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Coordination Compounds of Some Metals with *N,N'*-Bis(*m*-ethoxycarbonylphenyl)Urea

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Abstract—*N,N'*-bis(m-ethoxycarbonylphenyl)urea and its complex compounds with cooper, zinc and cadmium were syntesized. The structure of *N,N'*-bis(*m*-ethoxycarbonylphenyl)urea was investigated by XRD method. Ligand coordination process was determined. Some factors affecting the donor ability of the nitrogen and oxygen atoms in ligand molecule were discussed.

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Nowadays coordination compounds of urea and its different derivatives with transition metals are known [1–4]. It is established that in complex compounds urea and its derivatives are mostly coordinated by an oxygen atom. At the same time it is assumed that the coordination process depends of donor ability of nitrogen and oxygen atoms, and also of affinity of these atoms to the metals.

The investigation of the urea derivatives, containing two nitrogen atoms with different functional substituents affecting redistribution of electronic density of the molecule [5] due to inductive and mesomeric effects has shown that as observed from the data of the analyses of normal vibration of the urea molecule, the most characteristic are vibration frequencies of C=O, N–H, NCN and other bonds that change the most when urea is coordinated to metal.

In this research the results of the investigation of complexing properties of *N,N'*-bis(*m*-ethoxycarbonylphenyl)urea are reported. For preliminary estimate of coordinating ligand abilities a quantum-chemical calculation was used (PM3, AM-1). According to these calculations, the strongest negative charge is located on the oxygen atoms of the carbonyl group (–0.383) and ester group (–0.378). We may assume, that these oxygen atoms take part in the formation of a coordination bond with ions of metal during the complexing (Table 1).

The crystalline structure of the ligand molecule was investigated with XRD method (Fig. 1) [9]. The molecule has its own symmetry and is disposed in the crystal on the symmetrical axis of the second order that goes through atoms C^1 and O^1. The aromatic part of the molecule with neighbouring atoms (acetyl group) is planar within ±0.026 Å and turned by 51.3° relatively to the other planar atomic system $C^2NC^1O^1N'C^{2'}$ (±0.017 Å), consequently, the angle between two aromatic systems is 102.6°.

No anomalous interatomic dimensions or angles were observed in geometric parametres of the molecule. The lengths of the valent bonds in the aromatic ring and in the acetyl group are common [4]. The length of the C^1=O^1 bond [1.234(6) Å] is slightly increased comparing to the other carbonyl bond C^6=O^2 [1.204(4) Å] that indicates the conjugation of π-bond

Table 1. Distribution of effective charges (*q*, eV) on donor atoms in the *N,N'*-bis(*m*-ethocycarbonylphenyl)urea according to results of quantum-chemical calculations

Atom	PM-3	AM-1
O^1	–0.383	–0.379
O^2	–0.378	–0.355
O^3	–0.266	–0.279
O^4	–0.378	–0.355
O^5	–0.266	–0.279
N^1	0.030	0.304
N^2	0.030	0.304

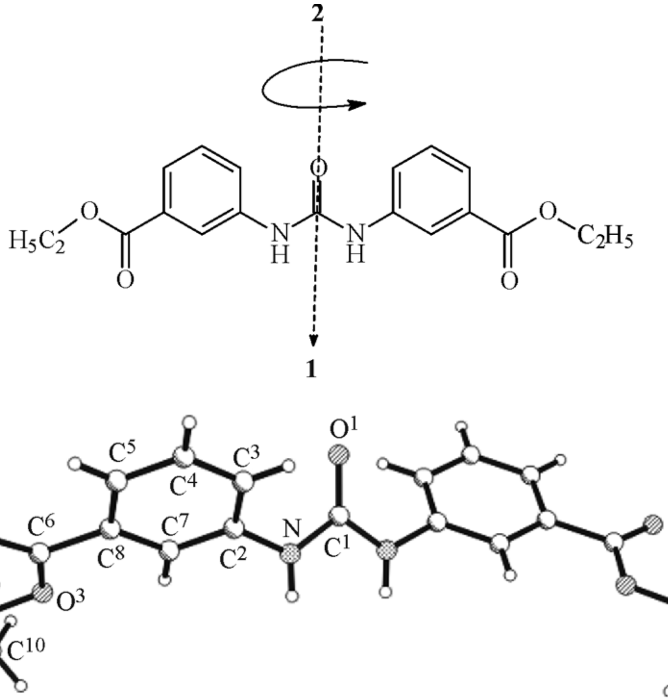


Fig. 1. General view of *N,N'*-bis(*m*-ethocycarbonylphenyl)urea molecule (assymetric part of the molecule is numbered).

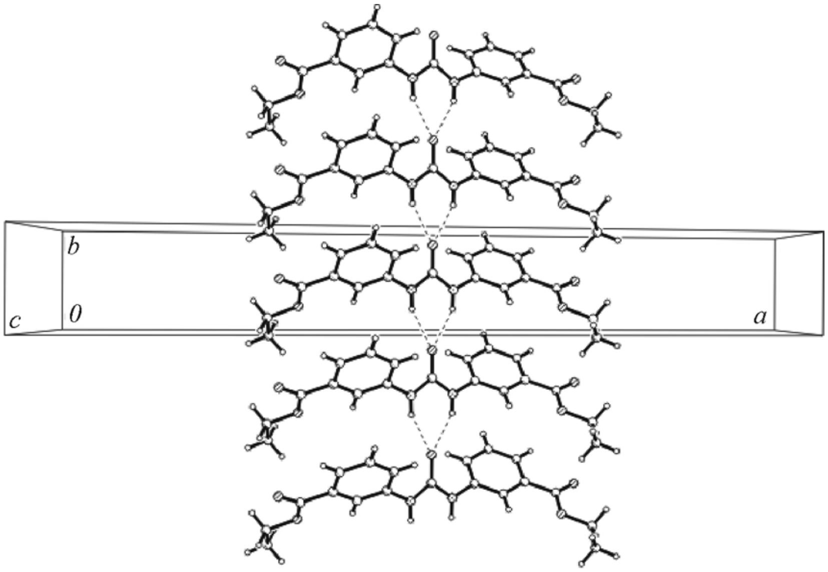


Fig. 2. The packing of the molecules in the crystal.

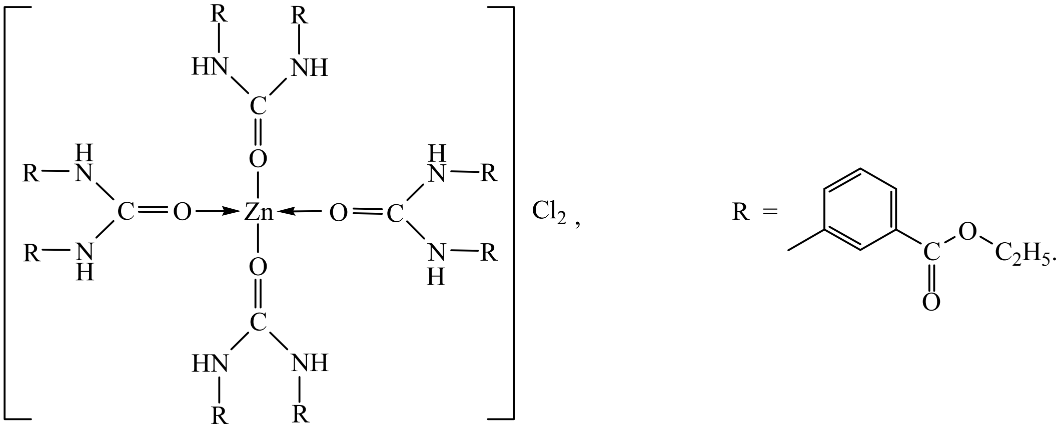
C^1=O^1 with unshared electron pairs of the two nitrogen atoms. However, the conjugation between π-electronic systems of acetyl and aromatic groups does not show itself in changing the length of bonds in these groups.

The packing of the molecule in crystalline structure is shown on the Fig. 2. There is an intermoleculer hydrogen bond of N–H···O···H–N type in the crystal. The carbonyl atom of oxygen O^1 from the source molecule interacts with two hydrogen atoms of the NH group of the molecule, translated along the *b*-axis. The intermoleculer bifurcated H-bond has the following parameters: O···N 2.896 Å, O···H–N 2.10 Å, angle O···HN 154°.

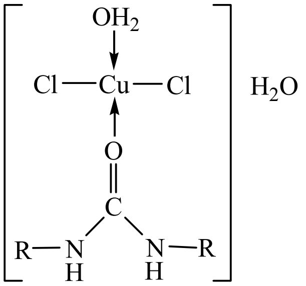
Due to translation elements, infinite band forms along the *b*-axis. The findings of the XRD analysis were deposited in Cambridge Structural Data Center (CCDC-73-42-11).

The data from elementary analyses of the complexes obtained are presented in Table 2.

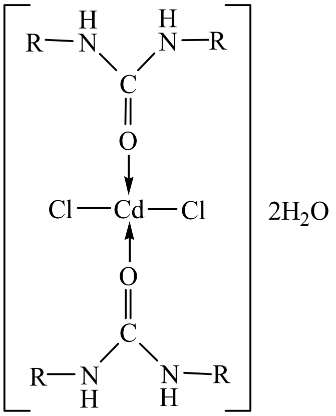
In order to determine the ligand coordination mode its IR spectrum and those of the complexes were investigated (Table 3). The comparison of the IR spectrum of the ligand and of the zinc complex shows that the vibration frequencies of NH-groups shift in high-frequency area, at the same time the vibration frequency of the carbonyl group is reduced by 15–20 cm^{-1}. These changes let us conclude, that the ligand in this complex is coordinated with the oxygen atom. In favor of this fact testify the vibration frequencies in the region of 400–420 cm^{-1} that are missing in the spectrum of a free ligand. Basing on the spectroscopic data for $ZnCl_2 \cdot 4L$ complex, the following structure is proposed.



In the IR spectrum of the cooper complex in the 1600–500 and 900–700 cm^{-1} range the absorption bands of hydrate and coordinated water molecule [9] are observed. In low frequency area an absorption band 400-450 cm^{-1} was found that may be attributed to the Cu–O bond vibrations. The spectroscopic data mentioned above allow to conclude that the ligand is coordinated with an oxygen atom of carbonyl group. One of the water molecules is coordinated to the central atom. For the cooper complex the following structure is proposed.



In the IR spectrum of the complex $CdCl_2 \cdot 2L \cdot 2H_2O$ absorption frequencies of NH and C=O groups were found. In low frequency area the absorption band at 410 cm^{-1} was discovered, missing in the spectrum of the free ligand. So, basing on the IR spectroscopic data the following structure is proposed for the cadmium complex.



According to the spectroscopic results mentioned above, *N,N'*-bis(*m*-ethoxycarbonylphenyl)urea in complex compounds of zinc, cadmium and cooper(II) is coordinated with an atom of oxygen of a carbonyl group.

The derivatives of the urea and thiourea, depending on the nature of the central atom and functional substituents in complexes may be coordinated with an atom of nitrogen. For example, in complex compounds of nickel with diphenyl- and ditolylurea coordination occurs with an atom of nitrogen that is proved with the XRD data [11]. Probably, the electron density of the phenyl group is conjugated with unshared electrons of the nitrogen atom. Consequently, the NH group gets

Table 2. Data of elemental analyses of synthetised complex compounds

Compound	C		N		M		Formula
	found, %	calculated, %	found, %	calculated, %	found, %	calculated, %	
$ZnCl_2$·4L	58.42	58.45	7.14	7.18	4.01	4.19	$ZnC_{76}H_{80}N_8O_{20}Cl_2$
$CuCl_2$·L·$2H_2O$	43.01	43.32	5.11	5.32	11.85	12.07	$CuC_{19}H_{24}N_2O_7Cl_2$
$CdCl_2$·2L·$2H_2O$	48.87	48.98	5.92	6.02	11.91	12.03	$CdC_{38}H_{44}N_4O_{12}Cl_2$

Table 3. Basic parameters (ν, cm^{-1}) of IR spectra of the ligand and its complexes with Zn, Cd, and Cu(II)

Соединение	ν(NH) ν(OH)	ν(CH)	ν(CO) ν(H_2O)	ν_k	ν(NH) ν(NCN)	ν(M–O)
N,N'-bis(*m*-ethocycarbonylphenyl)urea (L)	3251	3000	1660	1566	1611	–
	3353	2980		1528		
				1050		
$ZnCI_2$·4L	3450	3000	1740	1690	1640	400–420
	3360		1640	1550	1615	
				1100		
$CuCI_2$·L·$2H_2O$	3450	2990	1760	1590	1620	400–450
	3290	2980	1640	1050		
			1620			
$CdCI_2$·2L·$2H_2O$	3300	2980	1700	1570	1625	410
	3250		1630	900		
			1620	1020		

additional electron density. That, in its turn, increases the mobility of the hydrogen atom of the NH group. Therefore, in some diphenyl derivatives of the urea atom of hydrogen is replaced by metal and it is coordinated by atom of nitrogen.

In complex compounds of *N,N*'-bis(*m*-ethoxycarbonylphenyl)urea atom of nitrogen of NH group does not take part in coordination. Evidently, it is related to the repulsion of the phenyl rings because of the ethoxy group and some lengthening of C–NH bonds. Therefore the complex ligand compounds we have synthesized are mostly coordinated with the oxygen atom of the carbonyl group.

As a result of the investigation of the crystalline structure of *N,N′*-bis(*m*-ethoxycarbonylphenyl)urea we found that this compound has symmetric axis of second order (C_{2v}) along the C=O bond. So two ethoxyphenyl substituents are located symmetricaly. Such location of substituents on the nitrogen atom must affect the donor properties of atoms of nitrogen and oxygen when complexing with transition metals. We should mention that quantum-mechanical calculations and XRD proved, that the urea molecule has a planar structure. Unshared pairs of *p*-electrones of the nitrogen atoms are located normally to the molecular plane [12]. Therefore in the most complex metal compounds the urea is coordinated with the oxygen atom that conforms with the data of quantum-mechanical calculations.

EXPERIMENTAL

N,N′-bis(*m*-ethoxycarbonylphenyl)urea (L) is synthesized by a known method [7].

Synthesis of complex compounds was carried out by mixing the ethanol solutions of 0.01 mol of *N,N′*-bis(*m*-ethoxycarbonylphenyl)urea and of 0,0025 mol of zinc chloride. The reaction mixture was evaporated till 1/2 volume and then left to crystallize. After 4 days the precipitated crystals were filtered and analyzed.

Chloride complexes for Cu(II) and Cd(II) were obtained in the same way.

The XRD of the monocrystals was performed on an automatic diffractometer STOE Stadi 4 (λMoK_α, graphite monochromator). Experimantal data has been collected at 293±2 K.

The IR spectra of compounds has been registered in the range of 400–4000 cm^{-1} on a spectrometer Avatar

System 360 FT-IR and Protege 460 Magna-IR (Nicolet Instrument Corporation, USA) in tablets with KBr.

Quantum-mechanical calculation of the reactivity of the ligands has been performed by semiempiric (PM-3, AM-1) methods of calculation in program complex HyperChem Data [8].

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