

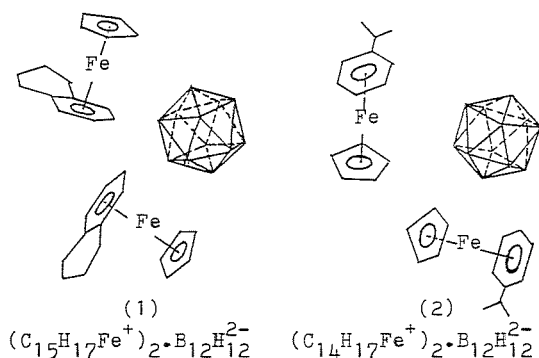
09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-8 CRYSTAL STRUCTURES OF (1) BIS(η^5 -CYCLOPENTADIENYL- η^6 -TETRAHYDRONAPHTHALENE-IRON) DODECAHYDRO-DODECABORATE AND (2) BIS(η^5 -CYCLOPENTADIENYL- η^6 -ISOPROPYLBENZENE-IRON) DODECAHYDRO-DODECABORATE. By Chen Liqing & Pan Kezhen, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, China and Zhang Lum & Hu Peizhi, Department of Chemistry, Wuhan University, Wuhan, China.

Compound 1 (see Title and Figure) Crystal data are : Orthorhombic s.g. Pbc_a, a=20.854(5), b=14.629(4), c=21.051(5) Å, Z=8. R=0.080 for 1899 reflections with $I \geq 3\sigma$. The cation ($C_{15}H_{17}Fe-C_{10}H_{12}$)⁺ has a sandwich conformation. The dihedral angle between the Cp ring and the conjugate six-member ring (Ph) in tetrahydronaphthalene is 2.6°. The anion B₁₂H₁₂²⁻ is a slightly distorted icosahedron. The more important distance and angle averages are Fe-C(Cp)=2.031, Fe-C(Ph)=2.085, C-C(Cp)=1.382, C-C(Ph)=1.416, C-C(single bond)=1.540, B-B=1.776 Å, B-B-B=60.0 (trigon) & 108.0° (pentagon). The distance between Fe and Cp ring is 1.658 Å, and that between Fe and Ph ring is 1.530 Å.

Compound 2 Crystal data are : Monoclinic s.g. C2/c, a=18.703(9), b=25.120(7), c=15.190(7) Å, $\beta=94.70(4)^\circ$, Z=8. R=0.070 for 2931 reflections with $I \geq 3\sigma$. It has a structure similar to that of Compound 1. The average bond lengths : Fe-C(Cp)=2.035, Fe-C(Ph)=2.075, C-C(Cp)=1.377, C-C(Ph)=1.394, B-B=1.777 Å. The distance from Fe to the Cp ring is 1.664 Å, and that to the Ph ring is 1.537 Å. The dihedral angle between Cp and Ph rings is 0.8°.

In both compounds, the cation and anion are of the distorted square and hexahedron coordinations, respectively.



09.3-9 CRYSTAL AND MOLECULAR STRUCTURES OF (η^5 -C₅H₅)₂Mo(SO₄) and |(η^5 -C₅H₅)₂MoI(CH₃CN)| (PF₆). By M. A.A.F. de C.T. Carrondo, A.M.T.S. Domingos* and M.T. Leal, Centro de Química Estrutural, Complexo I, I.S.T., Lisboa, Portugal. *Sector de Química, LNETI, Sacavem, Portugal.

Following our structural studies on Mo and Ti bis-cyclopentadienyl complexes (Carrondo and Domingos, J. Organomet. Chem. (1983), 253, 53) we now report the crystal structure determinations of the title compounds.

Crystal data for (η^5 -C₅H₅)₂Mo(SO₄) (I) - Mr=322.11, orthorhombic Ama₂, a=12.979(4), b=8.547(2), c=9.356(5) Å, V=1037.9 Å³, Z=4, MoK α radiation, 475 reflections with $F > 3\sigma(F)$.

Crystal data for |(η^5 -C₅H₅)₂MoI(CH₃CN)| (PF₆) (II) - Mr=538.94, triclinic P1, a=7.7989(6), b=10.3044(8), c=10.5565(5) Å, $\alpha=96.218(4)$, $\beta=94.466(4)$, $\gamma=102.697(5)^\circ$, V=818.2 Å³, Z=2, MoK α radiation, 4187 reflections with $F > 3\sigma(F)$.

The structures were solved by Patterson and difference electron density syntheses using Shelx and refined for compound (I) by full-matrix least-squares to R=0.025 and for compound (II) by blocked matrix least-squares (R=0.086, still in progress).

Molecules of (I) have the bent metallocene structure in which the Mo atom is attached to two oxygen atoms of the sulphate ligand and two η^5 -C₅H₅ groups in a distorted tetrahedron coordination. The Mo atom is at an average distance of 1.967(7) Å from the Cp rings and the angle between the ring normals is 134.8(4)°. The Mo-O(1) and Mo-O(2) bond lengths are respectively 2.057(9) and 2.162(8) Å and the O(1)-Mo-O(2) bond angle is 65.9(2)°. For the related compound [(C₅H₅)₂MoO₂PO₂Mo(C₅H₅)₂] (PF₆)₂ (Prout, Couldwell and Forder, Acta Cryst. (1977), B 33, 218) a mean Mo-O bond length of 2.126(3) Å and O-Mo-O bond angle of 67.8(1)° have been reported.

The structure of compound (II) consists of two discrete organometallic cations and two hexafluorophosphate anions per unit cell. The Mo atom coordinates two η^5 -C₅H₅ groups, one iodide and the nitrogen atom of one acetonitrile ligand. In each molecule the coordination geometry about the Mo atom is a distorted tetrahedron. At the present stage of refinement the Mo-I and Mo-N bond lengths and the N-Mo-I bond angle are respectively 2.840(4) Å, 2.172(23) Å and 80.8(6)° for one molecule and 2.822(4) Å, 2.096(21) Å and 81.4(5)° for the second.

Details of the molecular geometry will be given and comparison to similar compounds presented.