

COMPARISON OF GEOMETRIC PARAMETERS OF CATIONS IN COBALT (III) AND RHIDIUM (III) COMPOUNDS

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INTRODUCTION

It is known that many substances can form conformers, which with the same structural formula have different spatial structure (conformation). Under the conformation we understand the geometric shapes of molecules, passing into each other without changing the valence angles and bond lengths, for example, by rotation about single bonds [1]. The phenomenon of conformation is used in stereochemistry as one of the methods for studying the spatial structure of molecules of organic and inorganic substances, in particular complex and chelate compounds. The spatial structure of substances has a great influence on the physical and chemical properties (direction and speed of reaction and others).

In the work [2] is given the systematics of structural data of heteromolecular compounds built from heterogeneous molecules of polyatomic ions.

The main issues solved by the authors are: development of the principles of systematics of heteromolecular crystals, study of general laws of the structure of this class of compounds on the basis of statistical processing of data in the literature, study of peculiarity of particles packing into heteromolecular crystals of coordination compounds, study of contact conformation in crystals of coordination compounds, quantitative comparison of geometry of symmetrically independent complex molecules, as well as the impact of supersymmetry in heteromolecular crystals of coordination compounds.

In this paper we set out to explore the study of crystal structures in terms of determining the conformational differences, the quantitative comparison of the geometry of complex cations, transition metals of rhodium (III) and cobalt (III) with *TCS*, and rhodium (III) and cobalt (III) dioximins with two symmetric ligands of chalcogencarbamide (*Thio*, *Seu*) on the axial coordinate *Lig - M - Lig* [3].

1. TYPES OF CONFIRMATIONAL DIFFERENCES

The basis of the proposed systematics is the empirical approach of fixation, adequately studied and typical cases of conformation. For coordination compounds are distinguished the following types of specific differences affecting the first or second coordination sphere of transition metal:

1. Differences in the conformation of metallocycles.
2. Differences in the method of articulation of metallocycles.
3. Differences in rotations around single metal-ligand bonds.
4. Differences in the relative position of the ligands in equal (or close) coordination polyhedrons.
5. Differences in the chirality of mirror-equal metallocycles.

2. DIFFERENCES IN THE CONFORMATION OF METALLO-CYCLES

Uncoordinated thiosemicarbazide has a flat structure and exists in two stereoisomeric forms in *cis*- and *trans*-configurations depending on the rotation of hydrazine group *NH₂* around the *C-NH*-bond. Free *TSC* in crystalline state has a *trans*-configuration. Likewise, it also behaves in connection with silver, where *TSC* is a monodentate ligand. In other crystal structures, examined by us in the literature review and in this paper, *TSC* has the *cis*-conformation, being a bidentate ligand. In these compounds, as already noted, it forms stable five-membered chelate metallocycles *MTSC* - *RhSCN(1)N(2)*, coordinating with the metal through the sulphur and nitrogen atoms of the hydrazine group [3].

The question of the spatial structure of cycles is considered in detail in the paper [1]. There is also stated that any molecule, including cyclic, tends to take such a spatial form, in which the sum of all the "stresses" (Bayer - valences deviation from their

normal position unfavourably creates an increase in the energy storage of molecules; Pitzer - forced deviation from the most favourable odd conformation; tension caused by the mutual repulsion of converged atoms at the expense of Van der Waals forces; bond stress – (change of normal interatomic distances) and internal energy are minimal. Author [1] indicates that the cycles, starting with a four-membered one, have non-planar structure, thereby reducing the Pitzer stress. Each cycle is characterized by a geometric figure. For the five-membered ring the stable form is the envelope, for a six-membered – bath or chair.

According to data on X-ray structural analysis of crystal structures studied by us I - XI complex cations have octahedral structure. Analysis of plane equations passed by MLS through

metallocycles of coordination polyhedra I-VI shows that metalocycles have the shape of an envelope, their shape and spatial orientation being diverse. In the crystal structure $[(TSC)_3]Cl_3$ conformational envelopes of metalocycles of molecules *MTSC-I* and *MTSC-III* have an open triangular portion oriented upwards, in *MTSC-II* – downwards. A similar structure and opposite orientation of metalocycles is observed in the complex cation of crystal structure $[(TSC)_3]Cl_3 \cdot 3H_2O$ *Rh*, where *MTSC-III* is oriented with the triangular portion of the envelope downwards, and *MTSC-II* and *MTSC-I* – upwards. The equations of planes, passed OLS through the metalocycle atoms, and the relative deviations from them of these atoms are given in Table 1.

Table 1. Crystallographic characteristics of the investigated compounds.

№ of structure	Compound	A α	B β	C γ	Z	R	N
I	$[Rh(TCS)_3]Cl_3$	15,396(2) 90	9,193(3) 90	11,496(1) 80,0(1)	4	0,065	3664
II	$[Rh(TCS)_3]Cl_3 \cdot 3H_2O$	10,135(2) 90	9,726(4) 90	19,960(1) 108,10(2)	4	0,060	4043
III	$[Co(TCS)_3]Cl_3 \cdot 3H_2O$	10,043(2)	9,715(1)	20,013(4) 108,0(3)	4	0,150	660
IV	$[Co(TCS)_3]Cl_3 \cdot 3H_2O$ (violet modification)	14,801(5) 90	10,115(3) 90	12,662(4) 97,07(3)	4	0,030	1660
V	$[Rh(TCS)_3]Cl_3 \cdot 3H_2O$ (green modification)	13,507(4) 90	9,901(2) 90	16,131(2) 103,96(4)	4	0,071	1077
VI	$[Rh(TCS)_2Cl_2]Cl \cdot H_2O$	12,458(4) 94,75(3)	13,792(2) 107,21(4)	8,098(6) 96,82(2)	4	0,072	1200
VII	$[Co(DH)_2(Thio)_2]NO_3 \cdot H_2O$	7,905(1) 90	11,480(3) 90	23,141(6) 98,34(4)	4	0,048	2309
VIII	$[Co(DH)_2(Seu)_2]NO_3 \cdot H_2O$	7,978(2) 63,83(2)	11,558(3) 75,45(2)	12,935(4) 82,37(2)	2	0,088	3584
IX	$[Co(MH)_2(Thio)_2]$ $NO_3 \cdot H_2O$	17,703(3) 90	8,873(12) 90	12,477(7) 98,401(6)	4	0,051	1004
X	$[Rh(MH)_2(Thio)_2]$ $NO_3 \cdot H_2O$	17,820(2) 90	8,964(2) 90	12,572(3) 98,03(2)	4	0,031	1606
XI	$[Co(DH)_2(Thio)_2]NO_3$	19,624(4) 90	8,934(3) 90	12,338(2) 91,06(5)	4	0,056	1941

Table 1 shows the parameters of metallocycles, α -angle between the planes of the three- and four-membered parts of the envelope (folding angle) for each metallocycle. In complex cations of both modifications $[Co(TSC)_3]Cl_3 \cdot 3H_2O$ and V structures the spatial orientation of the two metallocycles is opposite [3]. The third metallocycle *MTSC-III* in structure IV and *MTSC-I* in V have practically a planar structure with the folding angle close to 180° . Consequently, thiosemicarbazide, as already noted, forms with the transition rhodium (III) and cobalt (III) metals stable metallocycles having the most favourable to it conformation of half-open or open envelope. In such cyclic compounds two main types of spatial isomerism – geometrical and optical may occur simultaneously. Chemical and physicochemical differences of the compounds appear to be explained by a conformational difference between them.

3. DIFFERENCES IN THE METHOD OF METALLO-CYCLES

Conformation of this type can be realized in fairly complex aggregates with polydentate ligands. Differences in rotations about single metal-ligand bonds in the examined structures are observed in cobalt (III) and rhodium (III) dioximins.

4. DIFFERENCES IN THE RELATIVE POSITION OF THE LI-GANDS

Trithiosemicarbazide compounds of cobalt (III) and rhodium (III) exist as two geometrically isomeric forms, differing in chemical and physicochemical properties, as well as the in geometric structure. Indeed, the X-ray analysis of these compounds I-VI shows a different location of *TSC* ligands in coordination octahedra. The spatial orientation of *TSC* ligands in structures I-IV is characteristic for the coordination octahedron of the cis-isomer, in structure V – for trans-isomer. *TSC* ligands in two independent complex cations of structure V occupy a cis-position [3].

Dioximins of trivalent cobalt and rhodium with the chalcogencarbamide also form coordination octahedra at the expense of four nitrogen atoms, dioximin molecules and two sulfur atoms. Dioximin molecules, in particular (*DH*) and (*MN*), are located in a plane and form conditionally the so-called equatorial segment. The remaining

two chalcogencarbamide ligands (*Thio* and *Seu*) occupy transpositions with respect to the equatorial moiety. Thus, the metal atom is located almost in the center of a distorted octahedron formed by six atoms: four *N* trans-ligands of dioximins and two S (Se) - chalcogencarbamide. By the mutual arrangement of ligands in the literature exist and are described the cis-dioximins and trans-dioximins of trivalent transition metals. The structure of investigated cobalt (III) and rhodium (III) dioximins of structures VII-IX is appropriate to refer to trans-dioximins.

5. DIFFERENCES IN THE GEOMETRY OF COORDINATION POLYHEDRAL

Comparing the same type of bond lengths and valence angles in the structures of rhodium (III) and cobalt (III) with sulphur- and selenium-containing ligands, we have not found significant geometric changes in the shape of octahedral polyhedra. Complex cations, formed by nitrogen and sulphur (selenium) atoms of *TSC Thio*, *DH* and *MH* ligands in the investigated crystal structures, are slightly distorted octahedra due to unequal radii of the atoms entering into the coordination of the metal and other factors associated with the change of bond lengths and valence angles.

Thus, in this paper are collected, compiled and analyzed data on the structure of transition metal coordination compounds with chalcogene-containing ligands: thiosemicarbazide and chalcogencarbamides.

CONCLUSIONS

1. The structure of coordination compounds of cobalt (III) and rhodium (III) with thiosemicarbazide is determined by the method of X-ray structural analysis. On the basis of structural material analysis is shown:

a) The octahedral coordination of *Co* and *Rh* with ligand joining by the chelate *S*, *N*-type is realized in compounds I-VI. Upon coordination there occurs a substantial delocalization of the electronic density in metallocycles.

b) The reason for the difference in the complex of physico-chemical properties consists in the isomerism thereof: in compounds I-IV is realized the face shape of the octahedron, in V – the edge one.

c) It is shown that the properties of one geometric isomer of $[M(TSC)_3]$ -type complex (II, III and IV) strongly depend on the nature of molecule packing in the crystal.

d) In the bis-ligand complex of V is revealed the presence of supersymmetry elements in the crystal.

2. The structure of cobalt and rhodium compounds with dioximins containing as axial ligand chalcogencarbamide molecules is determined. On the basis of information structural analysis is shown:

a) The octahedral coordination of the metal with the transposition of sulfur-containing ligand with respect to the equatorial moiety (EM) is realized in structures VII - XI.

b) For the first time is proven the fact of non-valence interaction of chalcogencarbamide with the metalocycle (EM), which leads to the effect of ligand-induced proton shift in the latter. After the example of compounds VI and VIII a new type of isomerism in cobalt (III) dioximins is revealed.

c) The isostructural properties of the complexes of different composition IX - XI are shown, which is determined by the major contribution of intermolecular hydrogen bonds in the formation of the crystal structure.

3. On the basis of crystal-structural analysis of compounds I - XI their conformational and geometric differences are revealed.

Bibliography

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