

07-Crystallography of Organometallic and Coordination Compounds

structure in dependence on the metal's nature and on the location of substituents in the quinoline ring. The buildup of structures of bis(2-methyl-5-methylthio-8-oxyquinolinates) of palladium (I), platinum (II) and oxovanadium (III) is examined. The monocrystals of the compounds are studied on the automatic diffractometer. The parameters of triclinic cells are the following:

I- $a=6.945(2)$, $b=10.893(3)$, $c=13.840(4)$ Å, $\alpha=85.37(2)$, $\beta=81.07(2)$, $\gamma=79.10(2)^\circ$, space gr. $P\bar{1}$, $Z=2$; II- $a=6.932(2)$, $b=10.908(3)$, $c=13.859(4)$ Å, $\alpha=85.63(3)$, $\beta=80.50(3)$, $\gamma=79.29(3)^\circ$, space gr. $P\bar{1}$, $Z=2$; III- $a=4.88(2)$, $b=15.694(4)$, $c=13.408(3)$ Å, $\alpha=82.98(2)$, $\beta=82.97(2)$, $\gamma=93.51(2)^\circ$, space gr. $P\bar{1}$, $Z=4$. In all three compounds there are two crystallographically independent molecules.

The compounds I and II are isostructural, coordination polyhedron of the Pd and Pt atom in both independent molecules is a centrosymmetrical trans-square ($2O+2N$). The distances Pd-O are 1.978(5) and 1.992(6) Å, Pd-N are 2.03(1) and 2.045(9) Å. The intermolecular interactions Pd(1)...Pd(2) 3.472 Å, Pt(1)...Pt(2) 3.446 Å unite the molecules of complexes I and II in dimers.

The coordination polyhedron of the oxovanadium atom in both molecules is a distorted trigonal bipyramid ($2N+2O+O_{oxo}$) with axial location of nitrogen atoms (angle N(1)-V-N(2) 157.9(3) and 158.7(3)°, resp., V-N aver. 2.10 and 2.12 Å). The surrounding chelate atoms ($2O+2N$) of the oxovanadium atom have a form of swings (angle O(1)-V-O(2) 127.9(3) and 127.5(3)° correspond.), which to the trigonally-bipyramidal one is supplemented by O_{oxo} at the distance V-O(3) 1.576(6) and 1.592(6) Å. The distances V-O are 1.950 and 1.935 Å. The chelate angles are 80.3(2) and 79.9(3)° in V(1) and 80.4(3) and 80.4(3)° in V(2). Metallo-cycles are non-planar. Twisting along the line O...N is 17.0 and 10.8° in V(1) and 10.8 and 12.8° in V(2).

The intermolecular distances: V(1)...O(3) 3.307, O(3)...O(1) 3.017, O(3)...O(2) 3.017, V(2)...O(3) 3.306, O(3)...O(1) 2.933, O(3)...O(2) 3.090 and S(1)A...S(2)B 3.620 Å. Complexes I and II as compared to the previously studied Pd and Pt complexes with 8-mercaptoquinolate and its derivatives.

As a result of comparative study of the complexes it has been established that the transition from 8-mercaptoquinolates to 8-oxyquinolates, judging by the existing structural data, causes substantial stereochemical changes.

PS-07.04.31 THE CRYSTAL AND MOLECULAR STRUCTURE OF [1,2-DIMETHYL-1,2-(DI-ISOBUTYL)ETHYL]BIS CYCLOPENTADIENYL ZIRCONIUM DICHLORIDE. By Shou-shan Chen, Xin-kan Yao and Hung-gen Wang, Institute of Elemento-organic Chemistry, Central Laboratory, Nankai University, Tianjin 300071, China.

The title compound, $C_{22}H_{32}Cl_2Zr$, is a new chiral bridged bis cyclopentadienylmetal complex. The sample was re-crystallized from a mixed solvent of dichloromethane and petroleum ether as colorless crystals. Intensities were collected on a CAD4 diffractometer, ω - 2θ scan mode, Mok_α in

the range of 2° to 25° . 2043 independent reflections were measured, of which 1721 were observed with $I > 3\sigma(I)$. The intensities were corrected for Lp factors and absorption.

The crystal is monoclinic, space group $C2/c$, with $a=13.330(3)$, $b=9.585(1)$, $c=16.492(3)$ Å, $\beta=94.76(2)^\circ$, $v=2099.8$ Å³, $M_r=458.63$, $Z=4$, $D_x=1.45$ g/cm³, $\mu=7.74$ cm⁻¹, $F(000)=952$.

The structure was solved by direct method (MALTAN-82) and difference Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H atoms led to R of 0.037 and R_w of 0.044.

The view of the molecule is shown in Figure 1. Its molecular structure possesses C_2 symmetry which belongs to the type of equivalent homotopic faces of cyclopentadienyl ligands. The dihedral angle between the two cyclopentadienyl planes is 57.33° .

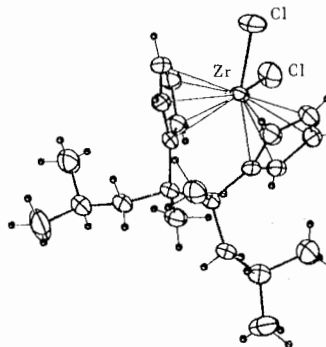


Fig. 1

PS-07.04.32 CRYSTAL STRUCTURE PECULIARITIES OF VOLATILE COMPLEXES USED AS PRECURSORS FOR CHEMICAL VAPOR DEPOSITION OF THIN-FILM SUPERCONDUCTORS. By T. M. Polyanskaya, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.

The crystal structures of the three types of volatile complexes used as molecular precursors for chemical vapor deposition of thin-film superconductors were discussed:

- I) Complexes of Cu(II), Ba, Ca, Sr and Y with β -diketons as ligands. The ligand substituents are as follows: CH_3 , CF_3 , $C(CH_3)_3$, $CF_2CF_2CF_3$.
- II) Alkaline-Earth-Metal β -diketonate complexes with the linear polyethers (di-, tri-, tetra-, hexaglyme).
- III) β -diketonate complexes with the macrocyclic polyethers, 18-crown-6 and 15-crown-5.

The only homoligand complexes of Cu and one of two forms of Y(dipivaloylmethanate)₃ are mononuclear ones among complexes of the type I, specified by donor-acceptor interaction of