fe(salen)]$_2$S[38]	300	0.33	0.60	
[Fe(saltol)$_2$]$_2$O[39]	77	0.32	1.41	
Fe(salen)[40]	95	1.29	2.41	
Fe(salphen)[40]	77	1.27	2.43	

[a] Measurements relative to α-Fe at 295 K. [b] Line width Γ, the half-width at half-maximum height. [c] The sample examined showed an additional component was present to the extent of 20% with parameters close to those for Fe^{II}(salphen).

or Fe(saltol)$_2$ in CH$_2$Cl$_2$, though whether this should be ascribed to steric effects or a change in variety of the azido nitrogens is unclear.

Attempts to convert [Fe(salen)$_2$]$_2$O directly into a bridged imido derivative by reaction with PhNCO have not been successful. This process was examined in the light of the successful synthesis of [(Cp)$_2$Mo(NPh)]$_2$N(Ph) by reacting [(Cp)$_2$Mo(O)]$_2$O with PhNCO.[29] However, the Fe^{III}–oxo complex showed no reaction with PhNCO in refluxing toluene nor did it react with the potential oxo–imide exchange reagent (Me$_3$Si)$_2$NMe. Neither [Fe(salen)]$_2$O nor [Fe(salen)]$_2$S reacted with arylamines such as aniline or p-toluidine.

Structure. The dinuclear, imido-bridged structure has been confirmed by an X-ray diffraction study of [Fe(salen)]$_2$N(Tol). The crystallographic asymmetric unit contains one discrete molecule of [Fe(salen)]$_2$N(Tol), which consists of two Fe(salen) units linked to the N atom of the tolylimido group. The tolyl ring lies between the two Fe(salen) systems as shown in Figure 2. A projection of the molecule viewed along the Fe···Fe axis is also shown in Figure 3. Selected bond distances and angles are given in Table IV.

The Fe–N–Fe angle is considerably lower at 129.6 (6)° than the 144.6 (6)° Fe–O–Fe angle in [Fe(salen)]$_2$O[30] but is still larger than that of Fe–S–Fe (121.8 (1)°) in the μ-sulfido derivative [Fe(salen)]$_2$S.[31] The additional bridge angles defining the imido compound are those including the tolyl carbon linked to the bridge N. They show slight differences, with Fe(1)–N(1)–C(1) = 113.6 (10)° and Fe(2)–N(1)–C(1) = 116.7 (10)°. The bridge N(1) is virtually coplanar with Fe(1), Fe(2), and C(1), its calculated distance above the least-squares plane of these atoms being 0.03 (1) Å.

The combination of short Fe–N(1) bonds, coplanarity of the three bands at N(1), and the values of the three bond angles at N suggest the possibility of multiple bonding in the Fe–N(1) linkages with involvement of the N lone pair. A similar combination of structural features has been reported for the phenylimido-bridged Ti(III) complex [(Cp)TiCl]$_2$(μ-NPh)(μ-N$_2$Ph$_2$).[32] This is not a necessary feature of an imido bridge, however, since the dibridged compound [(Me$_2$N)$_2$Zr]$_2$(μ-N^{t}Bu)$_2$ does not have coplanar Zr–N(^{t}Bu) and N–C(^{t}Bu) bonds.[33]

As in the μ-oxo and μ-sulfido complexes, the Fe atoms lie above the planes defined by the O$_2$N$_2$ donor atoms and toward the bridging N(1), Fe(1) at 0.594 (3) Å and Fe(2) at 0.589 (3) Å. The bridge distances Fe–N are equivalent and notably shorter at 1.87 (1) Å than the Fe–N distances within the chelate ring systems, the average value of which is 2.12 Å. The nitrido-bridged iron tetraphenylporphyrinato compound[34] [Fe(TPP)]$_2$N has a linear Fe–N–Fe array with Fe–N = 1.6605 (7) Å, but the Fe–N bonds have bond orders greater than 1.

The salen molecules are asymmetrically arranged with respect to each other with the salicylaldimine rings in one Fe(salen) unit bent away from the second Fe(salen) molecule along the chelate-ring ON axes to produce the characteristic "asymmetric umbrella" conformation of salen structures. The dihedral angles defining the intersections of the salicylaldimine group least-squares planes with the plane of the O$_2$N$_2$ donor sites as defined by Calligaris et al.[35] are shown in Table V. The distortion necessary to accommodate the tolyl group between two salicylaldimine fragments on neighboring Fe(salen) moieties is shown by the larger values of α and correspondingly smaller β values for this compound compared to those for the oxo and sulfido analogues.

The geometric relationship of the tolyl group to the nearest-neighbor salicylaldimine segments of the two Fe(salen) molecules can be described by a series of dihedral angles defining the intersections of the best least-squares planes representing the tolyl

---

(29) Green, M. L. H.; Moynihan, K. J. *Polyhedron* **1986**, *5*, 921.

(30) Davies, J. E.; Gatehouse, B. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1934.

(31) Dorfman, J. R.; Girerd, J.-J.; Simhon, E. D.; Stack, T. D. P.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 4407.

(32) Gambarrotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 1015.

(33) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(34) Scheidt, W. R.; Summerivlle, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623.

(35) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.

(36) Gerloch, M.; McKenzie, E. D.; Towl, A. D. C. *J. Chem. Soc. A* **1969**, 2850.

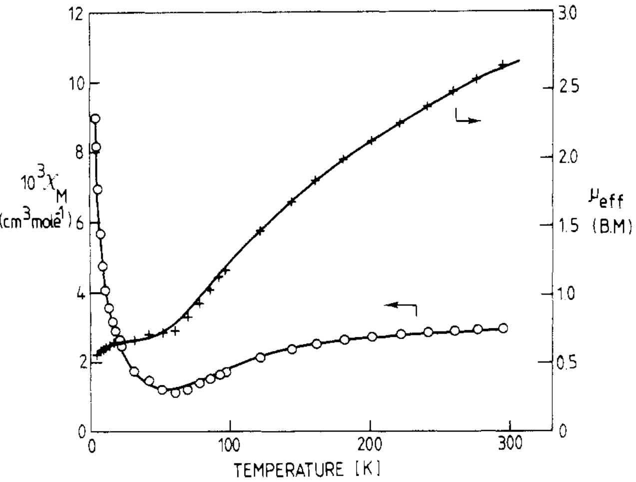

Figure 4. Plots of molecular susceptibility (O) and magnetic moment (per molecule) (+) for $[Fe(salen)]_2N(Tol)$. (The solid lines are based on values calculated from the best-fit parameters given in the text.)

ring or the appropriate salicylaldimine segments with the plane defined by Fe(1), Fe(2), N(1), and C(1), the tolyl ring carbon bonded to N(1). These angles are listed for the following ring planes: {C(1)–C(6)}, 96.3°; {O(2),C(17)–C(23),N(3)}, 90°; {O(3),C(24)–C(30),N(4)}, 85°.

Mössbauer Effect Spectra and Magnetism. The Mössbauer effect spectra of a number of the organoimido-bridged complexes were measured at 77 K. All show sharp, symmetrical quadrupole doublets. The isomer shifts (δ) and quadrupole splitting values (ΔE_Q) are given in Table VI together with those for related μ-oxo and μ-sulfido Fe(III) complexes for comparison. The isomer shift values are typical of those expected for high-spin ($S = {}^5/_2$) Fe(III) centers within the binuclear moiety.[41] The size of the quadrupole splitting is likewise symptomatic of a high-spin Fe(III) ion in a five-coordinate (N_3O_2) environment. The increase in ΔE_Q in going from tetradentate (salen) to bis-bidentate (saltol) ligand systems is indicative of small structural changes occurring around each Fe(III) entity that influence the precise ligand field symmetry around the metal but do not affect the spin state. A similar increase in ΔE_Q was observed between $[Fe(salen)]_2O$ and $[Fe(saltol)_2]_2O$.[39]

The δ and ΔE_Q values of the μ-oxo, -sulfido, and -organoimido Fe(III) salen complexes are very similar to each other, suggesting that the nature of the bridging (i.e. apical) atom does not affect either the spin state of Fe or the overall ligand field in any significant way.

The magnetic data lead to similar conclusions although there are differences in detail. The magnetic moments, per molecule, for a representative selection of the μ-organoimido complexes are shown in Table I. The values are grouped around 2.8 μ_B per dimer unit (i.e. ca. 1.9 μ_B per Fe) and are indicative of strong antiferromagnetic coupling of $S = {}^5/_2$ Fe(III) centers.[41] A variable-temperature susceptibility study of the compound $[Fe(salen)]_2N(Tol)$ plotted in Figure 4 confirms the antiferromagnetic coupling. The susceptibilities decrease gradually between 300 and 50 K, as expected for a ${}^5/_2$–${}^5/_2$ model with an $S' = 0$ ground state, but then increase at lower temperatures due to the presence of the traces of monomer impurity. A least-squares computer fitting of the data to the calculated susceptibility expression[41] gave the following best-fit set of parameters: $g = 1.98 \pm 0.03$; $J = -103 \pm 0.5$ cm^{-1} (% monomer impurity = 0.65 ± 0.005).

Plots similar to that in Figure 4 have been reported for $[Fe(salen)]_2O$[42] ($J = -89$ cm^{-1}) and $[Fe(salen)]_2S$[31] ($J = -88$ cm^{-1}) although the absolute values of χ_M were higher in those systems on account of the slightly smaller J values. The Fe–X–Fe bridge angles in this small series of $[Fe(salen)]_2X$ molecules vary over a range of 23° (Table V), making it difficult to determine which bridging atom can act as the best mediator of exchange coupling.

In a recent study, Holm and co-workers[43] have succeeded in keeping the Fe–X–Fe bridge angle almost constant by use of bulky 3-Bu^t-salen terminal ligands leading to the following Fe–X–Fe angles: $X = O^{2-}$, 174°; $X = S^{2-}$, 167°. The μ-sulfido system shows the stronger antiferromagnetic coupling.

To the best of our knowledge, there have been no previous reports on the influence of μ-organoimido groups on magnetic coupling in paramagnetic complexes. The geometry around the N atom of the *p*-tolylimido group is virtually planar, while the Fe–N–Fe angle of 130° and Fe–N–C(tolyl) angles of 114 and 117° give a pseudotrigonal arrangement of the various bonds to N. This arrangement suggests good overlap is possible between sp^2 type N orbitals and Fe d orbitals, allowing for strong antiferromagnetic coupling, as is observed. Any π-bonding contributions in the Fe–N–Fe bond framework, as was suggested in the structural discussion, would enhance the exchange coupling although it is not required to explain the observed magnetism. Similar strong coupling has been observed in many copper(II) dimeric complexes having pseudotrigonally coordinated oxygen as bridging atoms contained in exogenous alkoxide (RO$^-$) or endogenous phenolate or alcoholate groups.[44]

Another group of possible relevance to the planar, bridging imido group is the deprotonated amide $(N(R)C{=}O)^-$ acting as a bridge in fragments such as $Cu^{II}{-}N(R){-}C{=}O{\rightarrow}Cu^{II}$. This also has a trigonal-planar geometry about the N atom, and binuclear complexes containing this multiatomic bridge structure display very strong antiferromagnetic coupling.[45]

Acknowledgment. This work was supported by grants (to B.O.W. and K.S.M.) from the Australian Research Grants Scheme and the Monash University Special Research Fund. The authors are grateful to C. Delfs for assistance with the magnetic and Mössbauer measurements and Dr. E. N. Bakshi for aid in fitting the data.

Registry No. $[Fe(salen)]_2N(Tol)$, 113432-07-8; $[Fe(salphen)]_2N(Tol){\cdot}CH_2Cl_2$, 115186-41-9; $[Fe(salen)]_2N(Ph)$, 115186-42-0; $[Fe(salen)]_2N(ClPh)$, 115186-43-1; $[Fe(salphen)]_2N(Ph)$, 115204-20-1; $[Fe(salphen)]_2N(ClPh)$, 115186-44-2; $[Fe(saltol)_2]_2N(Tol)$, 115186-45-3; $[Fe(saltol)_2]_2N(Ph)$, 115186-46-4; $[Fe(saltol)_2]_2N(ClPh)$, 115204-21-2; $Fe^{II}(salen)py$, 24323-09-9; $Fe^{II}(salphen)$, 16828-80-1; $Fe^{II}(salmah)$, 65802-39-3; $Fe^{II}(saltol)_2$, 115186-47-5; $Fe(Et_2dtc)_2$, 15656-03-8; $Fe^{III}(Et_2dtc)_3$, 13963-59-2; $[Fe(salen)]_2O$, 18601-34-8; phenyl azide, 622-37-7; *p*-tolyl azide, 2101-86-2; *p*-chlorophenyl azide, 3296-05-7.

Supplementary Material Available: Table SI, listing angles and distances associated with the phenyl and chelate rings, the derived hydrogen positions, equations of least-squares planes, and distances of atoms from the planes (6 pages); Table SII, listing calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

---

(37) Reiff, W. M.; Baker, W. A.; Erickson, N. E. *J. Am. Chem. Soc.* **1968**, *90*, 4794.

(38) Mitchell, P. C. N.; Parker, D. A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1385.

(39) Buckely, A. N. Ph.D. Thesis, Monash Universioty, 1971; p 187.

(40) DeVries, J. L. K. F.; Trooster, J. M.; DeBoer, E. *J. Chem. Soc., Dalton Trans.* **1974**, 1771.

(41) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1.

(42) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 723.

(43) Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 1850.

(44) Murray, K. S. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine: New York, 1986; p 161.

(45) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063.