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**Registry No.** $CH_3$–$B_{12}$, 13442-55-4; $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; $H_2O$–$B_{12}^+$, 20623-12-5.

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# Structure and Magnetism of Monomeric Chlorobis(*N*-(2-phenylethyl)salicylideniminato)iron(III), Fe(SANE)$_2$Cl

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Determination of the crystal structure of the monomeric form of the title complex has allowed the identification of structural distortions associated with pairwise molecular interactions in the previously reported "dimeric" form. In the "dimeric" species the coordination geometry of the iron ion is severely distorted from the distinctly trigonal-bipyramidal geometry observed in the monomer. Magnetic moment measurements for the monomer confirm that the temperature dependence of the magnetic moment of the dimer arises from interaction between the component molecules. The monomer, $FeC_{30}H_{28}N_2O_2Cl$, is monoclinic with space group $C2/c$, $Z = 4$, $a = 30.13$ (3) Å, $b = 8.689$ (6) Å, $c = 10.859$ (8) Å, and $\beta = 106.33$ (3)° at 293 K.

## Introduction

In an examination of iron(III) Schiff base complexes, Bertrand, Breece, and Eller[1] discovered an unusual intermolecular interaction in the crystal structure of chlorobis(*N*-(2-phenylethyl)salicylideniminato)iron(III), Fe(SANE)$_2$Cl. In this material two molecules associate to form a "loose dimer", the components of which are related by a center of symmetry. The "dimers", however, differ from other species that contain four-membered $Fe_2O_2$ rings (for example, the dimeric form of Fe(salen)Cl[2]), in that the "intermolecular" Fe–O distance, 3.76 Å, is much longer than the corresponding "intramolecular" distance, 1.90 Å. Bertrand et al. suggest that the anomalous temperature dependence of the magnetic moment of this material could arise from a phase transition to a six-coordinate form at low temperature. Because of the similarity of the proposed transition to the structural transformation that often accompanies spin-state changes in ferric porphyrin complexes, several attempts were made in this laboratory to duplicate the reported synthesis of Fe(SANE)$_2$Cl. In all cases these efforts have resulted in the isolation of crystals with space group $C2/c$ rather than $P2_1/c$ as reported by the previous authors. For the determination of the relationship between the two materials, the investigation reported herein was undertaken.

## Experimental Section

**Preparation of Fe(SANE)$_2$Cl.** A solution of $FeCl_2 \cdot 4H_2O$ (0.695 g, 3.50 mmol) in 10 mL of methanol was added to *N*-(2-phenylethyl)salicylaldimine (1.70 g, 7.00 mm) in 10 mL of methanol. The mixture, exposed to the atmosphere, was stirred and then allowed to stand overnight. A small crop of red-black crystals formed. These were recrystallized from diethyl ether to produce crystals suitable for X-ray analysis.

**Data Collection.** Experimental parameters associated with the determination of the crystal structure are given in Table I.

**Magnetic Measurements.** The magnetic moments of the monomer were determined at a magnetic field of 0.62 T with a Princeton Applied Research FM-1 vibrating-sample magnetometer. $HgCo(SCN)_4$ was used as a standard. Magnetic moments of 5.96 (3) $\mu_B$ at 298 K and 5.81 (3) $\mu_B$ at 80 K (corrected for diamagnetism[3]) were obtained.

Table I. Experimental Parameters

formula: $FeC_{30}H_{28}N_2O_2Cl$
color: red-black
habit: parallelepipeds
lattice parameters: $a = 30.13$ (3) Å, $b = 8.689$ (6) Å, $c = 10.659$ (8) Å, $\beta = 106.33$ (3)°
wavelength: Mo $K\bar{\alpha}$, 0.71969 Å
temp: 293 K
radiation: Zr-filtered Mo
space group: $C2/c$
cryst dimens: 0.30 × 0.30 × 0.35 mm
abs coeff: 4.62 cm$^{-1}$
abs cor: none
diffractometer: Picker FACS-1
diffraction geometry: $\theta/2\theta$
scan width: base width = 2.0°
scan rate: 2.0°/min
bkgd: 20 s each side
reflctns measd: $2\theta(\max) = 50°$; 2571 reflctns with $h$ and $k \geq 0$
reflctns obsd ($I > 3\sigma$): 1147

Table II. Atomic Positions for the Monomeric Form of Fe(SANE)$_2$Cl

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Fe | 0.5000 | 0.2303 (1) | 0.2500 |
| Cl(1) | 0.5000 | 0.4899 (2) | 0.2500 |
| C(1) | 0.5834 (2) | 0.1426 (6) | 0.4475 (5) |
| C(2) | 0.6309 (2) | 0.1097 (6) | 0.4724 (6) |
| C(3) | 0.6601 (2) | 0.1249 (8) | 0.5954 (7) |
| C(4) | 0.6437 (2) | 0.1720 (7) | 0.6955 (6) |
| C(5) | 0.5969 (2) | 0.1981 (6) | 0.6734 (5) |
| C(6) | 0.5659 (2) | 0.1853 (5) | 0.5505 (5) |
| C(7) | 0.5172 (2) | 0.2046 (5) | 0.5358 (5) |
| C(8) | 0.4364 (2) | 0.2209 (6) | 0.4396 (5) |
| C(9) | 0.4144 (2) | 0.3764 (7) | 0.3995 (5) |
| C(10) | 0.3648 (2) | 0.3826 (7) | 0.4111 (6) |
| C(11) | 0.3297 (3) | 0.3028 (9) | 0.3274 (6) |
| C(12) | 0.2837 (3) | 0.3095 (10) | 0.3352 (8) |
| C(13) | 0.2745 (3) | 0.3968 (10) | 0.4262 (10) |
| C(14) | 0.3090 (4) | 0.4719 (10) | 0.5124 (9) |
| C(15) | 0.3542 (2) | 0.4640 (8) | 0.5048 (7) |
| N(1) | 0.4845 (1) | 0.2137 (4) | 0.4305 (4) |
| O(1) | 0.5561 (1) | 0.1286 (4) | 0.3283 (3) |

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(1) Bertrand, J. A.; Breece, J. L.; Eller, P. G. *Inorg. Chem.* **1974**, *13*, 125–131.

(2) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1900–1908.

Table III. Selected Bond Distances and Angles in the Monomeric and Dimeric Forms of Fe(SANE)$_2$Cl

Bond Distances (Å)

| atoms | dimer[1] ligand A | dimer[1] ligand B | monomer |
|---|---|---|---|
| Fe–Cl | 2.251 (5) | | 2.256 (3) |
| Fe–N | 2.14 (1) | 2.12 (1) | 2.143 (4) |
| Fe–O | 1.88 (1) | 1.86 (1) | 1.884 (3) |
| O–C(1) | 1.35 (1) | 1.36 (1) | 1.330 (5) |
| C(1)–C(2) | 1.38 (2) | 1.36 (2) | 1.408 (7) |
| C(2)–C(3) | 1.41 (2) | 1.37 (2) | 1.384 (7) |
| C(3)–C(4) | 1.38 (2) | 1.37 (2) | 1.376 (8) |
| C(4)–C(5) | 1.39 (2) | 1.39 (2) | 1.380 (8) |
| C(5)–C(6) | 1.43 (2) | 1.41 (2) | 1.402 (7) |
| C(6)–C(1) | 1.37 (2) | 1.37 (1) | 1.413 (7) |
| C(6)–C(7) | 1.42 (2) | 1.46 (2) | 1.443 (7) |
| C(7)–N | 1.29 (1) | 1.29 (1) | 1.284 (6) |
| N–C(8) | 1.49 (2) | 1.51 (1) | 1.482 (6) |
| C(8)–C(9) | 1.50 (2) | 1.53 (2) | 1.515 (7) |
| C(9)–C(10) | 1.53 (2) | 1.52 (2) | 1.534 (7) |
| C(10)–C(11) | 1.42 (2) | 1.36 (2) | 1.374 (8) |
| C(11)–C(12) | 1.42 (2) | 1.42 (2) | 1.415 (9) |
| C(12)–C(13) | 1.29 (2) | 1.29 (1) | 1.33 (1) |
| C(13)–C(14) | 1.41 (2) | 1.41 (1) | 1.35 (1) |
| C(14)–C(15) | 1.43 (3) | 1.43 (2) | 1.391 (9) |
| C(15)–C(10) | 1.36 (2) | 1.36 (2) | 1.349 (7) |

Bond Angles (Deg)

| atoms | square pyramid[4] | dimer[5] | monomer | trigonal bipyramid |
|---|---|---|---|---|
| N–Fe–N′ | 150 | 161.6 (4) | 172.3 (2) | 180 |
| O–Fe–O′ | 150 | 142.6 (4) | 124.1 (2) | 120 |
| Cl–Fe–O | 105 | 108.6 (3) | 118.0 (1) | 120 |
| N–Fe–O | 86 | 86.9 (4) | 89.0 (1) | 90 |
| N–Fe–O′ | 86 | 87.3 (4) | 87.3 (1) | 90 |
| Cl–Fe–N | 105 | 99.1 (3) | 93.9 (1) | 90 |

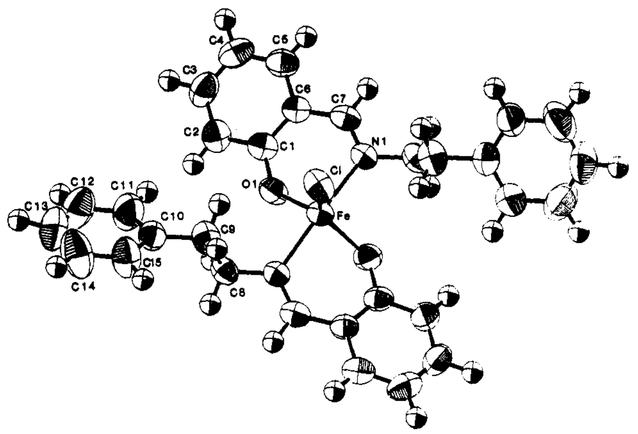

Figure 1. ORTEP drawing of the monomeric form of Fe(SANE)$_2$Cl.

## Structure Determination and Refinement

A Patterson function yielded the positions of the iron and chlorine atoms, and a difference Fourier synthesis revealed the remaining nonhydrogen atoms. Positions of the hydrogen atoms were obtained in subsequent difference maps or were calculated. Full-matrix least-squares refinement in which the hydrogen atom parameters were fixed converged with final $R$ factors $R = 0.041$ and $R_w = 0.043$. A final difference map showed no peaks greater than 0.2 e/Å$^3$. Final atomic positions are found in Table II, and a summary of bond distances and angles in both the monomer and the dimer is found in Table III. The numbering scheme used is shown in Figure 1.

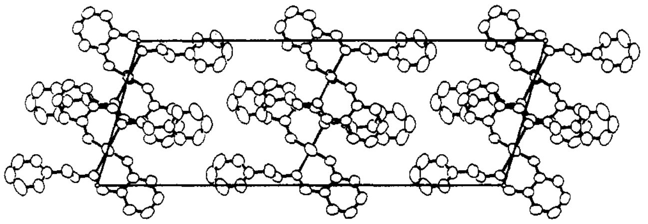

Figure 2. Packing diagram of the monomeric form of Fe(SANE)$_2$Cl projected down the $b$ axis.

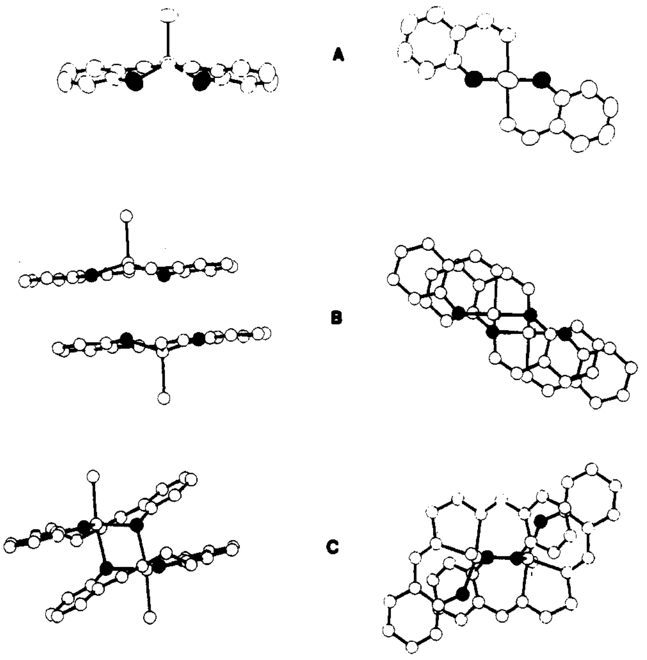

Figure 3. Molecular structures of (A) the monomeric form of Fe(SANE)$_2$Cl, (B) the dimeric form of Fe(SANE)$_2$Cl,[1] and (C) the dimeric form of Fe(Salen)Cl.[2] In structures A and B, the phenylethyl groups have been omitted for clarity. All hydrogen atoms have been omitted. The oxygen atoms in these drawings are black.

Programs in the UCLA VAX computer package include local versions of the ORFLS and ORXFFE programs originally written by Busing, Martin, and Levy and the ORTEP program by Johnson. Scattering factors and corrections for anomalous dispersion for all atoms were taken from ref 6.

## Discussion

In the $C2/c$ polymorph of Fe(SANE)$_2$Cl the complex is strictly monomeric. The iron and chlorine atoms lie on a crystallographic twofold axis, and the coordination geometry of the iron atom is only slightly distorted from trigonal bipyramidal with the nitrogen atoms in axial positions. Figure 2 shows the crystal packing viewed down the $b$ axis. Since there are no unusual intermolecular interactions in the $C2/c$ structure, it is reasonable to attribute the distortions observed in the $P2_1/c$ structure to "dimer" formation. The present structure thus allows one to pinpoint structural features that result from intermolecular interactions in the "loose dimer".

There are no significant differences in bond *distances* between the monomeric and the dimeric structures, but the coordination geometries are distinctly different. The bond angles about the iron ion, tabulated in Table III, show that the component molecules of the dimer have a coordination geometry that approaches an "ideal"[4] square pyramid, while the geometry of the monomer is well described as trigonal bipyramidal. The most pronounced effect of the distortion observed upon dimer formation is the increase in the O–Fe–O′

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(3) Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: London, 1968.

(4) Gillespie, R. J. *J. Chem. Soc.* **1963**, 4672–4685.

(5) These angles were calculated from the atomic positions given in ref 1. There are several errors in the angles tabulated in the text of this paper.

(6) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

bond angle from 124.1 to 142.6°.

Figure 3B suggests that the "dimer" is stabilized by interactions between the planar ligands of the component molecules. The angle between the normals to the least-squares planes defined by the two ligands is 28.9° for the "monomer" and 7.0° for the "dimer". Coplanarity of the two ligands optimizes the $\pi$ overlap. In the "dimer", the distance between the least-squares planes through all salicylideniminato atoms in the respective molecules is 3.47 Å, which is only slightly larger than the 3.31-Å[7] separation in naphthalene at room temperature and is in the range observed for many planar charge-transfer complexes.

Figure 3B also suggests that the small deviation from coplanarity of the two salicylaldimine ligands observed in the dimer could be the result of the weak iron–oxygen interaction. It is clear, however, that if a five-coordinate to six-coordinate transformation is to occur in the solid state, any significant shortening of the Fe–O′ bond must be accompanied by a drastic change in ligand orientation and at the expense of a significant amount of $\pi$ stabilization.

A related Schiff base complex, Fe(salen)Cl, has been crystallized in both monomeric[8] and dimeric[2] forms. In this case the dimer is a true dimer with 2.18-Å Fe–O bonds linking the component molecules. This complex differs from the SANE analogue in that an ethylene bridge links the two salicylaldimine components, forcing the complex to adopt a square-pyramidal geometry with the oxygen atoms in adjacent (rather than opposite) basal sites. Figure 3C shows, however, that the potential for $\pi$ overlap of the type observed in the "loose dimer" also exists in this complex. The distortion from coplanarity of the ligand ring systems observed for this compound is very similar to that required if the SANE dimer is to undergo the proposed transformation.

The anomalous temperature dependence of the magnetic moment of the dimeric form observed by Bertrand et al.[1] (from $\mu = 3.12\ \mu_B$ at 80 K to 5.95 $\mu_B$ at 298 K) is certainly consistent with the proposed "loose" dimer to "tight" dimer transformation. This interpretation is supported by the observation that the magnetic moment of the monomer is nearly constant over the same temperature range. There are, however, at least three possible types of transformations in accord with the limited amount of experimental data available. The first is an abrupt (first-order) transition. The second possibility is a continuous (second-order) transition in which at intermediate temperatures there exists an equilibrium mixture of "loose" and "tight" dimers. There is a large class of spin-equilibrium complexes in which processes of this type are known to occur. A third possibility is a continuous "displacive" transition in which there is a gradual decrease in the intermolecular distance with decrease in thermal energy. All molecular crystals in which planar molecules stack in a parallel fashion show a strong temperature dependence of the intermolecular separation. However, since formation of a strong Fe–O′ bond in this case requires major disruption of the ligand $\pi$ interaction, a transition of the third type is somewhat difficult to envision. Further, the drastic rearrangement of ligands that must accompany Fe–O′ bond formation is likely to significantly alter the crystal-packing interactions. Such a change increases the probability of a first-order transition. A transition of this type might preclude the direct single-crystal characterization of this transformation by multiple-temperature X-ray structural analysis.[9]

**Acknowledgment.** This work was supported by the National Science Foundation (Grant CHE79-06343) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.** Fe(SANE)$_2$Cl, 42294-92-8.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen positions, and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(7) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504.

(8) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1598–1608.

(9) In a review of this paper, J. A. Bertrand reported that when crystals of the dimeric form of Fe(SANE)$_2$Cl were cooled with liquid nitrogen, a cracking sound was heard and crystal movement was observed.

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# Uranyl Complexes of $\beta$-Polyketonates. Crystal and Molecular Structure of a Mononuclear Uranyl 1,3,5-Triketonate and a Novel Trinuclear Uranyl 1,3,5-Triketonate with a Trigonal-Planar Bridging Oxide

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Two uranyl complexes of 1,3,5-triketonate ligands have been crystallized and examined by X-ray diffraction techniques. The first is the mononuclear bis[1,5-diphenyl-1,3,5-pentanetrionato(1−)](methanol)dioxouranium(VI)–methanol, $[UO_2(C_{35}H_{30}O_7)(CH_3OH)]$, $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$, in which the uranium atom is bound to four enolic oxygens, two uranyl oxygens, and one methanolic oxygen. The triketonate ligands are in a cis configuration presumably due to the steric constraints of the methanol coordination. Crystal data are as follows: $P2_1/c$, $a = 9.932$ (4), $b = 30.29$ (4), $c = 11.671$ (4) Å; $\beta = 103.03°$, $V = 3421$ (2) Å$^3$; $Z = 4$, $R_1 = 0.048$, $R_2 = 0.050$. The second is a trinuclear $UO_2^{2+}$ anion containing a trigonal, tribridging oxide ion that results during attempts to prepare binuclear $UO_2^{2+}$ complexes of 1,3,5-triketonates. The compound bis(triethylammonium) tris(2,2′,8,8′-tetramethyl-3,5,7-nonanetrionato)-$\mu_3$-oxo-tris(dioxouranate)(2−), $[(C_2H_5)_3NH]_2[U_3O_6(C_{39}H_{60}O_9)O]$, $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$, contains a nearly equilateral triangle of $UO_2^{2+}$ ions with a central $O^{2-}$ ion trigonally bonded to the three U atoms. One triketonate occupies each edge of the triangle with the central enolic oxygen bridging two U atoms and the terminal oxygens bound to one U atom. Each U is seven-coordinate in nearly pentagonal-bipyramidal geometry. Crystal data are as follows: $C2/c$, $a = 27.90$ (2), $b = 15.65$ (2), $c = 31.81$ (3) Å; $\beta = 107.8$ (1)°, $V = 13220$ (20) Å$^3$; $Z = 8$, $R_1 = 0.062$, $R_2 = 0.078$.

## Introduction

During the past decade it has become increasingly apparent that the 1,3,5-triketones and their Schiff-base derivatives are an extremely versatile class of binucleating ligand. Part of our efforts during this period have been directed toward developing synthetic methods to produce pure samples of binu-