

## 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+Ooxo) 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 Ooxo 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,  $\omega$ - $2\theta$  scan mode,  $Mok_\alpha$  in

the range of  $2^\circ$  to  $25^\circ$ . 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,  $\beta=94.76(2)^\circ$ ,  $v=2099.8$  Å<sup>3</sup>,  $M_r=458.63$ ,  $Z=4$ ,  $D_x=1.45$  g/cm<sup>3</sup>,  $\mu=7.74$  cm<sup>-1</sup>,  $F(000)=952$ .

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  $57.33^\circ$ .

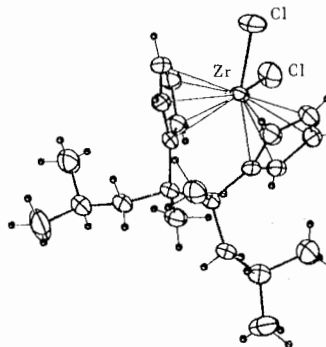


Fig. 1

**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  $\beta$ -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  $\beta$ -diketonate complexes with the linear polyethers (di-, tri-, tetra-, hexaglyme).
- III)  $\beta$ -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)<sub>3</sub> are mononuclear ones among complexes of the type I, specified by donor-acceptor interaction of

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Cu(2+) with the carbon atoms of neighbouring molecules. In Cu(acetylacetonate)<sub>2</sub>, for instance, they are arranged in such a way that to form the chains along the shortest unit cell edge. Mixed-ligand complexes of Cu(II) are pseudodimeric and the second form of Y(dipivaloylmethanate)<sub>3</sub> is the dimeric one.

$\beta$ -Diketonate complexes of alkaline-earth-metals are oligomeric ones. Oligomerization extent depends on synthesis conditions. Complexes of the type II and III are "the guest-host complexes". The influence of the additional neutral ligands on oligomerization extent of complexes in condensed phase has been considered by those examples. The Cu complexes with crown ethers are chain polymers. Maxidentant binding of the donor atoms of the additional ligands by the metal atoms has been shown to result in monomeric complexes with high coordination numbers of metal atoms and normal Van-der-Waals interactions between the complexes. Conformation and symmetry changing of the additional ligands in complex formation of this type were considered.

The coordination polyhedra of metal atoms in volatile complexes and in the high-T<sub>c</sub> superconducting oxides were compared. It was revealed a lack of direct analogies between them in many cases.

Topological features of the central metal atoms arrangement in the complexes were treated. They have been shown to be represented by unclose-packed nets, having, for example, Schläfli symbols, 4<sup>4</sup>, 6<sup>3</sup>, and the shortest distances between metal atoms arranged in the nodes of the nets.

A correlation between structures of the complexes and their volatility and thermostability has been discussed.

Introduction of additional ligands into guest-host complexes of type II and III has been shown to improve useful qualities of compounds.

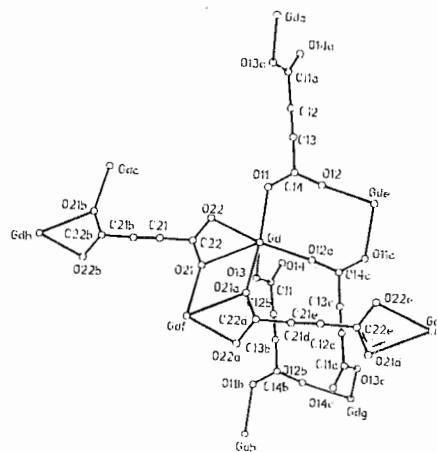


Fig.1. Molecular structure of Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O.

a single chain, which intersects the double chain above at each Gd atom, presenting a two dimension network structure. The Gd ion is 9-coordinate, bonded to six oxygen atoms from five carboxylic groups and to the three oxygen atoms of water molecules. There are two free water molecules in the unit cell. The Gd-O bond lengths range from 2.34 to 2.64 Å, one distance, namely, the Gd-O(21) of 2.64 Å, being significantly longer than the mean Gd-O bond length, 2.46 Å, the O(21) atom is the upper vertex of the tetragonal pyramid. The Gd-O(bridging bidentate) averaged distance of 2.35 Å is the shortest, but the Gd-O(chelating bidentate in bridging tridentate) averaged one of 2.50 Å is the longest in the three coordination forms. The rest Gd-O(water, unidentate, bridging part in tridentate) range from 2.42 to 2.49 Å with the mean bond length of 2.45 Å. The bond lengths and angles of the ADA in this paper are about the same as those of the literature(Allen and Don, 1973).

## References

Allen, C.L., and Don, T.C.(1973). Acta Cryst. B29, 1579-1583.

**PS-07.04.33** STRUCTURE OF GADOLINIUM COMPLEX WITH ACETYLENE DICARBOXYLIC ACID (ADA). By Yan Xing, Zhong-Sheng Jin, Zhi-Band Duan and Jia-Zuan Ni, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, People's Republic of China

Abstract Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O, Mr=794.8, triclinic, P $\bar{1}$ , a=8.254(2), b=8.605(2), c=9.066(2) Å,  $\alpha$ =95.38(2),  $\beta$ =115.82(2),  $\gamma$ =110.39(2)°, V=519.8(2) Å<sup>3</sup>, Z=1, D<sub>x</sub>=2.54 g cm<sup>-3</sup>,  $\lambda$ (Mo)K $\alpha$ =0.71069 Å, R=0.035 for 2694 observed reflections.

There are one and half ligands in an asymmetric unit. The molecular formula is Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O. The molecular structure is shown in Fig.1. The ligands are coordinated in three different forms in the molecule, firstly, only one of the two carboxylic oxygen atoms is bonded to a metal ion, and the other one is free, secondly, two carboxylic oxygen atoms are coordinated to two different metal ions, forming a carboxyl bridge, presenting a double chain structure, thirdly, two carboxyl oxygen atoms are bridging tridentate, bonded two Gd atoms, forming a four membered ring. Such the carboxylic groups form

**PS-07.04.34** THE STRUCTURE OF AQUOTETRAACETANILIDE OF EDTA COBALT (II) PERCHLORATE. By J.L. Briansó\*<sup>1</sup>, J.F. Piniella<sup>1</sup>, A. Alvarez-Larena<sup>1</sup>, A. Namor<sup>2</sup>, and J. Cárdenas<sup>2</sup>.

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In the context of a study on the use of Tetraacetanilide of EDTA for the recovery and purification of metals, we present here the X-ray crystal structure determination of the title compound.

The crystallographic results show a coordination seven around the cobalt, one water molecule being coordinated with the metal.