Crystal structure of (5-ferrocenyl-2-hydroxybenzenecarboxylato-*O,O'*)-titanocene(IV), (C₅H₅)Fe(C₁₂H₇O₃)Ti(C₅H₅)₂

Z.-W. Gao*, G.-F. Wang, L.-X. Gao, C.-Y. Zhang, D.-H. Wu, W.-R. Yu and Z.-T. Liu

Shaanxi Normal University, Key Laboratory of Macromolecular Science of Shaanxi, Xian, Shaanxi, 710062 P. R. China

Received September 2, 2005, accepted and available on-line December 5, 2005; CCDC no. 1267/1637

Abstract

C₂₇H₂₂FeO₃Ti, monoclinic, *P*1₂/c1 (no. 14), *a* = 13.752(4) Å, *b* = 12.180(4) Å, *c* = 12.468(3) Å, β = 92.42(2)°, *V* = 2086.5 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.064, *wR*_{ref}(*F*²) = 0.158, *T* = 273 K.

Source of material

The ligand 5-ferrocenylsalicylic acid was prepared from the modified literature procedure [1–2]. For 5-ferrocenylsalicylate titanocene, a solution of Cp₂TiCl₂-acac (1.0 mmol) in 10 ml H₂O was added to 1.1 mmol 5-ferrocenylsalicylic acid in 30 ml CHCl₃. The mixture was stirred for about 1 h at RT. The organic layer was separated and washed with an aqueous saturated solution of sodium carbonate and water, respectively, dried with anhydrous magnesium sulfate and filtered. The filtrate was evaporated to dryness under vacuum. The solid product was recrystallized from a dark green dichloromethane/hexane solution. Greenish-black crystals of 5-ferrocenylsalicylate titanocene complex suitable for single-crystal X-ray diffraction were obtained over a period of between one and two days at 4 °C (decomp. 187–188 °C).

Experimental details

The *N*_{gt}/*N*_{param} ratio is low due to the small size and the low quality of the crystals.

Discussion

5-Ferrocenylsalicylate titanocene molecules have the structure in which the Ti atom is attached to one oxygen atom of hydroxyl and one oxygen atom of carboxyl of 5-ferrocenylsalicylate ligand and two cyclopentadienyl groups. Z1 and Z2 refer to the centers of the Cp rings, C18 – C22 and C23 – C27, respectively. The coordinated oxygen atoms, Z1 and Z2 define a distorted tetrahedron with Z1–Ti1–Z2 angle being 131.9(2)°, and the O3–Ti1–O2 an-

gle being 86.9(2)°, the type of crystal structure is similar to salicylate titanocene(IV) [3]. The Ti–C(Z1) and Ti–C(Z2) distances are ranging from 2.329(9) Å to 2.398(8) Å and from 2.352(7) Å to 2.418(7) Å, respectively. The Ti1–Z1 distance (2.073(5) Å) is somewhat longer than Ti1–Z2 (2.058(5) Å). The O1–C17 bond length is 1.231(9) Å. The uncoordinated oxygen atoms are far removed from the Ti atom (*d*(Ti1...O1) = 4.016 Å) and the non-bonded contacts between the oxygen atom and the cyclopentadienyl C atoms are longer than 3.3 Å.

Table 1. Data collection and handling.

Crystal:	greenish-black block, size 0.09 × 0.09 × 0.10 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	11.07 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
2θ _{max} :	50.56°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	8324, 3754
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1347
<i>N</i> (<i>param</i>) _{refined} :	289
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.5964	−0.0286	0.2372	0.075
H(2)	4e	0.7251	0.1164	0.2143	0.080
H(3)	4e	0.7706	0.1956	0.3973	0.105
H(4)	4e	0.6612	0.1024	0.5352	0.117
H(5)	4e	0.5561	−0.0415	0.4274	0.085
H(6)	4e	0.4372	0.1628	0.1837	0.060
H(7)	4e	0.3853	0.1525	0.3813	0.063
H(8)	4e	0.4900	0.2908	0.4925	0.053
H(10)	4e	0.5733	0.3084	0.1787	0.060
H(12)	4e	0.5894	0.4407	0.5285	0.066
H(13)	4e	0.7057	0.5649	0.5790	0.054
H(16)	4e	0.6979	0.4226	0.2400	0.059
H(18)	4e	0.7306	0.7446	0.2736	0.094
H(19)	4e	0.7334	0.8166	0.4644	0.111
H(20)	4e	0.8755	0.9437	0.4853	0.095
H(21)	4e	0.9612	0.9599	0.3120	0.087
H(22)	4e	0.8712	0.8278	0.1776	0.091
H(23)	4e	1.0383	0.5874	0.5702	0.090
H(24)	4e	1.1073	0.5729	0.3838	0.094
H(25)	4e	1.1292	0.7691	0.3174	0.085
H(26)	4e	1.0788	0.8975	0.4606	0.083
H(27)	4e	1.0175	0.7850	0.6139	0.085

* Correspondence author (e-mail: zwgao@snnu.edu.cn)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Fe(1)	4e	0.57835(7)	0.16435(9)	0.34417(8)	0.0441(6)	0.0447(8)	0.0455(7)	0.0035(5)	-0.0027(5)	0.0012(6)
Ti(1)	4e	0.92730(9)	0.7248(1)	0.3962(1)	0.0462(8)	0.039(1)	0.0406(8)	0.0013(7)	-0.0039(6)	-0.0010(7)
O(1)	4e	0.8395(4)	0.5134(5)	0.1647(4)	0.091(4)	0.107(6)	0.051(4)	-0.029(4)	0.013(3)	-0.031(4)
O(2)	4e	0.9209(3)	0.6117(4)	0.2849(3)	0.054(3)	0.050(4)	0.043(3)	-0.006(3)	0.008(2)	-0.008(3)
O(3)	4e	0.8506(3)	0.6279(4)	0.4803(3)	0.054(3)	0.046(4)	0.033(3)	-0.009(2)	-0.001(2)	-0.003(2)
C(1)	4e	0.6268(6)	0.0150(8)	0.2956(7)	0.060(6)	0.064(7)	0.064(7)	0.010(5)	0.002(5)	-0.012(5)
C(2)	4e	0.6965(6)	0.0960(8)	0.2822(8)	0.047(5)	0.064(7)	0.089(7)	0.000(5)	0.006(5)	0.004(6)
C(3)	4e	0.7217(6)	0.1387(8)	0.382(1)	0.057(6)	0.073(8)	0.127(9)	0.020(5)	-0.045(6)	-0.022(8)
C(4)	4e	0.6606(9)	0.089(1)	0.4577(7)	0.132(9)	0.12(1)	0.041(6)	0.077(8)	-0.012(6)	-0.007(7)
C(5)	4e	0.6042(7)	0.0082(8)	0.3980(9)	0.100(7)	0.046(7)	0.068(7)	0.013(5)	0.020(6)	0.002(6)
C(6)	4e	0.4642(5)	0.2055(6)	0.2447(6)	0.050(5)	0.049(6)	0.049(5)	-0.007(4)	-0.014(4)	0.005(4)
C(7)	4e	0.4353(5)	0.2008(6)	0.3535(7)	0.041(4)	0.042(6)	0.075(6)	-0.007(4)	0.010(4)	0.017(5)
C(8)	4e	0.4931(5)	0.2780(6)	0.4151(6)	0.045(4)	0.041(5)	0.048(5)	0.006(4)	-0.002(4)	-0.006(4)
C(9)	4e	0.5568(4)	0.3300(7)	0.3463(5)	0.039(4)	0.051(6)	0.038(4)	0.000(4)	0.002(4)	0.005(4)
C(10)	4e	0.5385(5)	0.2873(6)	0.2424(6)	0.044(4)	0.053(6)	0.052(5)	-0.009(4)	-0.013(4)	0.013(4)
C(11)	4e	0.6300(5)	0.4136(6)	0.3776(6)	0.045(5)	0.036(5)	0.042(5)	-0.001(4)	-0.005(4)	0.006(4)
C(12)	4e	0.6357(5)	0.4603(7)	0.4797(6)	0.061(5)	0.058(7)	0.046(5)	-0.004(4)	0.006(4)	0.003(5)
C(13)	4e	0.7064(5)	0.5335(6)	0.5110(5)	0.053(5)	0.058(6)	0.027(4)	-0.003(4)	0.013(4)	-0.009(4)
C(14)	4e	0.7786(5)	0.5616(6)	0.4435(6)	0.054(5)	0.026(5)	0.038(4)	0.000(4)	-0.011(4)	-0.003(4)
C(15)	4e	0.7736(5)	0.5228(6)	0.3368(6)	0.041(4)	0.031(5)	0.044(5)	0.002(4)	-0.001(4)	0.001(4)
C(16)	4e	0.7004(5)	0.4499(7)	0.3098(6)	0.067(5)	0.045(6)	0.036(4)	0.010(4)	0.000(4)	0.007(4)
C(17)	4e	0.8479(5)	0.5486(7)	0.2571(7)	0.058(5)	0.038(6)	0.063(6)	-0.001(4)	0.004(5)	0.008(5)
C(18)	4e	0.7817(7)	0.7910(8)	0.307(1)	0.052(6)	0.056(7)	0.122(9)	0.015(5)	-0.037(6)	0.008(7)
C(19)	4e	0.7836(8)	0.828(1)	0.412(1)	0.088(8)	0.08(1)	0.12(1)	0.048(7)	0.051(7)	0.022(8)
C(20)	4e	0.8610(9)	0.8984(9)	0.4216(9)	0.118(9)	0.042(7)	0.075(8)	0.022(6)	-0.016(7)	-0.007(6)
C(21)	4e	0.9093(6)	0.9080(8)	0.328(1)	0.066(6)	0.047(7)	0.104(8)	-0.011(5)	-0.006(6)	0.042(6)
C(22)	4e	0.8591(8)	0.8357(9)	0.2542(7)	0.097(8)	0.082(8)	0.048(5)	0.034(6)	0.001(6)	0.025(6)
C(23)	4e	1.0486(6)	0.649(1)	0.521(1)	0.054(6)	0.069(9)	0.099(9)	-0.007(5)	-0.039(6)	0.039(7)
C(24)	4e	1.0852(6)	0.640(1)	0.419(1)	0.046(5)	0.09(1)	0.096(8)	0.027(5)	-0.020(5)	-0.027(8)
C(25)	4e	1.0967(5)	0.748(1)	0.3827(9)	0.044(5)	0.08(1)	0.085(8)	-0.009(5)	-0.005(5)	0.032(8)
C(26)	4e	1.0692(6)	0.8177(8)	0.460(1)	0.058(6)	0.052(7)	0.095(8)	-0.007(5)	-0.028(5)	-0.006(8)
C(27)	4e	1.0355(6)	0.756(1)	0.5442(8)	0.057(6)	0.11(1)	0.047(6)	0.000(6)	-0.020(4)	-0.013(7)

Acknowledgments. We would like to thank the National Natural Science Foundation of China (grant nos. 20101005, 20473051), Natural Science Foundation of Shaanxi Province (grant nos. 2003B04, 2004B12) and the National Basic Research Program of China ('973' program, no. 2004CCA00700) for research grants.

References

- Weinmayr, V.: The Condensation of Dicyclopentadienyliron with Aromatic Diazonium Salt. *J. Am. Chem. Soc.* **77** (1955) 3012-3014.
- Santis, G. D.; Fabbri, L.; Licchelli, M.; Monichino, A.; Pallavicini, P.; Perotti, A.; Poggi, A.: 5-Ferrocenyl-salicylate: a Convenient Ligand to Build up Multi-electron Redox System. *Inorg. Chem. Acta* **188** (1991) 1-3.
- Edwards, D. A.; Mahon, M. F.; Paget, T. J.; Summerhill, N. W.: The bis(cyclopentadienyl) titanium(IV)-salicylate system revisited and the characterisation of two 3,5-di-*t*-butylsalicylate analogues. The molecular structure of [Cp₂Ti(sal)], (sal = O₂CC₆H₄O²⁻). *Transition Met. Chem.* **26** (2001) 116-119.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.10. Bruker AXS, Madison, Wisconsin, USA 1998.