

oligomerization. However, concomitant electronic effects, especially the strong donor properties of the bis-ylidic ligand (Schmidbaur, 1983) resulting in an electronically more saturated Cu<sup>I</sup> center, may also be a contributing factor.

The support of the stay of one of us (GM) at the Max-Planck-Institut für Kohlenforschung by Deutsche Forschungsgemeinschaft is gratefully acknowledged.

#### References

- CAMUS, A., MARSICH, N., NARDIN, G. & RANDACCIO, L. (1973). *J. Organomet. Chem.* **60**, C39–C42.
- CHURCHILL, M. R., DEBOER, B. G., ROTELLA, F. J., ABU SALAH, O. M. & BRUCE, M. I. (1975). *Inorg. Chem.* **14**, 2051–2056.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- EDWARDS, P. G., GELLERT, R. W., MARKS, M. W. & BAU, R. (1982). *J. Am. Chem. Soc.* **104**, 2072–2073.
- HARDY, G. E., ZINK, J. I., KASKA, W. C. & BALDWIN, J. C. (1978). *J. Am. Chem. Soc.* **100**, 8001–8002.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JARDINE, F. H. (1975). *Adv. Inorg. Chem. Radiochem.* **17**, 115–163.
- JARVIS, J. A. J., PEARCE, R. & LAPPERT, M. F. (1977). *J. Chem. Soc. Dalton Trans.* pp. 999–1003.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- JUKES, A. E. (1974). *Adv. Organomet. Chem.* **12**, 215–322.
- KRÜGER, C., MÜLLER, G., ERKER, G., DORF, U. & ENGEL, K. (1985). *Organometallics*, **4**, 215–223.
- LEONI, P., PASQUALI, M. & GHILARDI, C. A. (1983). *J. Chem. Soc. Chem. Commun.* pp. 240–241.
- NARDIN, G., RANDACCIO, L. & ZANGRANDO, E. (1974). *J. Organomet. Chem.* **74**, C23–C25.
- PASQUALI, M., FLORIANI, C. & GAETANI-MANFREDOTTI, A. (1980). *Inorg. Chem.* **19**, 1191–1197.
- POSNER, G. H. (1980). *An Introduction to Synthesis using Organocopper Reagents*. New York: John Wiley.
- SCHMIDBAUR, H. (1983). *Angew. Chem.* **95**, 980–1000; *Angew. Chem. Int. Ed. Engl.* **22**, 907–927.
- SCHMIDBAUR, H., ADLKOEFER, J. & BUCHNER, W. (1973). *Angew. Chem.* **85**, 448–449; *Angew. Chem. Int. Ed. Engl.* **12**, 415–416.
- SCHMIDBAUR, H., ADLKOEFER, J. & HEIMANN, M. (1974). *Chem. Ber.* **107**, 3697–3705.
- SCHMIDBAUR, H., ZYBILL, CH., MÜLLER, G. & KRÜGER, C. (1983). *Angew. Chem.* **95**, 753–755; *Angew. Chem. Int. Ed. Engl.* **22**, 729–730.
- SCHMIDBAUR, H., ZYBILL, CH., NEUGEBAUER, D. & MÜLLER, G. (1985). *Z. Naturforsch. Teil B*, **40**, 1293–1300.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- VAN KOTEN, G. & NOLTES, J. G. (1982). *Comprehensive Organometallic Chemistry*, edited by G. WILKINSON, F. G. A. STONE & E. W. ABEL, Vol. 2, pp. 709–763. Oxford: Pergamon Press.
- VINCENT, A. T. & WHEATLEY, P. J. (1972). *J. Chem. Soc. Dalton Trans.* pp. 617–622.

*Acta Cryst.* (1986). **C42**, 1144–1148

## Structure of the Hexafluorophosphate Salts of $\mu$ -( $\eta^6$ : $\eta^6$ -Phenoxazine)-bis[ $\eta^5$ -cyclopentadienyliron(II)] (1) and ( $\eta^5$ -cyclopentadienyl)( $\eta^6$ -phenoxathiin)iron(II) (2)

BY V. M. LYNCH, S. N. THOMAS AND S. H. SIMONSEN

*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA*

AND A. PIÓRKO AND R. G. SUTHERLAND

*Department of Chemistry, The University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0*

(Received 16 September 1985; accepted 1 April 1986)

**Abstract.** (1): [C<sub>22</sub>H<sub>19</sub>Fe<sub>2</sub>NO](PF<sub>6</sub>)<sub>2</sub>, *M<sub>r</sub>* = 715.05, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 10.635 (2), *b* = 9.928 (1), *c* = 22.562 (7) Å,  $\beta$  = 92.41 (1)°, *V* = 2380.1 (9) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.00 g cm<sup>-3</sup> (163 K), Mo *K*α radiation,  $\lambda$  = 0.71069 Å,  $\mu$  = 14.63 cm<sup>-1</sup>, *F*(000) = 1424, *T* = 163 K, final *R* = 0.045 for 4787 reflections. (2): [C<sub>17</sub>H<sub>13</sub>FeOS]PF<sub>6</sub>, *M<sub>r</sub>* = 466.18, triclinic, *P* $\bar{1}$ , *a* = 8.461 (2), *b* = 10.273 (2), *c* = 10.562 (2) Å,  $\alpha$  = 93.75 (2),  $\beta$  = 110.41 (2),  $\gamma$  = 102.84 (2)°, *V* = 828.6 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.87 g cm<sup>-3</sup> (163 K), Mo *K*α radiation,  $\lambda$  = 0.71069 Å,  $\mu$  = 11.95 cm<sup>-1</sup>,

*F*(000) = 468, *T* = 163 K, final *R* = 0.046 for 3031 reflections. The cyclopentadienyliron(II) moieties, ( $\eta^5$ -Cp)Fe<sup>II</sup>, in (1) are *trans*. Coordination is to the terminal phenyl ring(s) in both complexes and results in a flattening of phenoxathiin in (2), while phenoxazine in (1) remains essentially unchanged. The heterocycles are nearly planar, with (1) having a dihedral angle between planes through the phenyl rings of 176.9 (1)° while (2) has a dihedral angle of 178.7 (1)°. Asymmetric C–O bond lengths are observed in (2) with the shorter bond being to the C atom of the coordinated ring,

1.387 (4) Å versus 1.419 (5) Å, which is apparently due to the inductive effect of the coordinated ( $\eta^5$ -Cp)Fe<sup>II</sup> group.

**Introduction.** Our interest lies in the synthesis and structural characterization of ( $\eta^5$ -cyclopentadienyl)-Fe<sup>II</sup>, *i.e.* ( $\eta^5$ -Cp)Fe<sup>II</sup>, complexes of a wide variety of tricyclic heterocycles. These complexes can be synthesized *via* a ligand exchange reaction where a Cp ring in ferrocene is directly replaced by the heterocycle (Lee, Steele & Sutherland, 1980; Lee, Piórko & Sutherland, 1983) or by way of a nucleophilic substitution reaction of an *o*-dichlorobenzene complex of ( $\eta^5$ -Cp)Fe<sup>II</sup> with an appropriately substituted arene (Sutherland, Piórko, Gill & Lee, 1982). While the mode of coordination by Fe<sup>II</sup> to the heterocycle is readily established by <sup>13</sup>C NMR data, the effect of complexation on the geometry of the heterocycle is not so easily ascertained. In addition, for the bis( $\eta^5$ -Cp)Fe<sup>II</sup> complexes, both *cis* and *trans* isomers may be obtained. As part of an ongoing study on such complexes, we report the crystal structures of the title compounds.

**Experimental.** Syntheses of (1) (Lee *et al.*, 1983) and (2) (Sutherland *et al.*, 1982) already described. (1) dark yellow crystal fragment, 0.28 × 0.17 × 0.17 mm; (2) dark yellow needle; 0.17 × 0.17 × 0.47 mm; both crystals from acetone–diethyl ether–methylene chloride (255 K). Data collected under identical experimental conditions, Syntex P2<sub>1</sub> diffractometer, graphite monochromator, Syntex LT-1 low-temperature delivery system (163 K). Lattice parameters from least-squares refinement of setting angles of 45 reflections for (1) (24.9 < 2θ < 29.2°), 60 reflections for (2) (23.2 < 2θ < 30.0°). ω-scan technique [6942 unique reflections for (1); 3797 for (2)], 2θ range 4–60° for (1), 4–55° for (2), 1° ω scan at 3–6° min<sup>-1</sup> [only unique data; *h* = 0→14, *k* = 0→13, *l* = -31→31 for (1); *h* = 0→10, *k* = -13→13, *l* = -13→12 for (2)]. Space group from systematic absences in (1) and by successful refinement of structure in (2). Four reflections [ $\bar{2}\bar{1}0$ , 008, 222 and  $\bar{2}\bar{1}1$  for (1) and 111, 002, 0 $\bar{2}0$  and  $\bar{3}00$  for (2)] remeasured every 96 reflections to monitor instrument and crystal stability. Max. decay correction <1% for (1) and (2) (Henslee & Davis, 1975). Data corrected for Lp effects and absorption [based on crystal shape; transmission-factor range 0.69–0.77 for (1) and 0.79–0.82 for (2)]. Data reduction described by Riley & Davis (1976). Reflections having  $F_o < n\sigma(F_o)$  considered unobserved [*n* = 4, 2155 reflections for (1); *n* = 6, 766 reflections for (2)]. Structures solved by heavy-atom and Fourier techniques and refined by full-matrix least-squares procedures with anisotropic thermal parameters for non-H atoms. H atoms located from difference map [except for H(N10) which was fixed with H–N bond length of 1.0 Å and C–N–H angles of 120°] and refined with isotropic thermal

parameters. For (1), 434 parameters refined\* in blocks of 257 and 178 parameters (scale factor refined in each block); for (2), 296 parameters refined.  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 1/[\sigma(F_o)]^2$  and  $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.04I)^2\}^{1/2}$ . Intensity, *I*, given by  $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$ , 0.04 used to down-weight intense reflections and to account for instrument instability, *k* is correction due to Lp effects, absorption and decay.  $\sigma(I)$  estimated from counting statistics;  $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$ . For (1), since geometry around O and N in phenoxazine ring (5 and 10 positions, respectively) expected to be similar, atoms in these positions initially refined as N. After several cycles of refinement with anisotropic thermal parameters, *U*<sub>*ii*</sub>'s for atom in 5 position quite low and much residual electron density around this atom. Therefore, this was concluded to be O-atom position and refined as such thereafter. For (1), final *R* = 0.045 for 4787 reflections, *wR* = 0.048 (*R*<sub>all</sub> = 0.078, *wR*<sub>all</sub> = 0.053), goodness of fit = 1.28; for (2), final *R* = 0.046 for 3031 reflections, *wR* = 0.061 (*R*<sub>all</sub> = 0.059, *wR*<sub>all</sub> = 0.063) and goodness of fit = 2.10. Max.  $|\Delta/\sigma| < 0.01$  in final refinement cycle for both structures and min. and max. peaks in final difference map -0.47 and 0.78 e Å<sup>-3</sup>, respectively, for (1) and -0.61 and 0.89 e Å<sup>-3</sup>, respectively, for (2). Scattering factors for non-H atoms from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), scattering factors for H atoms from Stewart, Davidson & Simpson (1965); linear absorption coefficient calculated from values from *International Tables for X-ray Crystallography* (1974). Least-squares-planes program supplied by Cordes (1983); other computer programs in reference 11 of Gadol & Davis (1982).

**Discussion.** Positional and thermal parameters for the atoms of (1) are listed in Table 1, those for (2) are listed in Table 2. ORTEP (Johnson, 1976) drawings showing the atom-labelling scheme for (1) and (2) are in Figs. 1 and 2, respectively. Bond distances and angles for the non-H atoms of both complexes are listed in Table 3. The PF<sub>6</sub><sup>-</sup> groups are reasonably well behaved and have P–F bond lengths ranging from 1.578 (3) to 1.599 (2) Å in (1) and from 1.548 (5) to 1.592 (4) Å in (2), while no F–P–F angle deviates from octahedral geometry by more than 1.1° in (1) and by more than 4.5° in (2). Several short F...H contacts are observed in both complexes. The shortest of these contacts are between F(22) and H(N10) (related by 0.5 + *x*,

\* Lists of anisotropic thermal parameters, bond distances and angles for H, P and F atoms, least-squares planes, unit-cell packing diagrams and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42956 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0.5 - y, 0.5 + z) at a distance of 1.99 (4) Å in (1) and between F(1) and H(C13) (x - 1, y, z) at a distance of 2.34 (5) Å. While most of these short contacts are probably due to electrostatic interactions between the PF<sub>6</sub><sup>-</sup> groups and Fe, the one involving H(N10) can be considered to be a conventional H bond. The dicationic complex in (1) is surrounded by twelve PF<sub>6</sub><sup>-</sup> groups. These groups are arranged in three parallel layers, each containing four anions, with the anions of the middle layer approximately equidistant from the two Fe atoms.

Table 1. *Positional and thermal parameters for μ-(η<sup>6</sup>:η<sup>6</sup>-phenoxazine)-bis[η<sup>5</sup>-cyclopentadienyliron(II)] hexafluorophosphate*

	x	y	z	U <sub>eq</sub> , U <sub>iso</sub> (Å <sup>2</sup> )*
Fe(1)	0.27240 (4)	0.25440 (4)	-0.05547 (2)	0.01906 (12)
Fe(2)	0.08018 (4)	0.27938 (4)	0.17829 (2)	0.01761 (12)
P(1)	0.27332 (8)	0.26288 (8)	0.42905 (4)	0.0237 (2)
P(2)	1.08357 (8)	0.22808 (9)	0.69233 (4)	0.0251 (2)
F(11)	0.2176 (2)	0.2358 (2)	0.49226 (10)	0.0489 (8)
F(12)	0.1725 (2)	0.1621 (2)	0.39900 (11)	0.0507 (9)
F(13)	0.3711 (2)	0.1419 (2)	0.43853 (10)	0.0457 (8)
F(14)	0.1765 (2)	0.3848 (2)	0.41901 (11)	0.0504 (9)
F(15)	0.3733 (2)	0.3648 (2)	0.45816 (10)	0.0478 (8)
F(16)	0.3287 (2)	0.2897 (2)	0.36569 (9)	0.0394 (7)
F(21)	0.9918 (2)	0.1210 (2)	0.66030 (11)	0.0507 (9)
F(22)	0.9905 (2)	0.3481 (2)	0.67279 (11)	0.0547 (9)
F(23)	1.1546 (3)	0.2464 (3)	0.63269 (12)	0.0722 (11)
F(24)	1.1747 (2)	0.3351 (2)	0.72462 (10)	0.0432 (8)
F(25)	1.1760 (3)	0.1098 (3)	0.71128 (15)	0.0789 (12)
F(26)	1.0115 (3)	0.2126 (3)	0.75167 (11)	0.0640 (10)
O(5)	0.0693 (2)	0.3312 (2)	0.03908 (9)	0.0249 (7)
N(10)	0.2935 (2)	0.2141 (3)	0.08518 (11)	0.0229 (7)
C(1)	0.4077 (3)	0.3222 (4)	0.0068 (2)	0.0280 (10)
C(2)	0.4052 (4)	0.4044 (4)	-0.0438 (2)	0.0344 (12)
C(3)	0.2923 (4)	0.4601 (3)	-0.0565 (2)	0.0336 (12)
C(4)	0.1796 (4)	0.4339 (3)	-0.0381 (2)	0.0271 (10)
C(4a)	0.1828 (3)	0.3544 (3)	0.01323 (13)	0.0203 (9)
C(5a)	0.0685 (3)	0.2429 (3)	0.08584 (12)	0.0196 (8)
C(6)	-0.0475 (3)	0.2169 (3)	0.11100 (14)	0.0231 (9)
C(7)	-0.0526 (3)	0.1304 (3)	0.16027 (15)	0.0272 (10)
C(8)	0.0580 (4)	0.0737 (3)	0.1846 (2)	0.0302 (11)
C(9)	0.1749 (3)	0.1015 (3)	0.16005 (15)	0.0254 (10)
C(9a)	0.1807 (3)	0.1837 (3)	0.10968 (12)	0.0199 (8)
C(10a)	0.2954 (3)	0.2985 (3)	0.03673 (13)	0.0231 (9)
C(11)	0.1695 (4)	0.0808 (4)	-0.0636 (2)	0.0348 (12)
C(12)	0.2987 (4)	0.0497 (4)	-0.0601 (2)	0.0368 (13)
C(13)	0.3565 (4)	0.1142 (4)	-0.1078 (2)	0.0344 (12)
C(14)	0.2625 (4)	0.1838 (4)	-0.1416 (2)	0.0375 (12)
C(15)	0.1467 (4)	0.1638 (4)	-0.1138 (2)	0.0361 (12)
C(21)	0.1819 (4)	0.4517 (4)	0.1937 (2)	0.0366 (12)
C(22)	0.0538 (4)	0.4827 (4)	0.1896 (2)	0.0377 (13)
C(23)	-0.0067 (4)	0.4100 (4)	0.2341 (2)	0.0347 (12)
C(24)	0.0853 (4)	0.3349 (4)	0.26583 (15)	0.0332 (11)
C(25)	0.2025 (4)	0.3604 (4)	0.2408 (2)	0.0363 (12)
H(C1)	0.479 (4)	0.276 (4)	0.021 (2)	0.038 (11)
H(C2)	0.480 (3)	0.416 (4)	-0.0655 (15)	0.030 (10)
H(C3)	0.286 (3)	0.504 (4)	-0.104 (2)	0.040 (11)
H(C4)	0.103 (3)	0.460 (4)	-0.053 (2)	0.035 (11)
H(C6)	-0.117 (3)	0.258 (4)	0.094 (2)	0.033 (10)
H(C7)	-0.128 (3)	0.123 (3)	0.181 (2)	0.031 (10)
H(C8)	0.055 (3)	0.022 (3)	0.2202 (14)	0.025 (9)
H(C9)	0.250 (3)	0.067 (4)	0.1765 (15)	0.031 (10)
H(N10)	0.3737 (2)	0.1749 (3)	0.10230 (11)	0.08 (2)
H(C11)	0.113 (4)	0.053 (4)	-0.037 (2)	0.058 (14)
H(C12)	0.341 (4)	0.008 (4)	-0.032 (2)	0.034 (11)
H(C13)	0.442 (4)	0.112 (4)	-0.116 (2)	0.042 (12)
H(C14)	0.275 (4)	0.247 (4)	-0.175 (2)	0.042 (11)
H(C15)	0.074 (4)	0.203 (4)	-0.129 (2)	0.056 (14)
H(C21)	0.240 (4)	0.485 (4)	0.168 (2)	0.038 (11)
H(C22)	0.014 (4)	0.535 (4)	0.162 (2)	0.038 (11)
H(C23)	-0.094 (4)	0.407 (4)	0.240 (2)	0.044 (12)
H(C24)	0.072 (4)	0.270 (4)	0.298 (2)	0.039 (11)
H(C25)	0.280 (4)	0.315 (4)	0.256 (2)	0.051 (13)

\* For anisotropic atoms, the U value is U<sub>eq</sub>, calculated as

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

where A<sub>ij</sub> is the dot product of the i<sup>th</sup> and j<sup>th</sup> direct-space unit-cell vectors.

The Fe...Fe separation in the dication is 5.741 (2) Å. The cation in (2) is surrounded by six PF<sub>6</sub><sup>-</sup> groups, with three of these being slightly closer than the other three.

The aromatic rings are all planar as expected. As is commonly observed, the C-C bonds of the complexed ring of the heterocycle in (2) are slightly longer than those of the uncomplexed ring. The Fe-C<sub>Cp</sub> bond lengths are normal for both complexes. The Fe-C<sub>heterocycle</sub> bond lengths show the long-short pattern observed in similar complexes (Simonsen, Lynch, Sutherland & Piórko, 1985) where the Fe-to-bridgehead-C bonds are slightly longer than the Fe-to-secondary-C bonds with the result that the Fe atom is not exactly centered over the arene ring. Because of the larger size of the arene ring, the Fe-to-ring-plane distance is shorter for the arene than for the Cp ring. The Fe-to-ring-plane distance is 1.544 (2) Å for the arene ring and 1.671 (2) Å for the Cp ring in (2), while, in (1), these distances are 1.554 (1) Å [Fe(1)] and 1.551 (1) Å [Fe(2)] and 1.664 (2) Å [Fe(1)] and 1.664 (2) Å [Fe(2)] for the arene and

Table 2. *Positional and isotropic thermal parameters for (η<sup>5</sup>-cyclopentadienyl)(η<sup>6</sup>-phenoxathiin)iron(II) hexafluorophosphate*

	x	y	z	U <sub>eq</sub> , U <sub>iso</sub> (Å <sup>2</sup> )*
Fe(1)	0.28880 (6)	0.21272 (5)	0.28270 (5)	0.0229 (2)
S(10)	0.63024 (12)	0.07542 (10)	0.28198 (10)	0.0342 (3)
O(5)	0.2482 (3)	-0.0149 (2)	0.0436 (3)	0.0343 (10)
C(1)	0.5294 (5)	0.3083 (4)	0.2778 (4)	0.0330 (14)
C(2)	0.4104 (6)	0.3889 (4)	0.2326 (4)	0.037 (2)
C(3)	0.2461 (5)	0.3343 (4)	0.1298 (4)	0.035 (2)
C(4)	0.1983 (5)	0.1982 (4)	0.0693 (4)	0.0308 (14)
C(4a)	0.3161 (4)	0.1176 (3)	0.1101 (3)	0.0250 (12)
C(5a)	0.3536 (4)	-0.1073 (3)	0.0737 (3)	0.0258 (12)
C(6)	0.2734 (5)	-0.2337 (4)	-0.0058 (4)	0.0305 (13)
C(7)	0.3607 (6)	-0.3334 (4)	0.0132 (4)	0.037 (2)
C(8)	0.5285 (6)	-0.3068 (4)	0.1110 (4)	0.034 (2)
C(9)	0.6080 (5)	-0.1803 (4)	0.1898 (4)	0.0295 (13)
C(9a)	0.5193 (4)	-0.0793 (3)	0.1719 (3)	0.0244 (12)
C(10a)	0.4817 (4)	0.1708 (3)	0.2158 (3)	0.0251 (12)
C(11)	0.1002 (6)	0.2256 (5)	0.3616 (4)	0.040 (2)
C(12)	0.2661 (6)	0.2790 (5)	0.4619 (4)	0.041 (2)
C(13)	0.3553 (6)	0.1778 (5)	0.4809 (4)	0.046 (2)
C(14)	0.2407 (7)	0.0593 (4)	0.3890 (5)	0.048 (2)
C(15)	0.0836 (6)	0.0902 (5)	0.3163 (5)	0.046 (2)
P(1)	-0.06625 (13)	0.36145 (10)	0.69523 (10)	0.0327 (4)
F(1)	-0.2375 (5)	0.2667 (4)	0.7002 (4)	0.096 (2)
F(2)	-0.1089 (5)	0.2757 (4)	0.5539 (3)	0.080 (2)
F(3)	0.1070 (6)	0.4497 (5)	0.6917 (4)	0.133 (2)
F(4)	-0.0308 (5)	0.4464 (4)	0.8385 (4)	0.090 (2)
F(5)	0.0364 (6)	0.2658 (5)	0.7741 (4)	0.112 (2)
F(6)	-0.1800 (8)	0.4534 (4)	0.6189 (5)	0.150 (3)
H(C1)	0.645 (5)	0.344 (4)	0.358 (4)	0.029 (10)
H(C2)	0.441 (5)	0.481 (4)	0.281 (4)	0.025 (9)
H(C3)	0.164 (5)	0.384 (4)	0.107 (4)	0.030 (10)
H(C4)	0.086 (5)	0.153 (4)	0.010 (4)	0.024 (10)
H(C6)	0.156 (6)	-0.249 (4)	-0.072 (4)	0.043 (12)
H(C7)	0.292 (6)	-0.419 (5)	-0.049 (5)	0.046 (12)
H(C8)	0.595 (6)	-0.364 (5)	0.124 (5)	0.047 (13)
H(C9)	0.720 (6)	-0.165 (4)	0.259 (4)	0.033 (11)
H(C11)	0.004 (6)	0.265 (5)	0.317 (4)	0.043 (12)
H(C12)	0.312 (6)	0.370 (5)	0.517 (5)	0.055 (14)
H(C13)	0.475 (6)	0.193 (5)	0.540 (5)	0.047 (13)
H(C14)	0.267 (6)	-0.026 (5)	0.379 (4)	0.045 (12)
H(C15)	-0.015 (7)	0.031 (5)	0.233 (5)	0.06 (2)

\* For anisotropic atoms, the U is U<sub>eq</sub>, calculated as

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

where A<sub>ij</sub> is the dot product of the i<sup>th</sup> and j<sup>th</sup> direct-space unit-cell vectors.

Cp rings, respectively. As is generally observed in such sandwich complexes (Churchill & Wormald, 1969), the coordinated aromatic rings are nearly parallel with no dihedral angle being greater than 3° in either complex.

While ( $\eta^6$ : $\eta^6$ -arene)bis( $\eta^5$ -Cp)Fe<sup>II</sup> dications of polyaromatic molecules have been known for some time (Morrison, Ho & Hendrickson, 1973; Lee, Sutherland & Thompson, 1972), this is the first reported example of a crystal-structure determination of such a compound. These complexes can be *cis* where the ( $\eta^5$ -Cp)Fe<sup>II</sup> moieties are on the same side or *trans* where they reside on opposite sides of the polyaromatic

molecule. The *trans* isomer is observed when the arene is planar or very nearly so, while both *cis* and *trans* isomers have been observed for several arenes that are folded (Morrison *et al.*, 1973; Lee *et al.*, 1983). For tricyclic arenes, steric effects due to the proximity of the cyclopentadienyl rings preclude the formation of the *cis* isomer for a planar or a nearly planar molecule. In addition, electrostatic effects will favor the *trans* isomer by maximizing the separation of the ( $\eta^5$ -Cp)Fe<sup>II</sup> moieties. Although such considerations would be of a lesser importance for some of the larger polyaromatic molecules such as chrysene, only a single isomer, inferred from <sup>13</sup>C NMR data to be *trans*, has been observed (Morrison *et al.*, 1973). Even though the monocation of phenoxathiin, (2), is nearly planar and the dication is prepared by reaction of the monocation with excess ferrocene, both *cis* and *trans* isomers of ( $\eta^6$ : $\eta^6$ -phenoxathiin)bis( $\eta^5$ -Cp)Fe<sup>II</sup> have been observed in solution (Lee *et al.*, 1983). This would require either a reduction in the dihedral angle of (2) prior to the formation of the dication to accommodate the two ( $\eta^5$ -Cp)Fe<sup>II</sup> groups on the same side of the molecule or the generation of free phenoxathiin followed by simultaneous or nearly simultaneous addition of two ( $\eta^5$ -Cp)Fe<sup>II</sup> groups. Such restrictions would not apply to the formation of the *trans* isomer. For thioxanthene, which is more folded than phenoxathiin [dihedral angle

Table 3. Bond distances and angles for the non-H atoms of the [( $\eta^5$ -cyclopentadienyl)iron(II)] complexes of phenoxazine (1) and phenoxathiin (2)

1	2	3	(1) (X = N)		(2) (X = S)	
			1-2	1-2-3	1-2	1-2-3
C(1)	Fe(1)		2.081 (3)		2.075 (4)	
C(2)	Fe(1)		2.062 (4)		2.071 (4)	
C(3)	Fe(1)		2.070 (3)		2.087 (2)	
C(4)	Fe(1)		2.082 (3)		2.095 (4)	
C(4a)	Fe(1)		2.102 (3)		2.119 (4)	
C(10a)	Fe(1)		2.130 (3)		2.104 (4)	
C(5a)	Fe(2)		2.115 (3)			
C(6)	Fe(2)		2.088 (3)			
C(7)	Fe(2)		2.073 (3)			
C(8)	Fe(2)		2.062 (3)			
C(9)	Fe(2)		2.083 (3)			
C(9a)	Fe(2)		2.140 (3)			
C(11)	Fe(1)		2.046 (4)		2.065 (6)	
C(12)	Fe(1)		2.055 (4)		2.056 (5)	
C(13)	Fe(1)		2.055 (4)		2.048 (5)	
C(14)	Fe(1)		2.064 (4)		2.043 (5)	
C(15)	Fe(1)		2.045 (4)		2.060 (5)	
C(21)	Fe(2)		2.046 (4)			
C(22)	Fe(2)		2.055 (4)			
C(23)	Fe(2)		2.054 (4)			
C(24)	Fe(2)		2.049 (3)			
C(25)	Fe(2)		2.043 (4)			
C(4a)	O(5)	C(5a)	1.382 (4)	117.7 (2)	1.387 (4)	119.6 (2)
C(5a)	O(5)		1.372 (4)		1.419 (5)	
C(9a)	X(10)	C(10a)	1.375 (4)	119.6 (2)	1.759 (3)	100.2 (2)
C(10a)	X(10)		1.378 (4)		1.748 (4)	
C(2)	C(1)	C(10a)	1.403 (5)	119.8 (3)	1.419 (6)	119.6 (3)
C(10a)	C(1)		1.415 (5)		1.424 (5)	
C(3)	C(2)	C(1)	1.400 (5)	120.9 (4)	1.396 (5)	120.8 (3)
C(4)	C(3)	C(2)	1.406 (6)	119.7 (3)	1.406 (6)	119.7 (4)
C(4a)	C(4)	C(3)	1.402 (4)	119.2 (3)	1.406 (6)	120.4 (3)
C(10a)	C(4a)	O(5)	1.403 (4)	121.4 (3)	1.413 (4)	125.8 (3)
C(10a)	C(4a)	C(4)		121.7 (3)		120.5 (3)
O(5)	C(4a)	C(4)		116.8 (3)		113.5 (3)
C(6)	C(5a)	C(9a)	1.404 (4)	120.7 (3)	1.386 (5)	121.2 (4)
C(6)	C(5a)	O(5)		117.5 (3)		113.6 (3)
C(9a)	C(5a)	O(5)	1.416 (4)	121.7 (3)	1.376 (4)	125.2 (3)
C(7)	C(6)	C(5a)	1.407 (5)	119.7 (3)	1.376 (6)	119.7 (3)
C(8)	C(7)	C(6)	1.396 (5)	119.8 (3)	1.388 (5)	120.0 (3)
C(9)	C(8)	C(7)	1.410 (5)	120.6 (3)	1.383 (5)	120.1 (4)
C(9a)	C(9)	C(8)	1.403 (4)	120.1 (3)	1.396 (6)	120.2 (3)
X(10)	C(9a)	C(5a)		119.5 (3)		124.9 (3)
X(10)	C(9a)	C(9)		121.5 (3)		116.1 (2)
C(5a)	C(9a)	C(9)		119.0 (3)		118.9 (3)
X(10)	C(10a)	C(1)		121.3 (3)		117.1 (2)
X(10)	C(10a)	C(4a)		119.9 (3)		123.8 (3)
C(1)	C(10a)	C(4a)		118.6 (3)		119.0 (3)
C(12)	C(11)	C(15)	1.408 (6)	107.9 (4)	1.392 (5)	108.5 (4)
C(15)	C(11)		1.413 (5)		1.401 (7)	
C(13)	C(12)	C(11)	1.415 (6)	108.2 (3)	1.401 (8)	108.6 (6)
C(14)	C(13)	C(12)	1.411 (6)	108.1 (4)	1.424 (6)	107.3 (4)
C(15)	C(14)	C(13)	1.419 (6)	107.6 (3)	1.402 (7)	107.7 (4)
C(11)	C(15)	C(14)		108.2 (3)		108.0 (3)
C(22)	C(21)	C(25)	1.396 (6)	108.2 (4)		
C(25)	C(21)		1.408 (5)			
C(23)	C(22)	C(21)	1.413 (6)	108.3 (2)		
C(24)	C(23)	C(22)	1.402 (5)	107.8 (4)		
C(25)	C(24)	C(23)	1.413 (6)	108.0 (3)		
C(21)	C(25)	C(24)		107.8 (4)		

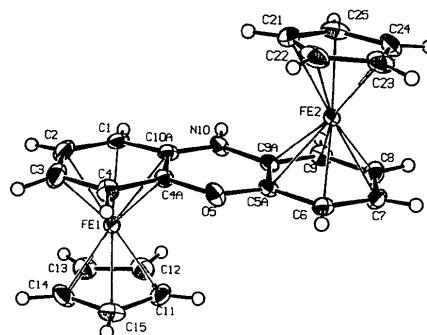


Fig. 1. View of complex in (1) showing the atom-labelling scheme.

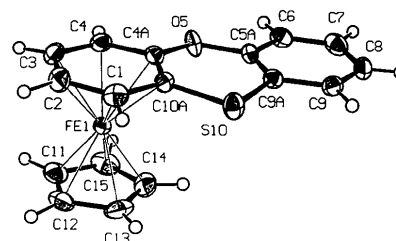


Fig. 2. View of complex in (2) showing the atom-labelling scheme.

of thioxanthene 135.3 (1)°; Gillean, Phelps & Cordes (1973)], only the *trans* dication has been reported (Lee *et al.*, 1980) although a recent reexamination of the <sup>13</sup>C NMR spectra of the dication of thioxanthene shows two CH<sub>2</sub> carbon signals. Work on such reactions with folded heterocycles is currently underway.

Coordination by the (η<sup>5</sup>-Cp)Fe<sup>II</sup> moiety results in flattening of phenoxathiin which has a dihedral angle of 147.71 (9)° (Kimura, 1981). In addition, asymmetric C—O bond lengths are observed with the shorter bond being to the C atom of the coordinated ring. The internal angles of the central ring of phenoxathiin increase upon coordination with the C—C—S(O) angles increasing by greater than 3° while the S...O distance increases from 3.049 (2) to 3.212 (3) Å in (2). These changes are consistent with previous results that indicate that electron-withdrawing groups substituted in or on the aromatic ring(s) of phenoxathiins result in a flattening of the molecule together with substantial changes in the geometry of the central ring (Lynch, Simonsen, Martin, Puig-Torres & Smith, 1984). Although the crystal structure of phenoxazine has not been reported, its geometry is expected to be similar to that of dibenzodioxin (where O replaces NH) which is planar (Singh & McKinney, 1978). It would appear that, insofar as the dihedral angle of the molecule is concerned, coordination by (η<sup>5</sup>-Cp)Fe<sup>II</sup> has little effect.

The financial support given by the Robert A. Welch Foundation to SHS (Grant F-017) and by the Natural Science and Engineering Research Council of Canada to RGS and AP is gratefully acknowledged.

*Acta Cryst.* (1986). C42, 1148–1151

## Structure of Dinitratobis(triphenylphosphine oxide)copper(II) Toluene Solvate (1/1)

BY M. BELICCHI FERRARI, G. FAVA GASPARRI, C. PELIZZI AND P. TARASCONI

*Istituto di Chimica Generale, Centro di Studio per la Strutturistica Diffraattometrica del CNR,  
43100 Parma, Via M. D'Azeglio 85, Italy*

(Received 2 September 1985; accepted 4 April 1986)

**Abstract.** C<sub>36</sub>H<sub>30</sub>CuN<sub>2</sub>O<sub>8</sub>P<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>, *M<sub>r</sub>* = 836.27, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 12.933 (3), *b* = 15.532 (3), *c* = 10.285 (3) Å, β = 100.68 (3)°, *U* = 2030.2 (9) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.37 Mg m<sup>-3</sup>, *Cu Kα*, λ̄ = 1.54178 Å, μ = 1.94 mm<sup>-1</sup>, *F*(000) = 866, room temperature, final *R* = 0.050 for 1759 unique observed reflections. The Cu atom lies on a symmetry centre and is six coordinated with two *trans* unidentate triphenylphosphine oxide (tppo) ligands and two *trans* bidentate nitrate groups. The nitrate groups are

0108-2701/86/091148-04\$01.50

## References

- CHURCHILL, M. R. & WORMALD, J. (1969). *Inorg. Chem.* **8**, 716–724.
- CORDES, A. W. (1983). Personal communication.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- GADOL, S. M. & DAVIS, R. E. (1982). *Organometallics*, **1**, 1607–1613.
- GILLEAN, J. A., PHELPS, D. W. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2296–2298.
- HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* **B31**, 1511–1519.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.)
- JOHNSON, C. K., (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KIMURA, M. (1981). Unpublished results.
- LEE, C. C., PIÓRKO, A. & SUTHERLAND, R. G. (1983). *J. Organomet. Chem.* **248**, 357–364.
- LEE, C. C., STEELE, B. R. & SUTHERLAND, R. G. (1980). *J. Organomet. Chem.* **186**, 265–270.
- LEE, C. C., SUTHERLAND, R. G. & THOMPSON, B. J. (1972). *J. Chem. Soc. Chem. Commun.* pp. 907–908.
- LYNCH, V. M., SIMONSEN, S. H., MARTIN, G. E., PUIG-TORRES, S. & SMITH, K. (1984). *Acta Cryst.* **C40**, 1483–1486.
- MORRISON, W. H., HO, E. Y. & HENDRICKSON, D. N. (1973). *J. Am. Chem. Soc.* **96**, 3603–3608.
- RILEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* **B32**, 381–386.
- SIMONSEN, S. H., LYNCH, V. M., SUTHERLAND, R. G. & PIÓRKO, A. (1985). *J. Organomet. Chem.* **290**, 387–400.
- SINGH, P. & MCKINNEY, J. D. (1978). *Acta Cryst.* **B34**, 2956–2957.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUTHERLAND, R. G., PIÓRKO, A., GILL, U. S. & LEE, C. C. (1982). *J. Heterocycl. Chem.* **19**, 801–803.

coordinated unsymmetrically. The CuO<sub>6</sub> chromophore has elongated rhombic octahedral stereochemistry in agreement with spectroscopic results.

**Introduction.** In the course of our studies on the synthesis of chlorobis[1-phenyl-3-(2-pyridyl)thiourea]-Cu<sup>I</sup>, obtained by the reaction of the ligand with tetrameric [Cu(PPh<sub>3</sub>)Cl]<sub>4</sub> and copper(II) nitrate (Belicchi Ferrari, Gasparri Fava, Pelizzi & Tarasconi, 1985) in toluene solution, [Cu(NO<sub>3</sub>)<sub>2</sub>(tppo)<sub>2</sub>] (tppo