

STRUCTURE OF A TRINUCLEAR μ_3 -VINYLIDENE CLUSTER $\text{CpMnFePt}(\mu_3\text{-C=CHPh})(\text{PPh}_3)(\text{CO})_6$

O. S. Chudin¹, V. V. Verpekin¹, A. D. Vasiliev^{2,3,4},
and A. I. Rubaylo^{1,3,4}

UDC 548.73

The single crystal X-ray diffraction study of the heterometallic cluster $\text{CpMnFePt}(\mu_3\text{-C=CHPh})(\text{PPh}_3)(\text{CO})_6$ is performed. The crystallographic characteristics are as follows: $a = 32.356(15)$ Å, $b = 11.754(5)$ Å, $c = 20.114(9)$ Å, $\beta = 115.707(6)^\circ$, $V = 6893(5)$ Å³, space group $C2/c$, $Z = 8$, $d_{\text{calc}} = 1.741$ g/cm³. The cluster molecule contains a bridging phenylvinylidene ligand coordinated to a metallic core in the form of a Mn–Fe–Pt chain (the Mn–Fe and Fe–Pt bond lengths are 2.6768(14) Å and 2.6280(11) Å respectively and the Mn···Pt distance is 3.6425(19) Å).

DOI: 10.1134/S0022476617030234

Keywords: manganese, iron, platinum, vinylidene complexes, heterometallic clusters, single crystal X-ray diffraction analysis.

Heterometallic cluster compounds are of both scientific and practical interest for a wide range of researchers [1-5]. Previously, a series of trinuclear vinylidene clusters of the $\text{CpMnFePt}(\mu_3\text{-C=CHPh})(\text{LL}')(\text{CO})_5$ ($\text{L} = \text{PPh}_3$ (**1**), $\eta^1\text{-Ph}_2\text{PCH}_2\text{P(=O)Ph}_2$ (**2**), P(OEt)_3 , $\text{P(OPr}^i)_3$, $\text{L}' = \text{CO}$; $\text{L} = \text{L}' = \text{P(OEt)}_3$, $\text{P(OPr}^i)_3$) type have been studied [6], but complex **2** was the only structurally characterized example [7]. Later, we synthesized a series of analogous complexes containing rhenium and determined the structures of $\text{CpReFePt}(\mu_3\text{-C=CHPh})(\text{LL}')(\text{CO})_5$ ($\text{L} = \text{PPh}_3$, $\text{L}' = \text{CO}$ (**3**) [8]; $\text{L} = \text{L}' = \text{P(OPr}^i)_3$ (**4**) [9]). Hence, to find out how the nature of the metal atom and its ligand environment affect the structural characteristics of clusters containing the μ_3 -vinylidene ligand coordinated to a trimetallic core MFePt ($\text{M} = \text{Re, Mn}$), the structure of $\text{CpMnFePt}(\mu_3\text{-C=CHPh})(\text{PPh}_3)(\text{CO})_6$ (**1**) cluster was studied by single crystal X-ray diffraction (XRD). Complex **1** was synthesized according to the procedure reported in [6].

Single crystal XRD study. The single crystal was examined on an automated SMART APEX II diffractometer (Bruker AXS) at the Krasnoyarsk Regional Center for Collective Use, the Siberian Branch of the RAS, equipped with a two-dimensional CCD detector. Absorption was taken into account by a multi-scan technique using the SADABS program [10]. The structure was solved by direct methods (the SHELXT software [11]) and refined by the full-matrix LSM technique in the anisotropic approximation using the SHELXL software [12]. The elongated thermal ellipsoids of carbon atoms of the $\eta^5\text{-C}_5\text{H}_5$ moiety indicate that this ring is disordered by rotation in its plane. Hence, the ring atoms were set in two positions and refined with the condition of equivalence of C–C and Mn–C distances. The positions of hydrogen atoms at carbon atoms

¹Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia; oschudin@mail.ru. ²Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia. ³Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia. ⁴Siberian Federal University, Krasnoyarsk, Russia. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 58, No. 3, pp. 628-630, March-April, 2017. Original article submitted April 4, 2016; revised May 11, 2016.

were calculated geometrically and refined in the rigid body approximation (the riding model); the others were located from the difference electron density maps and refined in the isotropic approximation. The crystallographic data and the details of the single crystal XRD experiment are as follows: $C_{37}H_{26}FeO_6PPtMn$, $M = 903.43$ g/mol, experimental temperature 296 K, monoclinic crystal symmetry, space group $C2/c$; the unit cell parameters: $a = 32.356(15)$ Å, $b = 11.754(5)$ Å, $c = 20.114(9)$ Å, $\beta = 115.707(6)^\circ$, $V = 6892(5)$ Å³, $Z = 8$; $d_{\text{calc}} = 1.741$ g/cm³, $\mu = 4.916$ mm⁻¹, $F(000) = 3520$, crystal size $0.43 \times 0.25 \times 0.21$ mm, MoK_α radiation ($\lambda = 0.71073$), 2θ range $4.036 \div 49.43^\circ$, $-37 \leq h \leq 37$; $-13 \leq k \leq 13$; $-23 \leq l \leq 23$, 23900 reflections, 5840 independent reflections [$R_{\text{int}} = 0.0574$, $R_{\text{sigma}} = 0.0501$], number of restrictions/parameters 90/382, $GOOF$ 1.011, $R1$ [$I \geq 2\sigma(I)$] 0.0319, $R1/wR2$ for all reflections 0.0534/0.0678, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, $e/\text{Å}^3 = 0.61/-0.50$.

The CIF file containing full information on the studied structure has been deposited with the Cambridge Crystallography Data Center (CCDC) under number 1457209 and is available free on request via the following website: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The central fragment of the molecule of cluster **1** is a metallic core in the form of a chain formed by three metal atoms Mn–Fe–Pt (Fig. 1a) and the phenylvinylidene ligand coordinated with it. The Mn–Fe, Fe–Pt bond lengths and the MnFePt, PtMnFe, FePtMn angles are 2.6768(14) Å, 2.6280(11) Å and $86.72(5)^\circ$, $46.08(5)^\circ$, $47.20(3)^\circ$ respectively. As noted above, the η^5 -C₅H₅ ligand is disordered over two equally occupied sites (Fig. 1b). The minimum distances from the hydrogen atoms of the η^5 -C₅H₅ ring to the nearest atoms consist of H–O contacts; only four of them are less than 2.7 Å (2.42 Å to 2.55 Å). Given the van der Waals radii of hydrogen (1.2 Å) and oxygen (1.5 Å) atoms, the η^5 -C₅H₅ ring may be thought to be free for rotation in its plane. As a result, the molecule of **1** in the crystal is a static superposition of two rotational isomers. The non-bonding Mn···Pt distance is 3.6425(19) Å, which exceeds the sum of the covalent radii of the Mn and Pt atoms by 0.5 Å [13].

In previously studied CpReFePt(μ_3 -C=CHPh)(PPh₃)(CO)₆ (**3**) cluster, with the same set of ligands as in the molecule of **1**, and in CpReFePt(μ_3 -C=CHPh)(PPh₃)[P(OPr^t)₃]₂(CO)₅ (**4**) cluster, the μ_3 -C=CHPh ligand forms two σ bonds with the Re and Pt atoms located on the chain end and an asymmetrical π bond with the central iron atom. Unlike complexes **3** and **4**, the μ_3 -C=CHPh ligand of cluster **1** forms σ bonds with the neighboring Mn and Fe atoms and is almost symmetrically η^2 bonded to the Pt atom located on the chain end. A similar symmetrical η^2 bonding of vinylidene with a metal atom on the chain end has been previously found for CpMnFePt(μ_3 -C=CHPh)(CO)₆[η^1 -Ph₂PCH₂P(=O)Ph₂] (**2**) cluster. The difference Δd between the Pt–C1 and Pt–C2 bond lengths in the molecule of **1** is 0.03 Å, 0 Å, and 0.05 Å for two independent molecules of complex **2** [7], while the Δd values in rhenium clusters **3** and **4** are 0.23 Å and 0.26 Å respectively. The Mn–C1, Fe–C1, and

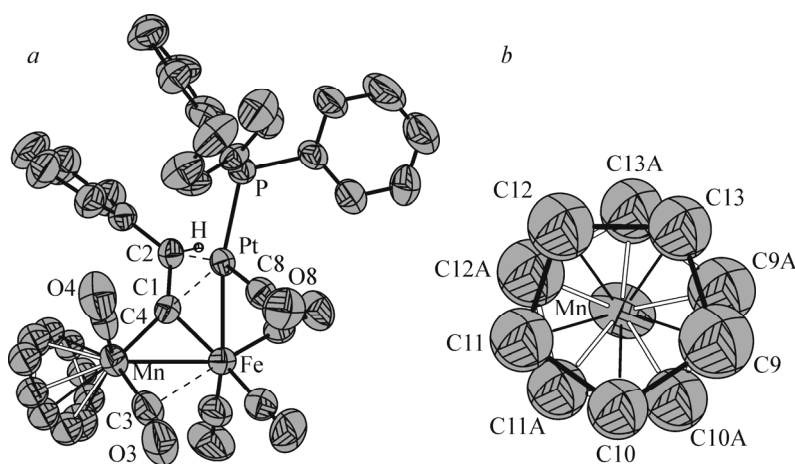


Fig. 1. Molecular structure of CpMnFePt(μ_3 -C=CHPh)(PPh₃)(CO)₆ (**1**) cluster (a) (hydrogen atoms, except the vinylidene ligand proton, are omitted); the projection of the [CpMn] moiety on the η^5 -C₅H₅ ring plane (b).

C1=C2 bond lengths in complex **1** are 1.939(8) Å, 1.863(5) Å, and 1.427(7) Å respectively. The C1=C2 bond length is comparable with those of the C=C bond in the known μ_3 -vinylidene complexes [14, 15]. The C3O3 group, due to the interaction with the neighboring Fe atom, is half-bridging, $\angle\text{Mn-C3-O3} = 165.9(6)^\circ$.

Therefore, in this work we determined the structure of $\text{CpMnFePt}(\mu_3\text{-C=CHPh})(\text{PPh}_3)(\text{CO})_6$ (**1**) cluster. It is shown that the geometry of the molecule of cluster **1** is similar to that of compound **2**, but differs from rhenium-containing clusters **3** and **4** in the nature of coordination of the vinylidene ligand to the metal core.

The work was supported by the Russian Academy of Sciences (the Integrated Program of Fundamental Research of the Siberian Branch of the Russian Academy of Sciences No. II.2 "INTEGRATION AND DEVELOPMENT").

REFERENCES

1. V. Ritleng and M. J. Chetcuti, *Chem. Rev.*, **107**, No. 3, 797 (2007).
2. R. D. Adams and B. Captain, *Angew. Chem. Int. Ed. Engl.*, **47**, No. 2, 252 (2008).
3. J. Xiao and R. J. Puddephatt, *Coord. Chem. Rev.*, **143**, 457 (1995).
4. S. Sculfort and P. Braunstein, *Chem. Soc. Rev.*, **40**, No. 5, 2741 (2011).
5. M. J. McGlinchey, et. al., *Coord. Chem. Rev.*, **143**, 331 (1995).
6. A. B. Antonova, et. al., *Inorg. Chim. Acta*, **230**, Nos. 1/2, 97 (1995).
7. A. B. Antonova, et. al., *J. Organomet. Chem.*, **577**, No. 2, 238 (1999).
8. A. B. Antonova, et. al., *J. Organomet. Chem.*, **694**, No. 1, 127 (2009).
9. V. V. Verpekin, O. S. Chudin, D. A. Piryazev, A. I. Rubaylo, S. A. Gromilov, O. V. Semeikin, *J. Struct. Chem.*, **56**, No. 4, 774-776 (2015).
10. G. M. Sheldrick, *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Goettingen, Germany (1997).
11. G. M. Sheldrick, *Acta Crystallogr.*, **A71**, 3 (2015).
12. G. M. Sheldrick, *Acta Crystallogr.*, **C71**, 3 (2015).
13. B. Cordero, et al., *Dalton trans.*, 2832 (2008).
14. M. I. Bruce, *Chem. Rev.*, **91**, No. 2, 197 (1991).
15. A. B. Antonova, *Coord. Chem. Rev.*, **251**, Nos. 11/12, 1521 (2007).