COMPLEXES OF 2-ACETYL-1,3-INDANDIONES

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Abstract: *2- acetyl-1,3-indanedione and its derivatives, are group of compounds with wide applications. It is proven that, when 2AIDs are included in complex compounds, their biological activity is increased. There is data about obtained complex compounds with metals of secondary groups of the periodic table like* Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+} *and* Fe^{3+} *. There are obtained and chelate complexes with elements of the lanthanide group* (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} *and* Gd^{3+}*). There is data for mixed-ligand complexes of 2-acetyl-1,3-indanedione and its derivatives.*

Keywords: *2-acetyl-1,3-indandiones, complexes, metal, ligand.*

INTRODUCTION

The term "complex compounds", in the broad sense of the word, encompasses a large number of compounds, such as molecular complexes, in which can be formed center, around which the complex forms. These compounds have a center (this may be a metal cation or oxo cation of the UO_2^{2+} type) around which they coordinate ligands (these may be particles of inorganic, organic or elemental organic nature). In chemistry, the two concepts are often mixed. 2-acetyl-1,3-indanedione (2-AID) and its derivatives are a broad application group. It has been shown that their biological activity also increases when they are incorporated into co-ordinating compounds. In general, the structure of 2-acetyl-1,3-indanedione and its derivatives is shown in Fig. 1.

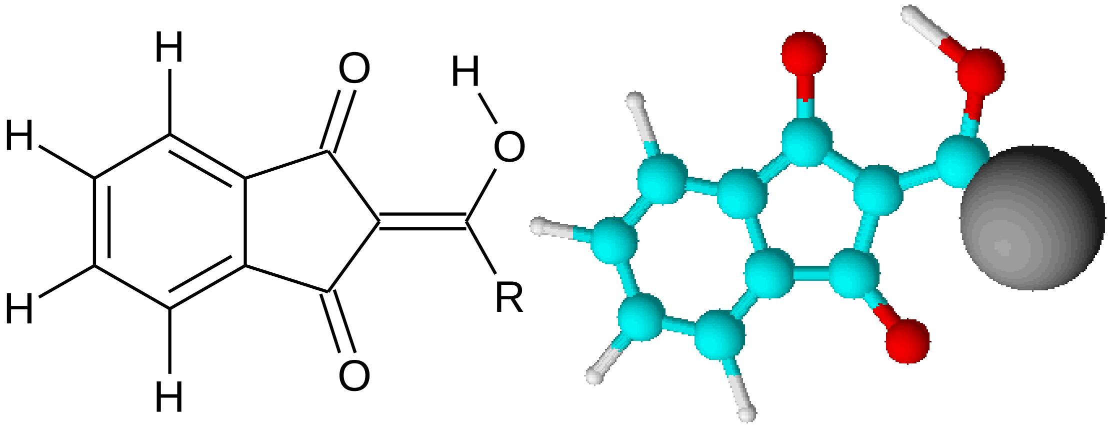

Fig. 1 Structure of 2-acetyl-1,3-indanediones

By incorporating them as ligands in coordination compounds, 2-acetyl-1,3-indanediones form chelate type complexes (Figure 2).

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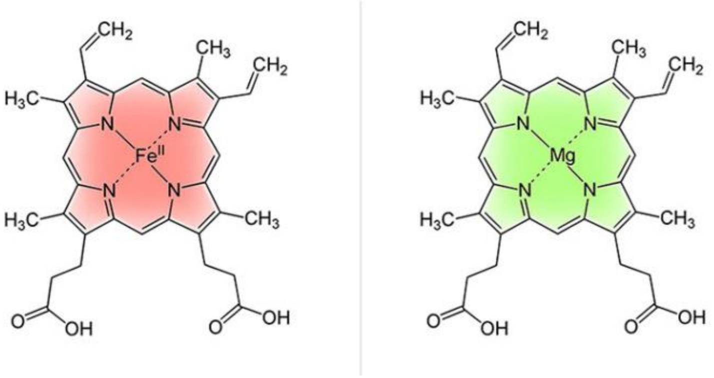


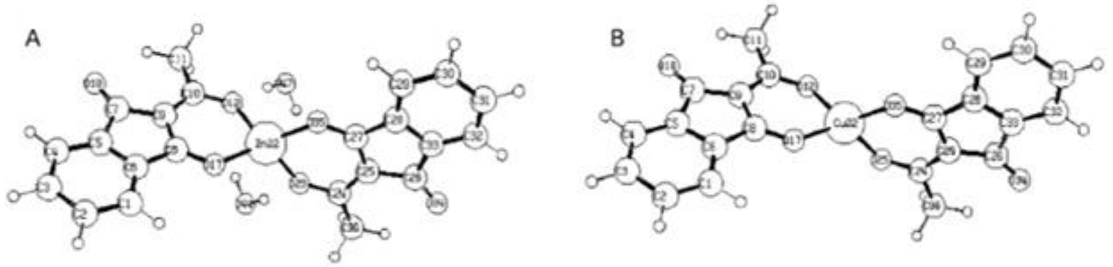
Fig. 2 Structural formulas of chelate complexes (left - hemoglobin, right - chlorophyll)

EXPLANATION

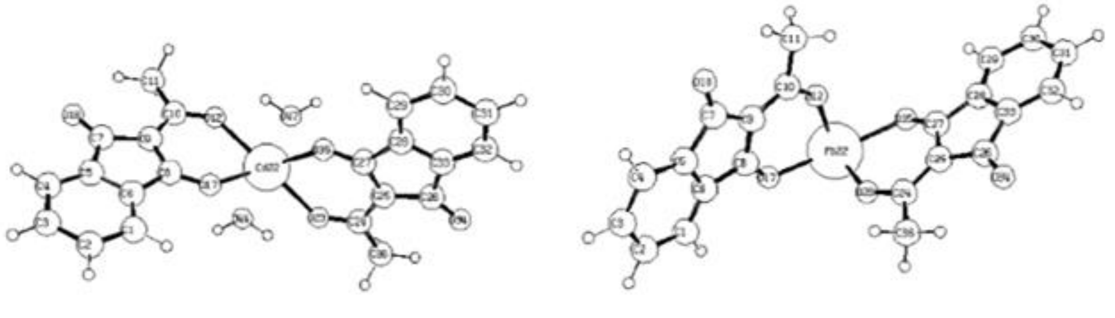
The co-ordinating compound 2-AID has been studied more often than usual for the complexation of a 2-acyl derivative of 1,3-indanedione, to relieve the effect of the acyl substitution of the substituents on the indanedione ring. The first-physiochemical investigations of the 2-AID coordinate coordinating compounds date back to 1969 (Zacharova-Kalavska D., I. Zelensky, A. Perjessy, A., 1969). The complexes 2-acetyl, 2-propenoyl and 2-benzoyl-1,3 indanediones with Fe^{3+}, Ti^{3+} and UO_2^{2+} were studied.

Coordination compounds of 2-acetyl-1,3-indanediones with Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}

A series of M (II) (M = Cu, Zn, Cd, Pb) complexes with 2-acetyl-1,3-indanedione (Figure 3) were synthesized. All complexes were obtained in a metal-ligand ratio of 1: 2. In complexes of Zn (II) and Cd (II), two molecules of water were found to be involved in the inner coordination sphere. It has been shown that the structure of the 2-AID complex with Pb (II) differs significantly from the deformed tetrahedral structure of the Cu (II), Zn (II) and Cd (II) complexes (Enchev, V., Ahmedova, Ivanova, G., Wawer, I., Stoyanov, N. and Mitewa, M., 2001).



$Zn(2AID)_2.2H_2O$ $Cu(2AID)_2$



$Cd(2AID)_2.2H_2O$ $Pb(2AID)_2$

Fig. 3 Optimized structures of the complexes of Cu (II), Pb (II), Zn (II) and Cd (II) with 2-AID

Coordination compounds of 2-acetyl-1,3-indanediones with Fe^{2+} and Fe^{3+}

Already with the establishment of methods for the synthesis of 2-acyl derivatives of 1,3-indanedione the ease with which they coordinate around Fe^{3+} was known (Figure 4). Therefore, the reaction with $FeCl_3$ is suggested as a qualitative response to their discovery (Rusanov V., Ahmedova A., Mitewa M., 2014).

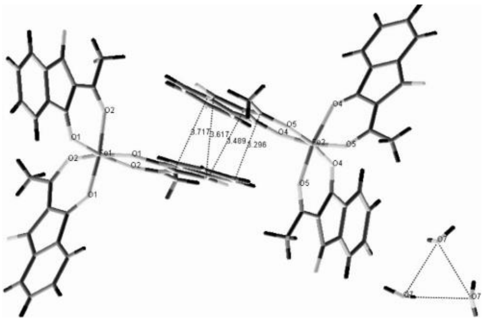


Fig. 4 Crystal structure of the Fe (III) complex with some intermolecular distances

A monocrystalline X-ray structure of the iron (III) complex of 2-acetyl-1,3-indanedione (Figure 5) was obtained which showed the presence of two types of stereoisomers. Both types have octahedral geometry but differ slightly. Details of the Mösbauer spectroscopy show a high spin electron structure of Fe (III) centers (Ahmedova, Rusanov V., Hazell A., Wolny J., Gochev G., Trautwein A., Mitewa M., 2006).

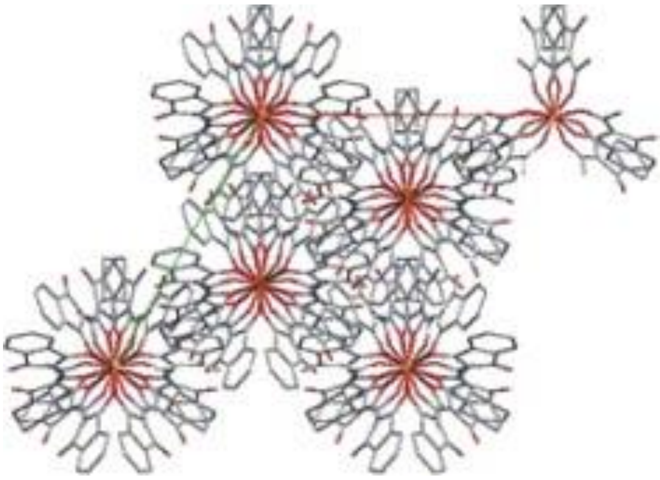


Fig. 5 Single cell view of Fe (2-AID) 3 complex

Iron complexes are prepared in aerobic conditions from two different Fe (II) - $Fe(NH_4)_2(SO_4)_2.6H_2O$ and $Fe(CH_3COO)_2.6H_2O$ starting Fe. The metal salt is dissolved in 1M HCl solution. The resulting solution is mixed with an ethanol solution of 2-AID in a metal ligand ratio of 1:2. An air-stable Fe (II) complex of β-trichloroethene, 2-acetyl-1,3-indanedione (2-AID) was obtained in two different ways and studied by Mösbauer spectroscopy. Based on the results of the theoretical calculations of the Mösbauer parameters of several different geometries and spin states of the Fe-complexes of 2-AID, it is concluded that the resulting Fe(II) complex has a pseudo-octadecimal geometry.

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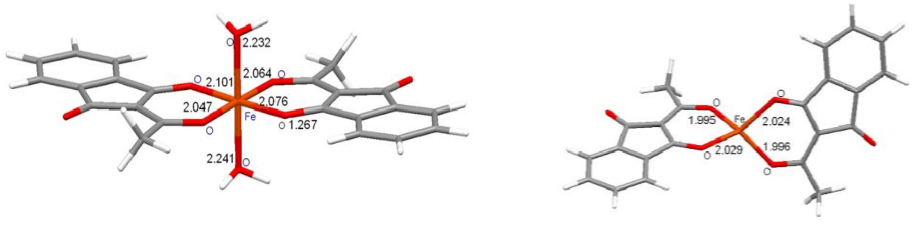

Octahedral model

Tetrahedral model

Fig. 6 Optimized Structures for high spin Fe (II) Complex of 2-AID - Octadecimal and tetrahedric model with selected bond lengths (Fe - O).

From Fig. 6 it is clear that Fe-centers are closely related to two ligand molecules, resulting in a total of four oxygen donor atoms (Rusanov V., Ahmedova A., Mitewa M., 2014).

Coordination compounds of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Gd^{3+}

Coordination compounds of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Gd^{3+} with 2-AID were also isolated in the solid state by reacting the corresponding lanthanide ions and solubilized 2-AID in ethanol followed by addition of dilute ammonia solution to pH 6-7 (Polluktov C., Zeltvai I., Tyshtenko M. et al., 1980). From data, obtained from thermogravimetric and elemental analysis, it was found that 3 molecules of 2-AID were coordinated with each lanthanide ion and the complexes crystallized as hexahydrate. Comparison of the IR spectra of the complexes with that of the free ligand, confirms the chelation with 2-AID deprotonated molecules as well as the presence of crystallization water.

Mixed ligand coordination compounds of 2-AID

Several scientific reports are known for the preparation of mixed ligand complexes of 2-AID with ions of transition metals (Zacharová-Kalavská D., Perjéssy A. & Zelenský I., 1970). Bater and co-workers describe the preparation of quaternary complexes of Mn, Fe, Co, Ni with a general composition ML'_2L_2, (HL-series of β-dicarbonyl compounds, including 2-acetyl- and 2-benzoyl-1,3- L'- nicotinamide) (BatyrD., Starysh M., 1994).

CONCLUSIONS

The presence of a hydroxyl and carbonyl bond in the immediate vicinity and the appearance of tautomerism in the structure of 2-acetyl-1,3-indanedione and its derivatives make them suitable for complex formation.

Complexes of various derivatives of 2-AID with metals from the primary and secondary groups of the periodic system were obtained. Coordinating compounds with elements of the lanthanide group have also been synthesized.

There are also data on mixed ligand complexes. From the literature references, it can be concluded that 2-AIDs are suitable for complex formation

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