

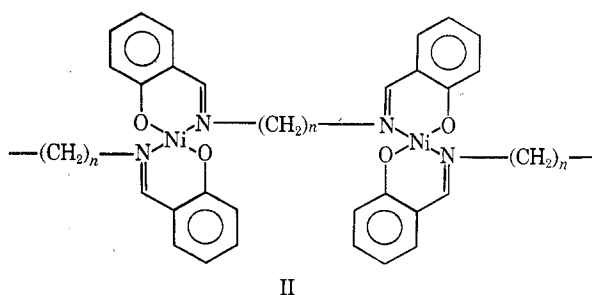
tra of bis(*N*-*m*-substituted arylsalicylaldiminato)nickel(II) complexes known to be extensively associated.<sup>9</sup> It is also found for complexes such as bis(*N*-*R*-salicylaldiminato)nickel(II), where  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ , which attains an octahedral ligand field through intramolecular coordination of the oxygens on the *R* groups.<sup>10</sup> The absorption at  $\sim 16,000 \text{ cm}^{-1}$  is found in the mull spectra of all complexes where  $n = 5-12$ . However, an absorption has been observed in this region not only for the diamagnetic complexes I where  $n = 3, 4^7$  but also for the associated bis(*N*-arylaldiminato)nickel(II) complexes<sup>9</sup> and the monomeric octahedral complex mentioned above where  $R = \text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ .<sup>10</sup> No absorption could be detected in the  $6800\text{-cm}^{-1}$  region where tetrahedral salicylaldimine complexes of Ni(II) characteristically absorb. Furthermore, the spectra of complexes I in the near-infrared region are quite unlike those reported for five-coordinate nickel(II) complexes of the salicylaldimine series.<sup>11</sup>

The spectral observations outlined above strongly imply that octahedrally coordinated nickel ions are present in the solid state of complexes I where  $n = 6-12$  and are responsible for the observed paramagnetism. However, most of the observed moments are considerably lower than the  $\sim 3.2 \text{ BM}$  expected for octahedral nickel(II). Infrared spectra of diamagnetic and strongly paramagnetic samples of the  $n = 12$  complex are quite similar and show no absorption which can be attributed to coordinated water. Also the elemental microanalyses give no indication of the presence of water. Paramagnetic impurities such as nickel acetate or nickel hydroxide would be detected by elemental analyses unless they are present to the extent of only  $\sim 3 \text{ mol } \%$  or less. In this case their maximum contribution to  $\mu_{\text{eff}}$  would be  $\sim 0.6 \text{ BM}$ , and their contribution to the absorption spectra would be negligible. It appears that the existence of a singlet-triplet equilibrium arising from a tetragonal ligand field<sup>12</sup> is not responsible for the anomalous moments, at least for the  $n = 11$  and  $12$  complexes. Moments of these complexes are unchanged (within  $0.05 \text{ BM}$ ) upon going from  $293$  to  $195^\circ \text{K}$ .<sup>13</sup>

We find the above results consistent with the presence of magnetically nonequivalent nickel ions in the solid samples: a fraction of the ions are octahedrally coordinated and high spin as a result of molecular association, whereas the others are planar and low spin. In order to determine if mixed crystals occur in samples having anomalous moments, X-ray powder patterns were made of three samples of the  $n = 12$  complex. The samples chosen had moments of  $0, 2.00,$  and  $3.03$

BM. It was expected that distinctly different patterns would be found for the samples having  $\mu_{\text{eff}} = 0$  and  $3.03 \text{ BM}$  and that the pattern for the sample with  $\mu_{\text{eff}} = 2.00 \text{ BM}$  would contain lines present in both of the other patterns. However, all three patterns contained common features, and resolution of the lines decreased markedly with increasing  $\mu_{\text{eff}}$ . These data do not unambiguously demonstrate the occurrence of mixed crystals in the  $2.00\text{-BM}$  sample, since it is not clear whether the high-spin form lacks crystallinity or is incapable of giving a good powder pattern for other reasons.

Some discussion of the mode of chelation is in order, especially for those ligands where the salicylaldimine groups are separated by a long hydrocarbon chain. In addition to a tendency to form molecular aggregates through sharing of donor oxygens, it is also quite possible that the complexes become polymeric through sharing of ligands. A possible structure is II, where the principal coordination is *trans* planar. Unfortunately, the low solubility of the complexes precludes molecular weight measurements. Space-filling molecular models



indicate, where  $n = 8-12$ , strained *trans*-planar and *cis*-planar monomers are possible, but an unstrained model of II is easily made. Furthermore, there is little steric inhibition to association by means of which a number of polymeric chains such as II could be joined laterally by sharing donor oxygens. Thus, we believe the most plausible structure for the higher homologs, at least, of the *N,N'*-polymethylenebis(salicylideniminato)nickel(II) complexes is II. In paramagnetic samples some of oxygens are shared, forming octahedrally coordinated nickel and joining the polymeric chains.

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## A New $\beta$ -Diketonate Complex of Silicon(IV)

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Received February 27, 1969

Recently there has been much interest in dichlorobis-(acetylacetonato) complexes of the group IV elements

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(13) Samples having intermediate moments ( $2.46 \text{ BM}$  for  $n = 11$  and  $2.64 \text{ BM}$  for  $n = 12$ ) were chosen for this experiment.

Ge, Sn, Ti, Zr, and Hf.<sup>1-8</sup> All of these complexes are nonionic and monomeric and have *cis* structures.<sup>1-3,7,8</sup> To this time, however, no analogous silicon complex has been reported. This work reports the preparation and some properties of a new complex which has a stoichiometry consistent with its being dichlorobis(acetylacetonato)silicon(IV),  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ .

#### Experimental Section

**Materials.**—Silicon tetrachloride and acetylacetone were purchased from Fisher Scientific Co. and were distilled under dry nitrogen before use. Methylene chloride and chloroform were also purchased from Fisher Scientific Co. Methylene chloride was distilled from calcium hydride prior to use. Chloroform was purified by extracting several times with water, drying over  $\text{CaSO}_4$ , and refluxing over and distilling from phosphorus pentoxide (under nitrogen) onto Linde Type 5A Molecular Sieves. No ethanol resonance peaks were observed at the most sensitive settings of the nmr spectrometers.

**Preparation of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ .**—Acetylacetone (8.7 g,  $8.7 \times 10^{-2}$  mol) dissolved in 10 ml of methylene chloride was added dropwise to silicon tetrachloride (14.8 g,  $8.7 \times 10^{-2}$  mol) in *ca.* 30 ml of methylene chloride at 0°. A small amount of white solid was evident after all of the acetylacetone was added. The final mixture was refluxed 10 hr with a slow stream of nitrogen flowing up the condenser (*ca.* 10 ml of methylene chloride was lost). The resulting solid was filtered off in Schlenk-type apparatus,<sup>9</sup> washed with 5 ml of methylene chloride, and dried under vacuum at room temperature. Yields of 10–15% were obtained. The compound does not melt (sealed capillary) below 350° but does turn brown over a range of *ca.* 175–200°. The compound is quite moisture sensitive and decomposes readily on standing in air. A positive qualitative test for silicon<sup>10</sup> was obtained.

Addition of hexane to the filtrate from above gave a large quantity of an off-white solid (sometimes light yellow) which was identified as  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl} \cdot \text{HCl}$  from ir and nmr data. An ir spectrum of the filtrate (thin film) showed the presence of only silicon tetrachloride and the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation; no free acetylacetone was observed. *Anal.* Calcd for  $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Si}$ : C, 40.41; H, 4.75; Cl, 23.86. Found: C, 39.94; H, 4.92; Cl, 23.79.

Ir spectrum, 2000–400  $\text{cm}^{-1}$  as a mull in Nujol: 1559 vs, br (slightly split), 1430 s, 1380 s, 1314 s, 1199 w, 1041 s, 1017 sh, 963 s, 818 m, 727 s, 656 m, 582 s (~445 vs, br, some shoulders—see text); 2000–400  $\text{cm}^{-1}$  in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ : 1561 s, 1549 vs, br, 1422 m, 1390 s, 1362 m, 1350 s, 1317 s, 1039 s, 1022 sh, 963 m, 945 sh, 618 w, 583 m, 542 m, 460 sh, 447 s, 420 sh(?). (Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.)

**Preparation of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ .**—This compound was prepared by an established procedure.<sup>11</sup> The compound did not melt below 300°, but did begin to decompose at *ca.* 180°. The purity of this compound was verified by nmr spectroscopy.

Ir spectrum, 2000–400  $\text{cm}^{-1}$  as a mull in Nujol: 1562 sh, 1546

vs, br, 1420 s, 1378 s, 1342 s, 1307 s, 1038 s, 1019 sh, 965 m, 942 m, 827 m, 726 s, 659 m, 622 m, 559 sh, 542 s, 463 m, 427 w; 2000–400  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ : 1557 sh, 1545 vs, br, 1392 s, 1349 s, 1317 s, 1038 s, 1020 sh, 963 m, 943 w, 651 w, 618 m, 557 sh, 542 s, 462 m.

**Spectra.**—Infrared spectra were taken on Beckman IR-9 and Perkin-Elmer 457 spectrophotometers. The nmr spectra were run on Varian A-60A and Perkin-Elmer R-20 spectrometers at *ca.* 35°. All spectral samples were prepared in a nitrogen-filled glove bag. The nmr tubes were sealed under nitrogen or vacuum. All solution ir spectra referred to in this work were run on 0.5-mm KBr cells. Spectra were run within a few hours after purification of the chloroform.

#### Results and Discussion

From the reaction of silicon tetrachloride and acetylacetone in equimolar quantities in an appropriate quantity of methylene chloride a white solid can be isolated in low yields having the empirical formula  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ . Until this time the only product reported to form from the reaction of acetylacetone and silicon tetrachloride in inert organic solvents is the hydrochloride of tris(acetylacetonato)silicon(IV) chloride,  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl} \cdot \text{HCl}$ .<sup>12,13</sup> The fact that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  does not melt before undergoing solid-state decomposition is not completely unexpected since it has been reported that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Br}$ <sup>11</sup> and  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ <sup>14</sup> behave similarly.

We have been unsuccessful in preparing  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Br}_2$  by reaction of silicon tetrabromide with acetylacetone under conditions similar to those described above. Also, we have been unable to prepare analogous complexes from the reaction of benzoylacetone and dibenzoylmethane with silicon tetrachloride. In all of the above attempts only the expected tris( $\beta$ -diketonate)-silicon(IV) type of complexes were isolated.

The infrared data show that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is a chelated enolate complex as its spectrum is similar to spectra observed for other chelated enolate complexes.<sup>15</sup> The strong broad band about 1559  $\text{cm}^{-1}$  is in the region of characteristic absorptions ( $\nu_{\text{C} \dots \text{O}}$  and  $\nu_{\text{O} \dots \text{C}}$ ) for chelated acetylacetonate complexes. The lack of bands from 1600 to 1800  $\text{cm}^{-1}$  indicates the absence of any open-chain oxygen-silylated species like that found by West<sup>13</sup> or any entities with a silicon-carbon bond. The mull spectrum of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  while similar to those of other chelated acetylacetonate complexes is noticeably different from that for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  which is evidence against  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  having a structure containing the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation. In the region above 400  $\text{cm}^{-1}$  similar ir spectra are observed for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ ,  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Br}$ ,<sup>16</sup> and  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{FeCl}_4$ <sup>17</sup> indicating that the anion has little influence on the spectrum of the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation.

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(2) W. H. Nelson, *ibid.*, **6**, 1509 (1967).

(3) (a) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965);

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(4) W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

(5) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).

(6) (a) K. C. Pande and R. C. Mehrotra, *Chem. Ind. (London)*, 1198 (1958);

(b) D. M. Puri and R. C. Mehrotra, *J. Less-Common Metals*, **3**, 247 (1961);

(c) D. M. Puri, K. C. Pande, and R. C. Mehrotra, *ibid.*, **4**, 481 (1962);

(d) R. C. Mehrotra and V. D. Gupta, *J. Indian Chem. Soc.*, **40**, 911 (1963).

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(8) V. Doron and C. Fischer, *Inorg. Chem.*, **6**, 1917 (1967).

(9) S. Herzog and J. Dehnert, *Z. Chem.*, **4**, 1 (1964).

(10) R. K. McAlpine and B. A. Soule, "Qualitative Chemical Analysis,"

D. Van Nostrand Co., New York, N. Y., 1933, p 486.

(11) R. C. Fay and N. Serpone, *J. Am. Chem. Soc.*, **90**, 5701 (1968).

(12) (a) W. Dilthey, *Ber.*, **36**, 923 (1903); (b) W. Dilthey, *Ann.*, **344**, 300 (1906).

(13) R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

(14) West<sup>13</sup> noted that when half of the HCl was removed from  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl} \cdot \text{HCl}$ , the remaining solid did not melt but gradually decomposed above 200°. We have prepared  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  by the method of Fay and Serpone and observed thermal characteristics similar to those described by West for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl} \cdot 0.5\text{HCl}$ .

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 215–220.

(16) D. W. Thompson, unpublished results.

(17) W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

Having established from ir data that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is a chelated enolate complex, the question remains as to the specific structure. Unfortunately  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is insoluble in carbon tetrachloride, hexane, and benzene and only very slightly soluble with decomposition in nitrobenzene, nitromethane, and acetonitrile. In ethanol-free chloroform and methylene chloride  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is sparingly soluble although it partially decomposes to a species containing the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation (see Figure 1). These solubility problems preclude molecular weight and conductivity measurements which would help establish the polymerization and any salt-like character of the complex.

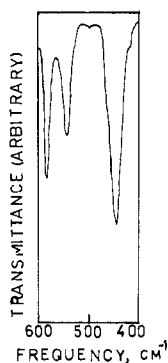


Figure 1.—Infrared spectrum (600–400  $\text{cm}^{-1}$ ) of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  in chloroform solution.

In attempting to suggest a structure for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  any species containing an  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation can reasonably be excluded on the basis of the above ir data and on the fact that known  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  salts are very soluble in chloroform and polar solvents.<sup>18</sup> Further, the very low solubility of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  in polar organic solvents does not seem consistent with a saltlike formulation as  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2^{2+} \cdot 2\text{Cl}^-$  or  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}^+ \cdot \text{Cl}^-$ .

It seems most probable that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is monomeric and nonionic. This conclusion is consistent with the following facts: (1) the monomeric, nonionic structure is well established for  $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  complexes where  $\text{M} = \text{Ge}, \text{Sn}, \text{Ti}, \text{Zr},$  or  $\text{Hf}$ ;<sup>1b,c,4,6b,c,d,19</sup> (2) the dicarboxybis(acetylacetonato)silicon(IV) complexes prepared by Pike and Lungo<sup>20</sup> are nonionic and monomeric; (3) the ir spectrum of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is similar to that for the analogous germanium<sup>18</sup> and tin complexes<sup>21</sup> except in the 500–400- $\text{cm}^{-1}$  region where a strong broad complex absorption occurs which may contain a silicon-chlorine stretching mode<sup>22,23</sup> (see Figure 2); and (4)  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is readily decomposed on standing in air giving off acidic fumes<sup>24</sup> (presumably HCl). This is to

(18) R. F. Riley, R. West, and R. Barbarin, *Inorg. Syn.*, **7**, 30 (1963).

(19) (a) G. T. Morgan and H. D. R. Drew, *J. Chem. Soc.*, 373 (1924); (b) *ibid.*, 1261 (1924).

(20) (a) R. M. Pike and R. R. Lungo, *J. Am. Chem. Soc.*, **87**, 1403 (1965); (b) *ibid.*, **88**, 2060 (1966).

(21) J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 183 (1967).

(22) I. R. Beattie, T. Gibson, M. Webster, and G. P. McQuillan, *J. Chem. Soc.*, 238 (1964).

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(24) A piece of moist litmus paper above the solid turns red within a few minutes (room conditions; 25° and ca. 65% relative humidity).

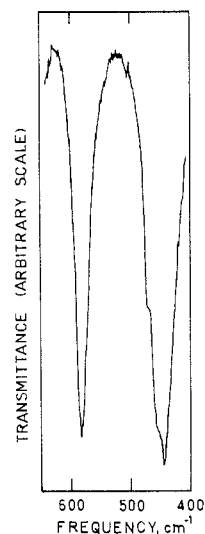


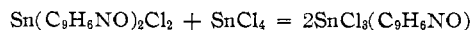
Figure 2.—Infrared spectrum (650–400  $\text{cm}^{-1}$ ) of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  as a mull in Nujol.

be expected if silicon-chlorine bonds are present because of their relative ease of hydrolysis.

Solution ir data (Figure 1) show that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  dissolves in chloroform and methylene chloride to yield a mixture of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  and  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ . The bands at 542 and 618  $\text{cm}^{-1}$  correspond to those for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ , which leaves the band at 583  $\text{cm}^{-1}$  due to  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ . Other bands in the 2000–400- $\text{cm}^{-1}$  region are identical within a few wave numbers to the solid-state bands for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  and  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ . The lack of bands in the 2000–1600- $\text{cm}^{-1}$  region shows the absence of free diketone and indicates that only the two oxygen-chelated complexes exist in solution. The  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3^+$  cation may form by the reaction



This type of reaction is known in the reverse direction for a tin-8-hydroxyquinolino complex<sup>25</sup>



Further, when  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  is refluxed in methylene chloride containing excess silicon tetrachloride, solid  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  can be isolated. Also, when  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is dissolved in chloroform containing  $4 \times 10^{-2}$  *M* silicon tetrachloride, there is noticeable suppression of the formation of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  as observed by the low intensity of the band at 542  $\text{cm}^{-1}$  compared to the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  band at 583  $\text{cm}^{-1}$ .

The observed nmr spectrum for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  in ethanol-free chloroform (or methylene chloride) is shown in Figure 3. The spectrum of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  consists of four resonance signals which is consistent with the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ — $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  mixture indicated by ir data. The signals from  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  were identified by direct comparison with the nmr spectrum of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  in the same solvent. Spectra at larger scale expansions than shown gave no indication that the methyl resonance signal for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is split.

(25) M. J. Frazer and B. Rimmer, 69 *J. Chem. Soc.*, **A**, (1968).

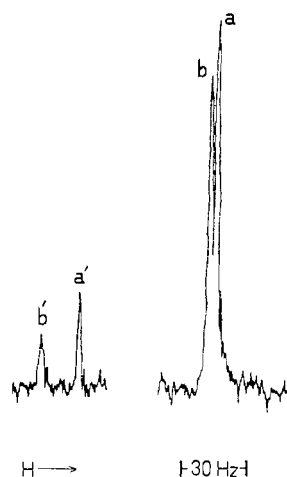


Figure 3.—Nmr spectrum (60 MHz, *ca.* 35°) of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  in chloroform. Chemical shifts (in ppm relative to the  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  methyl peak taken to be equal to  $-2.28$  ppm from TMS from ref 11): a,  $-2.22$ ; b,  $-2.28$ ; a',  $-5.93$ ; b',  $-6.23$ . a and a' refer to the methyl and ring protons of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ , and b and b' refer to the methyl and ring protons of  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$ , respectively.

Further, no splitting or significant line broadening was observed at low temperatures ( $-60^\circ$ ).

The observation of a single methyl resonance signal for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is consistent with a symmetrical structure, *i.e.*, a *trans* structure if, indeed, the complex is monomeric and nonionic. If the complex has a *cis* structure, one would expect to observe two methyl resonances since analogous *cis* tin and germanium complexes exhibit two methyl resonances near  $35^\circ$ .<sup>3b</sup> Also at *ca.*  $35^\circ$ , *cis*-diacetoxybis(acetylacetonato)silicon(IV) has two acetylacetonate methyl resonances,<sup>26</sup> and tris(benzoylacetonato)silicon(IV) chloride exhibits three methyl resonances (indicating a *cis,trans* structure for the cation).<sup>3b</sup> The above data make it unlikely that the observation of a single methyl resonance for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is due to rapid exchange on the nmr time scale.

On the other hand, the position of the ring proton resonance signal (5.93 ppm) for  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is most consistent with an unsymmetrical complex. According to recent workers<sup>3b,11</sup> acetylacetonate complexes having electrical asymmetry in the plane of the ring exhibit ring proton resonance signals which are significantly shifted relative to neutral and symmetrical complexes. Specifically for complexes of the type *cis*- $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  (M = group IV element) and for salts such as  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3\text{Cl}$  which ion pair to produce electrical asymmetry, the ring proton signals should occur from *ca.* 0.2 to 0.7 ppm downfield from the signals for the *trans* complexes. These recent observations suggest that  $\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$  is either ionic or unsymmetrical or both since the ring proton resonance signal is well into the region for unsymmetrical complexes. However, although the above correlation appears quite general for a number of representative acetylacetonates, it may be

that the silicon-acetylacetonate complexes are anomalous with respect to chemical shift data, and a *trans* monomeric and nonionic complex might also have a downfield ring proton signal. The supposition is supported by the fact that the chemical shift of the ring proton in *trans*-diacetoxybis(acetylacetonato)silicon(IV) is well into the region for unsymmetrical complexes.<sup>26</sup> Unfortunately, we have been unable to prepare other dihalobis( $\beta$ -diketonate)silicon(IV) complexes which would provide further data to clarify existing uncertainties.

**Acknowledgment.**—The author expresses appreciation to the Grant-in-Aid program of the College of William and Mary for support of this research.

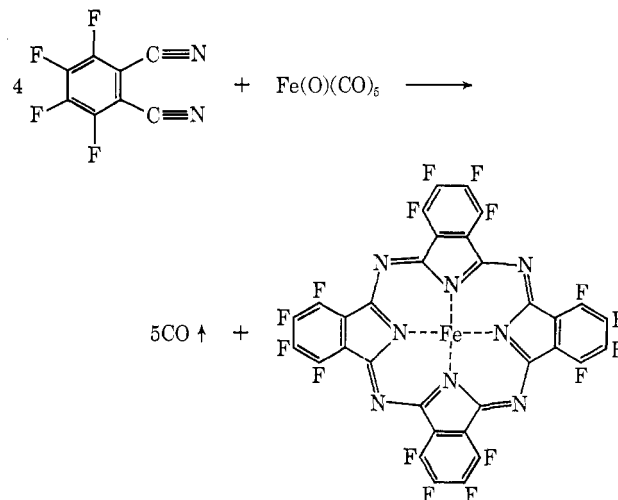
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## A Fluorinated Iron Phthalocyanine

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Received March 3, 1969

We are currently studying the rates of reaction of ferrous phthalocyanine with bases, these displacing weaker bases from the axial sites at the ferrous center.<sup>1</sup> Solubility limitations are irksome in such systems, and one approach, to sulfonate the peripheral phenylene groups, gives a product which dissolves in water but is a ferric, not a ferrous, phthalocyanine in solution.<sup>2</sup> Our approach has been to prepare a ferrous phthalocyanine with all of the hydrogen atoms of the four peripheral phenylene groups replaced by fluorine atoms. This note gives details of the synthesis, which is by the method of Meloni, Ocone, and Block,<sup>3</sup> and a preliminary account of some of the properties of this new compound.



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