Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Structure Studies of Iron(III) Salicylaldimine Complexes. Five-Coordinate Monomeric and Dimeric Complexes

J. A. BERTRAND,* J. L. BREECE, and P. G. ELLER

Received June 5, 1973

The preparations, structures, and magnetic properties of two five-coordinate iron(III) salicylaldimine complexes are reported. The complex with *N*-(3-hydroxypropyl)salicylaldimine (SALPA), Fe(SALPA)Cl, crystallized in space group $P2_1/c$ (a = 11.548 (3) Å, b = 9.143 (2) Å, c = 18.683 (4) Å, β = 134.43 (5)°) with four formula units of the compound and two disordered molecules of toluene per unit cell ($\rho_{\text{calcd}} = 1.48$ g cm^{-3}; $\rho_{\text{obsd}} = 1.47$ (2) g cm^{-3}). The structure, which was refined to a conventional R value of 0.099, contains dimeric, five-coordinate iron complexes in which the coordination is intermediate to the trigonal-bipyramidal and square-pyramidal arrangements. The room temperature magnetic moment is below the expected value for a high-spin d^5 complex and is indicative of antiferromagnetic coupling. The monomeric complex with *N*-(2-phenylethyl)salicylaldimine (SANE), Fe(SANE)$_2$Cl, crystallized in space group $P2_1/c$ (a = 13.325 (1) Å, b = 21.336 (1) Å, c = 10.168 (1) Å, β = 115.86 (1)°) with four formula units per unit cell ($\rho_{\text{calcd}} = 1.38$ g cm^{-3}; $\rho_{\text{obsd}} = 1.37$ (1) g cm^{-3}). The structure, which was refined to a conventional R value of 0.074, contains monomeric five-coordinate complexes in which the coordination is intermediate to the trigonal-bipyramidal and square-pyramidal arrangements. Above 196°K, the magnetic moment is typical for a high-spin d^5 complex. The magnetic moment at temperatures of 140°K and lower is greatly reduced and a phase transition is thought to occur between 140 and 196°K. The possibility of dimer formation at the temperature of the phase transition is suggested.

Introduction

Iron(III) complexes of Schiff base ligands have been the subject of several recent studies[1-9] and a number of different types of complexes have been reported. Among these complexes, there are several types that are interesting because of unusual coordination numbers and several types that are interesting because they exist as polynuclear species.

Since iron(III) complexes of Schiff base ligands usually have high-spin d^5 configurations, there is no ligand field stabilization effect and stereochemical considerations should be the same as for a nontransition metal ion. On the basis of VSEPR, a five-coordinate complex would be expected to have a trigonal-bipyramidal arrangement of donor groups, but a square-pyramidal arrangement, with the metal ion above the base (apex ligand–metal–basal ligand angles *ca.* 104°), should be almost as favorable.[10,11] Since the energy difference between these two possibilities is small, the size and shape of the ligands could be important in determining the arrangement and, in some cases, arrangements intermediate to these two might result. One example in which the ligand geometry appears to be important is the complex with the tetradentate ligand *N,N'*-ethylenebis(salicylidenimine), Salen, which has the formula Fe(Salen)Cl. The ligand geometry would favor a square-pyramidal arrangement with the tetradentate ligand occupying the basal positions, and this is the arrangement observed for the monomeric form of this compound.[2] With the bidentate ligand *N*-*n*-propylsalicylaldimine, Sal=NPr, an iron(III) complex of the formula Fe(Sal=NPr)$_2$Cl has been reported, and a preliminary communication of a structure study[12] indicated a five-coordinate geometry that is intermediate to a square pyramid and a trigonal bipyramid. The geometry is most easily indicated by the Cl–Fe–donor angles; for a square pyramid arrangement all four angles would equal *ca.* 104° and for a trigonal bipyramid arrangement two angles would be 90° and two would be 120°. In the case of Fe(Sal=NPr)$_2$Cl, two angles of 97° and two of 113° were observed.

Other examples of Schiff base complexes containing five-coordinate iron(III) are found among the oxygen-bridged dimeric complexes which are also of interest because of their magnetic properties. Oxygen-bridged dimers with a single oxo bridge[8,13] and oxygen-bridged dimers containing a four-membered iron–oxygen ring[3,9] have been reported and both types show antiferromagnetic coupling. The complex [Fe(Salen)]$_2$O, an example of an oxo-bridged species, has an Fe–O–Fe angle of approximately 140° and a coupling constant,[1] J, of the order of -100 cm^{-1}. The coordination about the iron, as in Fe(Salen)Cl, is square pyramidal with the bridging oxygen at the apex. A number of complexes of the type [Fe(Sal=NR)$_2$]$_2$O have been reported[5] and, although no structure studies have been reported, the fact that they show magnetic coupling similar in magnitude to that in [Fe(Salen)]$_2$O suggests a structure with a single oxo bridge between two five-coordinate iron(III) complexes. A number of additional oxo-bridged iron(III) complexes[14,15] with different coordination numbers and with Fe–O–Fe angles up to 180° show similar magnetic properties. One of these complexes[14] contains seven-coordinate iron(III) with a pentagonal-bipyramidal arrangement of the donors about the metal ion.

The dimeric form of Fe(Salen)Cl is an example of a complex with a four-membered iron–oxygen ring.[3] The monomeric units stack together in pairs so that an additional iron–oxygen bond is formed from each iron to an oxygen of the

---

[1] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 1014 (1967).

[2] M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).

[3] M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1900 (1967).

[4] M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 112 (1968).

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

[6] A. van den Bergen, K. S. Murray, and B. O. West, *Aust. J. Chem.*, 21, 1517 (1968).

[7] A. van den Bergen, K. S. Murray, B. O. West, and A. N. Buckley, *J. Chem. Soc. A*, 2051 (1969).

[8] M. Gerloch, E. D. McKenzie, and A. D. C. Towl, *J. Chem. Soc. A*, 2850 (1969).

[9] J. A. Bertrand, J. L. Breece, A. R. Kalyanaraman, G. J. Long, and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, 92, 5233 (1970).

[10] R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

[11] J. Zemann, *Z. Anorg. Allg. Chem.*, **324**, 241 (1963).

[12] J. E. Davies and B. M. Gatehouse, *Chem. Commun.*, 1166 (1970).

[13] F. E. Mabbs, P. Goggan, A. T. McPhail, and V. N. McLachlan, *J. Chem. Soc. A*, 1014 (1971).

[14] E. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, **89**, 720 (1967).

[15] S. J. Lippard, H. J. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967).

adjacent ligand and the coordination about the iron becomes six-coordinate. Although there is antiferromagnetic coupling of the iron atoms, the magnitude of the interaction is much less than in the oxo-bridged dimers as evidenced by the value[4] of J, -7.5 cm^{-1}. Complexes with terdentate Schiff base ligands have been prepared and these complexes, which have formulas of the type FeLCl, show magnetic coupling of the same order of magnitude as for $[\mathrm{Fe(Salen)Cl}]_2$. A binuclear oxygen-bridged structure was suggested for these complexes[7] and a preliminary communication of the structure of the FeLCl complex with *N*-(3-hydroxypropyl)-salicylaldimine as ligand confirmed the hypothesis of a dimer and showed square-pyramidal coordination of iron(III) with a four-membered iron-oxygen ring.[9]

We are making a systematic study of structures of iron(III) complexes of Schiff base ligands and in this paper report structures for a five-coordinate monomeric complex with bidentate ligands and for a five-coordinate dimeric complex with a terdentate ligand. Although a preliminary communication reported the crystal structure for the unsolvated form of the *N*-(3-hydroxypropyl)salicylaldimine complex, crystals large enough for a complete data set could not be obtained and the complete structure reported here involved crystals that contain toluene of crystallization.

Experimental Section

$\mathrm{Fe(SANE)_2Cl}$. Preparation. A solution of $\mathrm{FeCl_2{\cdot}4H_2O}$ (0.695 g, 3.50 mmol) in 6 ml of 80% methanol was slowly added to a solution of *N*-2-phenylethylsalicylaldimine (1.70 g, 7.00 mmol) in 10 ml of methanol. The resulting intensely red-black solution was stirred for 15 min then allowed to stand overnight. A small crop (0.078 g) of deep red-brown microcrystals formed; reducing the volume of solvent to one-half and addition of ether produced a second crop of $\mathrm{Fe(SANE)_2Cl}$.

Anal. Calcd for $\mathrm{FeC_{30}H_{28}N_2O_2Cl}$: C, 66.74; H, 5.22; N, 5.19; Cl, 6.57. Found: C, 66.50; H, 5.13; N, 5.33; Cl, 6.88.

Well-formed crystals suitable for single crystal X-ray analysis were obtained by recrystallization from diethyl ether.

Magnetic Susceptibility. The magnetic moment of the compound was determined by the Faraday method using $\mathrm{HgCo(CNS)_4}$ as a calibrant. Diamagnetic corrections were made using published atomic values.[16] The moment was determined at several temperatures and the values obtained (in BM), with the temperature of the measurement in parentheses (°K), were 5.95 (298), 5.81 (196), 4.19 (144), and 3.12 (77).

Crystallographic Data Collection. A well-formed crystalline block of approximate dimensions 0.25 × 0.25 × 0.25 mm was mounted on a glass fiber and precession photographs were taken, using zirconium-filtered Mo Kα radiation, λ 0.7107 Å. Precession photographs of the $h0l$, $h1l$, $h2l$, $hk0$, and $hk1$ reciprocal lattice levels were consistent with Laue symmetry $2/m$ and the systematic absence of the $0k0$ reflections with $k = 2n + 1$ and $h0l$ reflections with $l = 2n + 1$ uniquely defined the monoclinic space group $P2_1/c$ (No. 14).[17] The crystal was transferred to a Picker four-circle automated diffractometer and 16 medium intensity reflections, at various values of 2θ, were accurately centered. The setting angles for these reflections were used to refine cell parameters by a least-squares procedure; the cell parameters obtained are:[18] $a = 13.325$ (1) Å, $b = 21.336$ (1) Å, $c = 10.168$ (1) Å, and $\beta = 115.86$ (1)°. The calculated density of 1.378 g/cm^3 for four formula units per cell agrees well with the experimental density of 1.37 (1) g/cm^3 measured by the flotation method using a mixture of carbon tetrachloride and heptane. With four formula units per cell, there is no symmetry imposed on the structure by space group requirements and the asymmetric unit consists of one formula unit.

Intensity measurements were made using zirconium-filtered molybdenum radiation, with crystal-counter and source-crystal distances of 26 and 21 cm, respectively. The takeoff angle was adjusted to 1.9°, at which point the peak height of a medium intensity reflection was reduced to 90% of its maximum value. The width at half-height of ω scans of typical medium intensity reflections was 0.25°, indicating a satisfactory mosaic spread for the crystal.[19] Using a scan rate of 1 deg min^{-1}, a symmetrical scan of 2° was taken about the calculated position (λ 0.7109 Å) for each reflection, and stationary background counts for 20 sec were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/sec. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak. Three reflections occurring in diverse regions of reciprocal space (400, 060, 004) and a null reflection (14, 0, 0) were measured after every 150 reflections as a check on crystal and instrument stability. Since the standards varied randomly by less than 4% of the average corrected intensities, no scaling of the data was required. Corrected intensities (I) were obtained by subtracting three times the total measured background from the total integrated peak count (CT), where t_c is the scan time and t_b

$$I = \mathrm{CT} - 0.5(t_c/t_b)(\mathrm{bgd1} + \mathrm{bgd2})$$

is the counting time of each background (either bgd1 or bgd2). The corrected intensities were assigned standard deviations according to the formula[20]

$$\sigma(I) = [\mathrm{CT} + 0.25(t_c/t_b)^2(\mathrm{bgd1} + \mathrm{bgd2}) + (pI)^2]^{1/2}$$

A total of 4256 reflections were collected in a complete quadrant of data out to $2\theta = 50°$. Of these, 1955 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.50 with $p = 0.02$. Corrections for Lorentz and polarization effects were made but no corrections were made for absorption since both the crystal size and the linear absorption coefficient ($\mu = 7.25$ cm^{-1}) for molybdenum radiation are relatively small. The maximum error introduced by neglect of absorption corrections is estimated to be less than 4% on I.

Solution and Refinement of the Structure. Computations were carried out on the Burroughs 5500 and the Univac 1108 computers. Programs employed include Carter's cell and diffractometer setting angle program, Zalkin's FORDAP Fourier summation program, Iber's NUCLS5 modification of the Busing-Martin-Levy ORFLS full-matrix least-squares program, the Martin-Busing-Levy ORFFE function and error program, Johnson's ORTEP plotting program, and various locally written programs. In structure factor calculations, the scattering factors were taken from Cromer and Waber's tabulation[21] for all atoms except hydrogen; Stewart's hydrogen atom scattering factors were used.[22] The scattering factors for iron and chlorine were corrected for the real and imaginary anomalous dispersion components, using the dispersion factors tabulated by Cromer.[23] The agreement factors are defined in the usual way as $R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$. In all least-squares refinements, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$.

A three-dimensional Patterson synthesis revealed trial coordinates for iron, chlorine, and one oxygen atom. Three successive difference Fourier syntheses, calculated with phases derived from least-squares refined positions of atoms located on the Patterson and the previous Fourier syntheses, revealed the remaining nonhydrogen atoms. Four cycles of full-matrix least-squares refinement of an overall scale factor and individual positional and isotropic thermal parameters for the 36 nonhydrogen atoms (145 variables) reduced R to 0.179 and R_w to 0.281. A further refinement, using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$), gave $R = 0.212$ and $R_w = 0.219$.

At this point, an examination of the diffractometer scans indicated that the initial $\sigma(I)/I$ value of 0.50 was unrealistically high and allowed very weak or nonexistent reflections to be included. After the data set was reprocessed with a $\sigma(I)/I$ value of 0.33, 1448 statistically significant reflections remained. Two cycles of refinement, with variable anisotropic temperature factors for iron and

---

(16) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Wiley-Interscience, New York, N. Y., 1960, p 403.

(17) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965.

(18) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(19) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(20) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(21) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(23) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

Table I. Final Atomic Parameters for $Fe(SANE)_2Cl$

(A) Positional and Isotropic Thermal Parameters,[a] with Esd's[b]

Atom[c]	x	y	z	B	Atom	x	y	z	B
Fe	0.1087 (2)	0.0354 (1)	0.2376 (3)	*d*	H2	0.3832	−0.1001	0.3751	3.7
Cl	0.1475 (4)	0.0773 (2)	0.4577 (5)	*d*	H3	0.5811	−0.0869	0.4114	3.7
LAO	0.2268 (8)	−0.0193 (5)	0.2644 (12)	4.4 (2)	H4	0.6309	0.0123	0.3347	4.7
LACl	0.3312 (12)	−0.0094 (7)	0.2797 (17)	3.3 (3)	H5	0.4942	0.0963	0.2166	5.4
LAC2	0.4075 (12)	−0.0572 (7)	0.3421 (18)	3.9 (4)	H7	0.3189	0.1336	0.1220	4.1
LAC3	0.5177 (13)	−0.0496 (8)	0.3611 (18)	4.6 (4)	H8A	0.0390	0.1457	−0.0103	3.7
LAC4	0.5487 (15)	0.0059 (9)	0.3202 (22)	5.6 (4)	H8B	0.1647	0.1823	0.0143	3.7
LAC5	0.4717 (13)	0.0532 (8)	0.2550 (19)	4.9 (4)	H9A	0.0829	0.1800	0.2500	5.1
LAC6	0.3603 (10)	0.0459 (7)	0.2379 (16)	3.5 (3)	H9B	0.0486	0.2410	0.1205	5.1
LAC7	0.2871 (13)	0.0968 (7)	0.1711 (19)	4.0 (3)	H11	0.1862	0.3178	0.1239	5.9
LAN	0.1856 (9)	0.1025 (5)	0.1535 (14)	3.3 (2)	H12	0.3132	0.3689	0.3456	7.2
LAC8	0.1235 (12)	0.1593 (8)	0.0748 (18)	4.1 (3)	H13	0.5006	0.3245	0.5100	6.1
LAC9	0.1124 (14)	0.2058 (8)	0.1785 (21)	5.1 (4)	H14	0.4521	0.2205	0.6030	6.9
LAC10	0.2202 (12)	0.2393 (8)	0.2775 (18)	4.1 (3)	H15	0.2669	0.1694	0.4408	5.3
LAC11	0.2471 (15)	0.2971 (9)	0.2319 (22)	5.5 (4)	H17	−0.1780	0.1547	−0.0208	4.5
LAC12	0.3504 (16)	0.3243 (9)	0.3285 (24)	6.2 (5)	H18	−0.3690	0.1474	−0.0413	4.7
LAC13	0.4210 (16)	0.2998 (9)	0.4489 (23)	6.0 (5)	H19	−0.4387	0.0523	0.0309	5.5
LAC14	0.3972 (18)	0.2430 (11)	0.5003 (27)	6.9 (5)	H20	−0.2967	−0.0291	0.1754	3.0
LAC15	0.2940 (15)	0.2141 (8)	0.4070 (22)	5.2 (4)	H22	−0.1323	−0.0811	0.2405	4.5
LBO	−0.0252 (9)	0.0670 (5)	0.0959 (13)	5.2 (3)	H23A	0.1184	−0.1322	0.2929	3.2
LBC1	−0.1300 (12)	0.0637 (7)	0.0852 (17)	3.4 (3)	H23B	0.0531	−0.1260	0.4105	3.2
LBC2	−0.2039 (13)	0.1110 (8)	0.0203 (20)	4.3 (4)	H24A	−0.1969	0.4271	−0.0961	4.4
LBC3	−0.3115 (13)	0.1091 (8)	0.0040 (20)	4.8 (4)	H24B	−0.0716	0.4496	0.0532	4.4
LBC4	0.3464 (14)	0.0582 (8)	0.0550 (21)	4.9 (4)	H26	−0.1331	0.3514	−0.2157	6.5
LBC5	−0.2728 (12)	0.0097 (7)	0.1262 (18)	3.8 (3)	H27	0.1313	−0.2627	0.7653	7.1
LBC6	−0.1623 (11)	0.0137 (7)	0.1417 (17)	3.2 (3)	H28	0.3562	−0.2847	0.7549	6.4
LBC7	−0.0923 (10)	−0.0403 (8)	0.2129 (15)	3.4 (3)	H29	−0.3894	0.2383	0.3794	6.8
LBN	0.0137 (8)	−0.0419 (6)	0.2516 (12)	3.1 (2)	H30	−0.2908	0.3613	−0.1758	4.5
LBC8	0.0689 (11)	−0.1020 (7)	0.3283 (17)	3.2 (3)					
LBC9	−0.1316 (13)	0.4111 (8)	0.0081 (19)	4.3 (4)					
LBC10	−0.1818 (12)	0.1487 (8)	0.4240 (19)	4.1 (4)					
LBC11	−0.1286 (14)	0.3164 (9)	−0.1378 (21)	5.5 (4)					
LBC12	0.1821 (17)	−0.2385 (11)	0.7159 (25)	7.2 (5)					
LBC13	0.2825 (16)	−0.2555 (9)	0.7304 (22)	6.0 (5)					
LBC14	−0.3351 (17)	0.2248 (10)	0.3279 (25)	6.6 (5)					
LBC15	−0.2881 (14)	0.3318 (9)	0.0857 (20)	5.3 (4)					

(B) Anisotropic Thermal Parameters for Iron and Chlorine Atoms[e]

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Fe	440 (14)	163 (6)	1013 (32)	23 (11)	268 (17)	19 (17)
Cl	1025 (41)	180 (12)	1267 (77)	73 (18)	599 (50)	63 (24)

[a] Each hydrogen atom was assigned the temperature factor of the carbon to which it was bound at the time the hydrogen atom was introduced. Parameters of hydrogen atoms were not refined. [b] Estimated standard deviations, esd's, are right adjusted to the least significant digit of the preceding number. [c] LA and LB refer to ligand A and ligand B, respectively. [d] Atoms refined anisotropically. [e] The anisotropic thermal parameter is defined as: $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}kl - \beta_{23}kl]$.

chlorine (155 variables), resulted in agreement factors of $R = 0.096$ and $R_w = 0.081$. A difference Fourier synthesis revealed positions corresponding to 26 of the 28 hydrogen atoms among the strongest peaks. All hydrogen atoms were included, but not refined, in subsequent calculations at positions of idealized geometry (C-H distance of 1.08 Å and angles at carbon of 120.0 or 109.5°). Further refinement reduced R to 0.094 and R_w to 0.079.

Close examination of the data set indicated that the $\sigma(I)/I$ and the "ignorance factor," p, were still unrealistic and their values were reset to 0.25 and 0.03, respectively. After rejection of an additional seven reflections which had excessively long scan times due to instrumental difficulties, four cycles of least-squares refinement resulted in $R = 0.074$ and $R_w = 0.072$ for the remaining 1171 reflections. In the refinement with the reprocessed data, only seven of the 115 variables shifted by more than two estimated standard deviations (the maximum shift was 3.1σ), indicating that the reduction in agreement factors with the reprocessed data resulted from the elimination of randomly poor data. A weighting analysis showed no dependence of the function $\Sigma w(|F_o| - |F_c|)^2$ on $\sin\theta/\lambda$ or on F_o, indicating that an ignorance factor of 0.03 gives reasonable weights for the data. In the final refinement, the largest parameter shift (the x coordinate of C12) was 0.08 times its estimated standard deviation; the final agreement factors are $R = 0.074$ and $R_w = 0.072$. The final positional and thermal parameters are given in Table I.

$[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$. Preparation. The Schiff base ligand was prepared by direct reaction of salicylaldehyde and 3-aminopropanol. To the ligand (0.01 mol) was added a methanol solution (100 ml) of lithium methoxide (0.02 mol); the resulting solution of the dianion of the ligand was added dropwise to a stirred methanol solution of $FeCl_3 \cdot 6H_2O$ (0.01 mol). Upon heating the solution to reflux, a dark-brown crystalline product precipitated and was filtered off. The product was recrystallized from toluene to give $[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$.

Anal. Calcd for $Fe_2C_{27}H_{30}N_2O_4Cl_2$: C, 51.54; H, 4.77; N, 4.27. Found: C, 51.58; H, 4.74; N, 4.67.

Magnetic Susceptibility. The magnetic moment of the compound was determined by the Faraday method as described for $Fe(SANE)_2Cl$. A moment of 4.52 BM was obtained at room temperature and the value at 77°K was 2.37 BM.

Crystallographic Data Collection. The crystal chosen for the structure determination was a plate of approximate dimensions 0.75 × 0.45 × 0.15 mm; it was mounted along the long dimension (a^* axis). Precession photographs, using Zr-filtered Mo Kα radiation (λ 0.7107 Å), indicated a monoclinic unit cell; the absence of $h0l$ reflections for odd values of l and the absence of $0k0$ reflections for odd values of k uniquely defined the space group as $P2_1/c$ (No. 14).[17]

The crystal was transferred to an automated Picker four-circle diffractometer and 20 reflections, which were located and centered manually, were used to refine cell parameters by a least-squares procedure; the cell parameters obtained are: $a = 11.548$ (3) Å, $b = 9.143$ (2) Å, $c = 18.683$ (4) Å, $\beta = 134.43$ (5)°, and $V = 1408.6$ Å^3 (25°, Mo Kα radiation). The calculated density of 1.48 g/cm^3 for two dimers and two molecules of toluene per unit cell agrees well with the observed density of 1.47 (2) g/cm^3 measured by the flotation method using a mixture of hexane and methylene iodide.

The X-ray intensity measurements were made on the same crystal as used for the unit cell determination and Mo Kα radiation was again used. The data collection procedure was the same as described for the preceding crystal. A total of 850 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30 with $p = 0.01$. The intensities were corrected for Lorentz and polarization effects but no corrections were made for absorption. The linear absorption coefficient, μ, was 12.8 cm^{-1} and the value of $e^{-\mu t}$ ranged from 0.56 to 0.83; the actual range in integrated transmission factors is smaller than this.

Solution and Refinement of the Structure. Coordinates for the iron and chlorine atoms were obtained from a three-dimensional Patterson synthesis; an electron density calculation, using calculated phases based on the heavy atom contribution, revealed the positions of all nonhydrogen atoms except those of the toluene. After least-squares refinement of coordinates and isotropic temperature factors for all atoms located, the value of R was 0.147. A difference Fourier map at this point revealed a region of high electron density around the inversion center at ($^1/_2$, $^1/_2$, 0), and the toluene was introduced as a rigid group centered on the inversion center. Due to the inversion symmetry, only three-ring carbon atoms were required and these were positioned 1.37 Å from the inversion center with C-C distances of 1.37 Å. The methyl group, which is required to be disordered, was positioned on a line through one of the carbon atoms at a distance of 2.95 Å from the inversion center and was assigned an occupancy factor of 0.5. Four cycles of full-matrix least-squares refinement using a weighting scheme based on counting statistics ($w = 4I/\sigma(I)^2$) and refining an overall scale factor, individual positional parameters for all nonhydrogen atoms except those of the toluene group, anisotropic temperature factors for iron and chlorine and isotropic temperature factors for the other atoms, and three orientation angles and an isotropic group temperature factor for the toluene group gave $R = 0.099$ and and $R_w = 0.091$. The region around the toluene still showed some intensity in difference Fourier maps but attempts to treat disorder of the toluenes by including a second rigid group did not improve the refinement. No attempt was made to locate hydrogen atoms. Final positional and thermal parameters are given in Table II.

Description of Structures

$Fe(SANE)_2Cl$. Relevant bond distances and angles for the $Fe(SANE)_2Cl$ structure are given in Tables III and IV. The asymmetric unit, Figure 1, contains an iron(III) atom whose coordination is intermediate to a square pyramid and a trigonal bipyramid. Considering it as square pyramidal, the trans-chelate groups occupy the basal plane and the chlorine atom occupies the apical position. The base is distorted somewhat from planarity, with the four donor atoms deviating as much as 0.16 Å from the least-squares plane through the four atoms, and the iron atom is displaced 0.40 Å toward the apex from the least-squares plane of the four basal donor atoms. The fact that the coordination is intermediate to the square-pyramidal and trigonal-bipyramidal arrangements is indicated by the values of the chlorine-iron-basal ligand angles. These angles should all be 104° for a square pyramid while a trigonal bipyramid would have two of 90° and two of 120°; the observed values (97.2 and 100.8° for Cl-Fe-N; 107.1 and 111.0° for Cl-Fe-O) are very close to the values obtained by averaging these two sets of values.

The Fe-Cl bond (2.251 (5) Å) is within the normal range for iron(III)-chlorine bonds. The independent Fe-N (2.142 (11) and 2.122 (11) Å) and Fe-O bond (1.863 (11) and 1.882 (10) Å) distances agree well internally and fall in the range normally observed.

As indicated in Table V, the nine-atom salicylaldehyde fragments are very nearly planar as expected from the nature of the bonding and from previous structures. Each salicylaldehyde fragment, however, is distinctly canted with respect to the corresponding Fe-O-N plane. Thus, the dihedral angles, Table VI, between the Fe-O-N plane and the salicylaldehyde plane are 19.1 (18) and 28.5 (16)° for ligand A and ligand B, respectively. This structural feature, previously observed in other salicylaldimine complexes, presumably results from the requirement of iron for an O-Fe-N angle closer to 90° than the 120° favored for a planar six-membered ring containing five sp^2 hybridized atoms. The two phenyl rings are very nearly planar and the internal angles and bond lengths for these and for the two ethyl groups are normal.

Table II. Atomic Parameters for $[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$

(A) Positional and Isotropic Thermal Parameters, with Esd's[a]

Atom	x	y	z	B, Å^2
Fe	0.1389 (3)	0.0335 (3)	0.0072 (2)	b
Cl	0.3412 (6)	0.1576 (7)	0.1449 (4)	b
O2	0.0798 (14)	0.1092 (14)	−0.1066 (8)	5.12 (30)
O14	0.0538 (12)	−0.1208 (15)	0.0298 (8)	4.53 (30)
C3	0.1409 (20)	0.0849 (18)	−0.1469 (12)	3.45 (40)
C4	0.0848 (24)	0.1850 (24)	−0.2266 (15)	6.01 (52)
C5	0.1442 (25)	0.1596 (25)	−0.2711 (15)	6.03 (52)
C6	0.2643 (24)	0.0677 (24)	−0.2331 (15)	6.09 (51)
C7	0.3223 (22)	−0.0301 (26)	−0.1530 (14)	5.44 (46)
C8	0.2582 (19)	−0.0145 (19)	−0.1107 (11)	3.39 (38)
C9	0.3234 (19)	−0.1233 (20)	−0.0320 (12)	3.71 (39)
N10	0.2768 (15)	−0.1213 (10)	0.0142 (9)	3.25 (31)
C11	0.3541 (24)	−0.2396 (25)	0.0942 (15)	5.81 (52)
C12	0.2212 (21)	−0.3383 (22)	0.0659 (13)	4.70 (45)
C13	0.1222 (21)	−0.2604 (21)	0.0846 (13)	4.41 (44)

(B) Anisotropic Thermal Parameters[c] for Iron and Chlorine

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Fe	136 (5)	94 (4)	54 (2)	20 (5)	67 (2)	3 (3)
Cl	188 (12)	203 (12)	77 (5)	−53 (9)	86 (6)	−54 (6)

(C) Positional and Isotropic Thermal Parameters of the Toluene[d]

Atom[e]	x	y	z	B
TC1	0.5760	0.5692	−0.0231	13.1
TC2	0.6631	0.5277	0.0739	13.1
TC3	0.4129	0.5414	−0.0969	13.1
TC4	0.3157	0.5878	−0.2052	13.1

[a] Esd's are right adjusted to the least significant digit of the preceding number. [b] Atoms refined anisotropically. [c] The form of the anisotropic thermal ellipsoid is: $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. [d] Treated as rigid body in refinement. [e] TC1, TC2, TC3 are toluene ring carbon atoms, TC4 is the toluene methyl group.

Table III. Interatomic Distances (with esd's) for the $Fe(SANE)_2Cl$ Molecule

	Distance, Å		
Atoms		Ligand A	Ligand B
Fe-Cl	2.251 (5)		
Fe-Cl[a]	2.262 (5)		
Fe-N		2.14 (1)	2.12 (1)
Fe-O		1.88 (1)	1.86 (1)
O-C1		1.35 (1)	1.36 (1)
C1-C2		1.38 (2)	1.36 (2)
C2-C3		1.41 (2)	1.37 (2)
C3-C4		1.38 (2)	1.37 (2)
C4-C5		1.39 (2)	1.39 (2)
C5-C6		1.43 (2)	1.41 (2)
C6-C1		1.37 (2)	1.37 (1)
C6-C7		1.42 (2)	1.46 (2)
C7-N		1.29 (1)	1.29 (1)
N-C8		1.49 (2)	1.51 (1)
C8-C9		1.50 (2)	1.53 (2)
C9-C10		1.53 (2)	1.52 (2)
C10-C11		1.42 (2)	1.36 (2)
C11-C12		1.42 (2)	1.42 (2)
C12-C13		1.29 (2)	1.29 (1)
C13-C14		1.41 (2)	1.41 (1)
C14-C15		1.43 (3)	1.43 (2)
C15-C10		1.36 (2)	1.36 (2)

[a] Corrected for "riding" motion (Cl on Fe).

Although corresponding bond lengths and angles in the two independent ligands agree well, the two ligands adopt distinctly different conformations. The β-phenyl fragment for ligand B is directed away from the coordination sphere

Table IV. Bond Angles (deg) within the Fe(SANE)$_2$Cl Molecule

	Angle		
Atoms[a]		Ligand A	Ligand B
LAN-Fe-LBN	161.6 (4)		
LAN-Fe-LBO	104.4 (4)		
LAO-Fe-LBN	89.6 (4)		
LAO-Fe-LBO	148.3 (4)		
Cl-Fe-N		100.9 (3)	97.3 (3)
Cl-Fe-O		106.7 (3)	99.8 (3)
N-Fe-O		87.5 (4)	69.7 (4)
Fe-O-C1		132.5 (8)	130.4 (8)
O-C1-C2		116.9 (12)	120.1 (14)
O-C1-C6		121.3 (12)	120.7 (13)
C6-C1-C2		121.8 (10)	119.2 (12)
C1-C2-C3		119.6 (15)	122.2 (16)
C2-C3-C4		119.4 (15)	119.9 (17)
C3-C4-C5		121.0 (14)	120.6 (14)
C4-C5-C6		119.6 (14)	118.4 (13)
C5-C6-C1		118.6 (12)	120.3 (13)
C5-C6-C7		115.9 (13)	114.6 (13)
C6-C7-N		126.7 (13)	123.2 (14)
Fe-N-C7		122.5 (9)	124.4 (10)
Fe-N-C8		120.5 (7)	121.6 (7)
N-C8-C9		111.3 (13)	108.6 (13)
C8-C9-C10		114.9 (13)	110.9 (13)
C9-C10-C11		119.4 (15)	122.1 (15)
C15-C10-C11		118.7 (15)	120.4 (14)
C10-C11-C12		115.9 (17)	118.4 (15)
C11-C12-C13		125.3 (19)	121.4 (15)
C12-C13-C14		120.9 (20)	122.5 (17)
C13-C14-C15		115.7 (21)	114.5 (17)
C14-C15-C10		123.5 (18)	115.5 (17)

[a] LA and LB before an atom designation refer to ligand A and ligand B, respectively.

Table V. Least-Squares Planes within the Fe(SANE)$_2$Cl Molecule[a, b]

Atom	Dev, Å	Atom	Dev, Å
(A) Basal Plane of Square Pyramid			
Equation:	$-0.1999x + 0.4356y + 0.8777z - 1.7011 = 0$		
LAO	−0.1273	LBO	−0.1562
LBN	0.1258	LBN	0.1165
(B) Salicylaldehyde Group of Ligand A			
Equation:	$-0.1633x + 0.3886y + 0.9068z - 1.728 = 0$		
O	0.0031	C4	0.0155
C1	−0.0037	C5	−0.0132
C2	−0.0025	C6	0.0150
C3	−0.0083	C7	−0.0063
(C) Salicylaldehyde Group of Ligand B			
Equation:	$-0.1009x + 0.4662y + 0.8789z - 1.5337 = 0$		
O	−0.0192	C4	−0.0221
C1	−0.0020	C5	0.0010
C2	0.0167	C6	0.0240
C3	0.0035	C7	−0.0031
(D) Phenyl Group of Ligand A			
Equation:	$-0.7286x + 0.4919y + 0.4767z - 2.4831 = 0$		
C10	−0.0031	C13	−0.0161
C11	−0.0030	C14	0.0095
C12	0.0134	C15	−0.0009
(E) Phenyl Group of Ligand B			
Equation:	$0.0860x + 0.5446y + 0.8343z - 2.6417 = 0$		
C10	0.0162	C13	−0.0109
C11	−0.0025	C14	0.0051
C12	−0.0118	C15	−0.0183

[a] Planes are derived using unit weights for all atoms. [b] The planes are in cartesian coordinates with the *x* axis coincident to *a* and the *z* axis coincident to *c**.

whereas ligand A is folded back toward the apical chlorine atom. This causes one proton (H9A) bonded to carbon C9 to be directed toward the chlorine atom; the distance (2.90 Å) is slightly less than the sum of the van der Waals radii of hydrogen and chlorine and is indicative of a weak hydrogen-bonding interaction. The interaction is not expected to contribute significantly to the overall stability and the ligand conformations are probably the result of crystal packing.

Table VI. Dihedral Angles between Selected Planes in Fe(SANE)$_2$Cl

Plane 1	Plane 2	Angle, deg
Fe-LAO-LAN	LAC1-LAC6-LAC7	19.1 (18)
Fe-LBO-LBN	LBC1-LBC6-LBC7	28.5 (16)
Fe-LAO-LAN	Fe-LBO-LBN	40.9 (4)

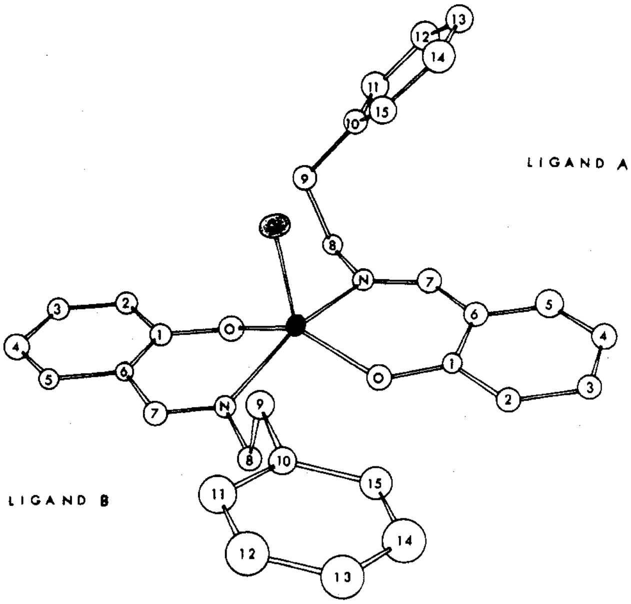


Figure 1. A perspective view of the molecular structure of Fe(SANE)$_2$Cl.

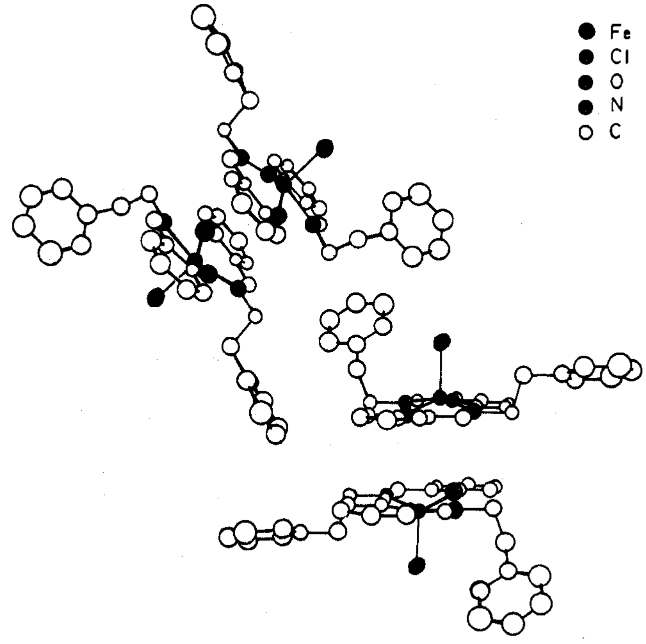


Figure 2. Packing diagram of the Fe(SANE)$_2$Cl structure.

The crystal packing for Fe(SANE)$_2$Cl is shown in Figure 2. Asymmetric units are seen to be linked by inversion centers into very loose "dimers" with the iron of one complex positioned below an oxygen, LBO, of the other. The resulting iron-oxygen four-membered planar ring has angles of 73.3 and 106.7° at the iron and oxygen, respectively. This four-membered ring is, thus, very similar to those found in other dimeric complexes of iron(III) and copper(II) except for the very large difference in the two iron-oxygen distances in the present structure (1.90 and 3.76 Å). The resulting iron-iron distance is extremely long (4.67 Å) and no magnetic interactions would be expected.

$[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$. Relevant bond distances and angles for the $[Fe(SALPA)Cl]_2 \cdot C_6H_5CH_3$ structure are given in Table VII. The dimeric unit, Figure 3, is very similar to that reported for the unsolvated material.[9] The iron atoms of the dimer are bridged by the alkoxide oxygens to form a four-membered ring with iron-oxygen distances of 1.983 and 1.934 Å and angles of 75.9 and 104.1° at iron and oxygen, respectively. The coordination of the iron is intermediate to a square-pyramidal and a trigonal-bipyramidal arrangement with the donors of the tridentate ligand and the bridging alkoxide oxygen in the basal plane. The chlorine-iron-basal ligand angles vary from 97.9 to 113.8°. This arrangement is very different from that found[24] for the dimeric copper(II) complex of the protonated form of the same ligand, $[Cu(SALPA\text{-}H)Cl]_2$ (where SALPA-H represents the monoanion of the Schiff base of salicylaldehyde and 3-aminopropanol). In the copper structure, the phenolic oxygen served as the bridging group and the coordination, with chlorine-iron-basal ligand angles ranging from 92.5 to 126.2°, was closer to trigonal bipyramidal than to square pyramidal. Considering the present structure as a square pyramid, the distortion is indicated by calculation of the least-squares plane through the four basal ligands and the distances of the four atoms from the plane; O14′ and N10 show the greatest deviations from this plane (0.32 Å). As in other structures, the iron is displaced out of the basal plane and toward the apical chlorine by 0.55 Å.

As in both the copper compound and the unsolvated iron compound, the four-membered iron-oxygen ring is exactly planar due to the presence of an inversion center. However, the coordination of the bridging oxygen deviates more from planarity in this structure than in either of the previous structures. This deviation is indicated in Table VIII by the distance of the attached carbon from the plane of the four-membered ring; that distance was 0.08 Å in both the copper structure and the structure of the unsolvated iron compound and is 0.28 Å in the present structure.

Discussion

In the structure of both $Fe(SANE)_2Cl$ and $[Fe(SALPA)Cl]_2$, the coordination of iron(III) is intermediate to the square-pyramidal and trigonal-bipyramidal arrangements. The actual coordination is most easily indicated by the angles at the metal, and in Table IX the values obtained for the present structures are compared to values obtained for similar structures and to values for the two ideal geometries. In all of the structures listed, chlorine occupies the apical position of the square pyramid and the donor atoms of the base plane are numbered from one to four; positions one and two are the axial positions of the trigonal bipyramid. The coordination in $[Cu(SALPA\text{-}H)Cl]_2$ is closer to trigonal bipyramidal than that of the iron compounds. The differences between the various iron compounds are small and probably reflect the different steric requirements of the ligands.

The molecular units of the present two structures are, of course, different since $Fe(SANE)_2Cl$ is monomeric and $[Fe(SALPA)Cl]_2$ has a dimeric structure with bridging oxygens. This difference is reflected in the room temperature magnetic moments of the two compounds. The value obtained for $Fe(SANE)_2Cl$, 5.95 BM, is very close to the spin-only value for five unpaired electrons (5.92 BM) and is the

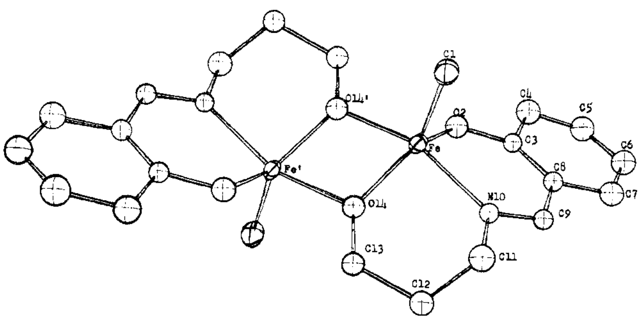


Figure 3. A perspective view of the molecular structure of $[Fe(SALPA)Cl]_2$.

Table VII. Interatomic Distances and Angles (with esd's) for the $[Fe(SALPA)Cl]_2$ Molecule

(A) Distances, Å

Atoms	Length	Atoms	Length
Fe-Fe′	3.089 (6)	C5-C6	1.33 (2)
Fe-Cl	2.226 (6)	C6-C7	1.44 (2)
Fe-O2	1.85 (1)	C7-C8	1.42 (2)
Fe-O14	1.93 (1)	C3-C8	1.35 (2)
Fe-O14′	1.98 (1)	C8-C9	1.48 (2)
Fe-N10	2.06 (1)	C9-N10	1.31 (2)
O2-C3	1.37 (2)	N10-C11	1.53 (2)
C3-C4	1.46 (2)	C11-C12	1.52 (3)
C4-C5	1.42 (3)	C12-C13	1.58 (2)
		C13-O14	1.47 (2)

(B) Angles, Deg

Atoms	Angle	Atoms	Angle
Fe-O14-Fe′	104.1 (6)	C4-C5-C6	122.2 (20)
O2-Fe-O14′	91.4 (6)	C5-C6-C7	120.7 (19)
N10-Fe-O14′	158.1 (5)	C6-C7-C8	117.7 (17)
Cl-Fe-O2	112.5 (5)	C7-C8-C3	121.9 (18)
Cl-Fe-O14	113.8 (4)	C7-C8-C9	112.2 (15)
Cl-Fe-N10	97.9 (4)	C3-C8-C9	125.9 (14)
Cl-Fe-O14′	102.2 (4)	C8-C9-N10	119.2 (15)
O14-Fe-N10	88.2 (5)	C9-N10-Fe	128.8 (12)
O14-Fe-O2	133.6 (5)	C11-N10-Fe	116.5 (10)
N10-Fe-O2	88.8 (5)	C9-N10-C11	114.0 (14)
O14-Fe-O14′	75.9 (6)	N10-C11-C12	108.8 (14)
Fe-O2-C3	130.8 (11)	C11-C12-C13	111.5 (16)
O2-C3-C4	115.4 (16)	Fe-O14-C13	132.9 (9)
C4-C3-C8	120.1 (16)	Fe′-O14-C13	121.2 (10)
C8-C3-O2	124.2 (15)	O14-C13-C12	110.7 (13)
C3-C4-C5	116.7 (19)		

Table VIII. Least-Squares Planes within the Fe(SALPA)Cl Molecule[a, b]

Atom	Dev, Å	Atom	Dev, Å
(A) Four-Membered Iron-Oxygen Ring			
Equation: $-0.1229x + 0.3128y + 0.9418z + 0.000 = 0$			
Fe1*	0.00	C11	0.14
Fe1′*	0.00	C12	−0.35
O14*	0.00	C13	0.28
O14′*	0.00		
(B) Basal Plane of Square Pyramid			
Equation: $0.2949x + 0.5223y + 0.8020z - 0.1306 = 0$			
O2*	−0.07	N10*	0.33
O14*	0.06	Fe1	0.55
O14′*	−0.32		
(C) Salicylaldehyde Group			
Equation: $0.3638x + 0.6713y + 0.6458z - 0.5820 = 0$			
C3*	−0.04	C8*	−0.01
C4*	0.04	C9	−0.09
C5*	−0.04	N10	−0.11
C6*	0.04	O2	0.01
C7*	0.00		

[a] Planes are derived using unit weights for atoms marked with asterisks and zero weights for all other atoms. [b] The planes are in cartesian coordinates with the x axis coincident to a and the z axis coincident to c^*.

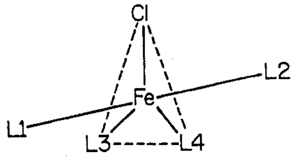
---

(24) J. A. Bertrand, J. A. Kelley, and J. L. Breece, *Inorg. Chim. Acta*, 4, 203 (1970).

Table IX. Comparison of Angles at the Metal Ion for some Related Salicylaldimine Complexes

Atoms[a]	Ideal square pyramid	[Fe(SALPA)Cl]$_2$ unsolvated	[Fe(SALPA)Cl]$_2$·$C_6H_5CH_3$	Fe(SANE)$_2$Cl	Fe(Sal=NPr)$_2$Cl	[Cu(SALPA-H)Cl]	Ideal trigonal bipyramid
L1-Fe-L2	150	148.3	158.1	161.9	166	168.9	180
L3-Fe-L4	150	143.6	133.6	141.9	134	123.4	120
L1-Fe-L3	86	90.9	88.2	87.4	87	76.0	90
L1-Fe-L4	86	88.1	88.8	86.1	87	104.0	90
L2-Fe-L3	86	71.0	75.9	88.9	87	99.6	90
L2-Fe-L4	86	91.7	91.4	86.0	87	69.7	90
Cl-Fe-L1	105	103.9	97.9	100.8	97	92.5	90
Cl-Fe-L2	105	106.2	102.2	97.2	97	98.6	90
Cl-Fe-L3	105	106.8	113.8	107.1	113	110.1	120
Cl-Fe-L4	105	108.7	112.5	111.0	113	126.2	120

[a] Atoms designated L1 and L2 would be the axial groups of a trigonal bipyramid:



expected value for a high-spin d^5 complex. The room temperature magnetic moment obtained for [Fe(SALPA)Cl]$_2$, 4.52 BM, is considerably lower and is indicative of antiferromagnetic coupling through the bridging oxygens. The room temperature value and the value at 77°K (2.37 BM) are very close to the values obtained for the unsolvated form of the same compound; since the toluene of solvation is not coordinated to the metal ions, it would not be expected to affect the magnetic properties of the complex. The temperature dependence of the magnetic moment of unsolvated [Fe(SALPA)Cl]$_2$ was reported previously and the magnetic moment was observed to drop from 4.50 BM at room temperature to 2.30 BM at 77°K. The experimental data for the unsolvated species could be fit to the equation[25] for binuclear complexes of metal ions with spins of $^5/_2$ by a J value of -17 cm^{-1}. From the bond angle at the bridging oxygen, 104.1°, antiferromagnetic coupling *via* a σ pathway would be expected[26] and, since the angle is almost the same as that in the dimeric form of Fe(Salen)Cl, a coupling constant similar to that in [Fe(Salen)Cl]$_2$, 7.5 cm^{-1}, would be expected if only coupling *via* the σ pathway were involved. The larger coupling constant for [Fe(SALPA)Cl]$_2$ may be indicative of an additional coupling mechanism and the possibility of antiferromagnetic coupling *via* a π pathway has been suggested for dinuclear copper(II) complexes that contain similar planar four-membered rings.[27]

Although no change was expected, the magnetic moment of Fe(SANE)$_2$Cl was measured at several temperatures below ambient. At the temperature of a Dry Ice-acetone slurry (196°K), the magnetic moment (5.81 BM) had changed very little and the compound appeared to be a normal, magnetically dilute compound. However, at the temperature of an *n*-pentane slurry (144°K), the moment was drastically reduced (4.19 BM), and at the temperature of liquid nitrogen (77°K), the observed value was even lower (3.12 BM). The sample was repeatedly warmed to room temperature and recooled to 77°K and the same magnetic moments were obtained. The values obtained at 144 and 77°K, respectively, are approximately 1 BM higher than the corresponding values for [Fe(SALPA)Cl]$_2$ at these temperatures and indicate a similar type of antiferromagnetic coupling with a smaller J value. The most reasonable explanation for the discontinuity that occurs between 144 and 196°K would be a phase change accompanying a change in molecular structure. The arrangement into loose dimers with an Fe-Fe distance of 4.67 Å and Fe-O distances of 3.76 and 1.90 Å was noted above and is apparent in Figure 2. These distances are large enough to rule out significant magnetic interactions, but a phase transition at a lower temperature could lead to a dimeric unit with shorter Fe-Fe and Fe-O distances and substantial coupling. Although such monomer-dimer transformations have not been observed previously as phase transitions, structure studies of monomeric and dimeric forms of Fe(Salen)Cl have been reported and the properties of the two forms are comparable to those of Fe(SANE)$_2$Cl above and below the transition temperature.

Acknowledgment. This work was supported by NSF Grant GP-20885. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged. The help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.

Registry No. Fe(SANE)$_2$Cl, 42294-92-8; [Fe(SALPA)Cl]$_2$·$C_6H_5CH_3$, 42294-93-9.

Supplementary Material Available. Observed and calculated structure factors (in electrons) for Fe(SANE)$_2$Cl will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-125.

---

(25) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(26) D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 11, 1958 (1972).

(27) J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, 6, 248 (1972).