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Synthesis, IR Spectroscopy and X-Ray Diffraction Analysis of Copper (II) Complexes Based on 1-Benzoyl-3-Phenyl-5-Hydroxy-5-Trifluoromethyl-2-Pyrazoline and its Derivatives

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ABSTRACT

Mononuclear copper (II) complexes were synthesized on the basis of 1-benzoyl-3-phenyl-5-hydroxy-5-trifluoromethyl-2-pyrazoline and its derivatives [1]. The synthesized complexes are researched with application of methods of the element analysis, IR spectroscopy. The molecular and crystal structure of a complex of copper (II) with benzoylhydrazone of 1,1,1-trifluor-4- (4-bromphenyl)-butane-2,4-dion (H_2L^5) structure $CuL^5 \cdot NH_3$ is established by a method X-ray diffraction analysis.

KEYWORDS: *benzoylhydrazone, aroyltrifluoroacetylmethane, spin-hamiltonian, hyperfine structure, additional hyperfine structure, square structure, crystal structure*

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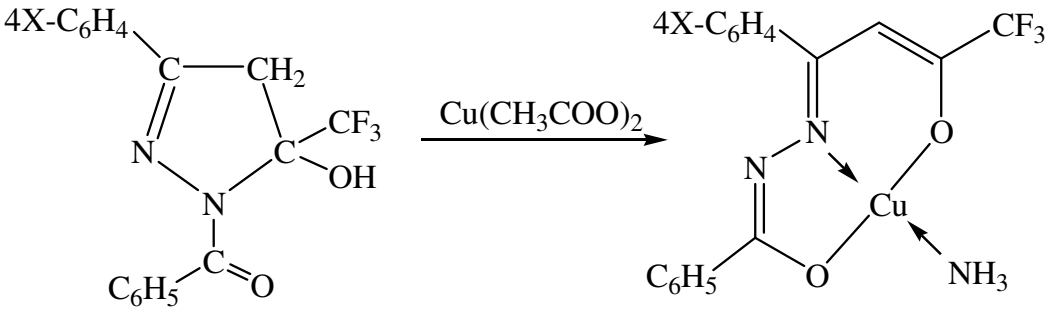
1. INTRODUCTION

To date, little time and attention has been devoted to the study of the geometric and electronic structure of complex copper (II) compounds with ligands such as acylhydrazones of fluorinated β-dicarbonyl compounds [1-3, 5, 12-17]. Meanwhile, the study of the magnetic properties of copper-containing complexes, along with the consideration of their geometric and electronic structure, allows us to draw reasonable conclusions and predict the ways of directed synthesis of complex compounds with specified properties [4-6, 9].

We synthesized complex compounds of copper (II) with benzoylhydrazones of aroyltrifluoroacetylmethanes. The results of elemental analysis and spectroscopic studies allowed us to attribute $CuL \cdot NH_3$ to the compounds:



X = H ($CuL^1 \cdot NH_3$); CH_3 ($CuL^2 \cdot NH_3$); OCH_3 ($CuL^3 \cdot NH_3$); Cl ($CuL^4 \cdot NH_3$); Br ($CuL^5 \cdot NH_3$).

2. EXPERIMENTAL PART

Synthesis of $CuL^1 \cdot NH_3$. To a hot solution of 0.5 g (0.0015 mol) of 1-benzoyl-3-phenyl-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H_2L^1) in 25 ml of ethanol, an aqueous-ammonic solution of 0.0015 mol (0.30 g) of copper (II) acetate in 15 ml of 25% ammonia solution was added. The reaction flask was heated with a reverse refrigerator for 30 minutes. After 2 days, the green precipitate was filtered out, washed with water, ethanol and dried in the air. Output of the CuL^1 complex.NH3 was 0.46 g (72 %) with T. sol. 223 °C.

Other copper (II) complexes have been synthesized similarly. The outputs and data of the elemental analysis of complex copper (II) compounds are given in table 1.

Table 1 Yields, melting points, and results of elemental analysis of copper (II) $Cu \cdot NH_3$ complexes based on benzoylhydrazones of aroyltrifluoroacetylmethanes

Compound	Yield, %	$T_{sol.}$, °C	Brutto-formula	Found/ Calculated, %			
				Cu	C	H	N
$CuL^1 \cdot NH_3$	72	223	$CuC_{17}H_{14}F_3N_3O_2$	15,34/15,39	49,41/49,46	3,40/3,42	10,22/10,18
$CuL^2 \cdot NH_3$	65	256	$CuC_{18}H_{16}F_3N_3O_2$	14,83/14,89	50,60/50,64	3,75/3,78	9,87/9,84
$CuL^3 \cdot NH_3$	79	233	$CuC_{18}H_{16}F_3N_3O_3$	14,30/14,35	48,77/48,82	3,61/3,64	9,51/9,49
$CuL^4 \cdot NH_3$	86	247	$CuC_{17}H_{13}ClF_3N_3O_2$	14,18/14,21	45,62/45,65	2,89/2,93	9,42/9,39
$CuL^5 \cdot NH_3$	36	*	$CuC_{17}H_{13}BrF_3N_3O_2$	12,88/12,92	41,49/41,52	2,64/2,66	8,57/8,55

Single crystals of $CuL^5 \cdot NH_3$ were grown during recrystallization of the complex from ethanol. X-ray diffraction was performed using an automatic Xcalibur diffractometer (CuKa radiation, λ=1.54 Å, graphite monochromator, ω scanning, $2\theta_{max}$= 50°).

3. RESULT AND DISCUSSIONS

3.1. IR spectroscopy

In the IR spectrum of the $CuL^5 \cdot NH_3$ complex (Fig. 1., Table 2.), the vibrational frequency $\nu_{(C=N)}$ (1607 sm^{-1}) is compared to the IR spectrum of the free ligand (the absorption band $\nu_{(C=N)}$= 1633 sm^{-1}) shifted to the low frequency region by 26 sm^{-1}. This suggests the coordination of the ligand to the metal via two amide and β – diketone oxygen atoms and an azomethine nitrogen atom [4, 7-13, 15].

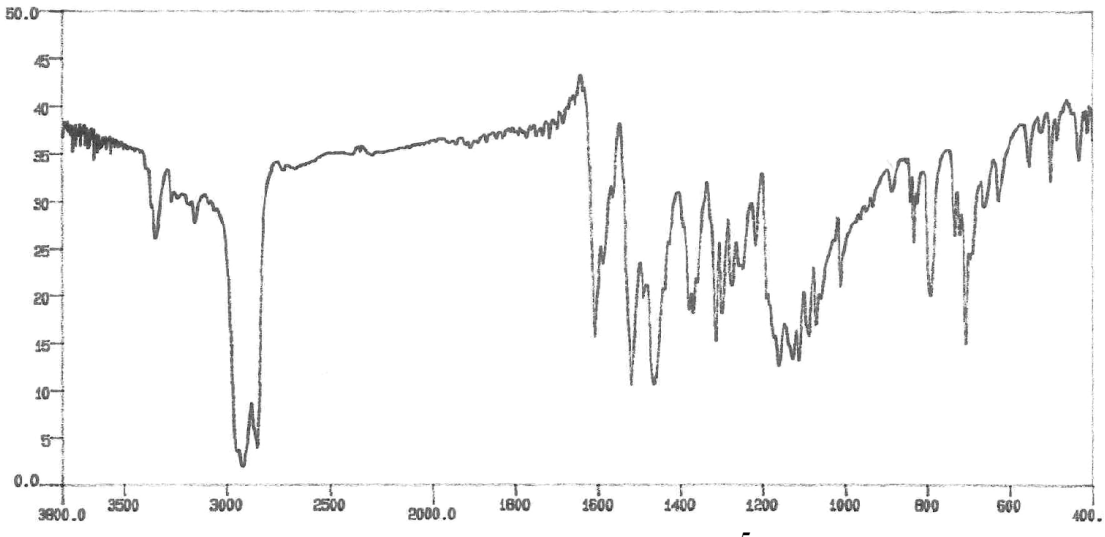


Figure 1 IR spectrum of a complex copper (II) compound $CuL^5 \cdot NH_3$ based on benzoyl hydrazone 1,1,1-trifluoro4 - (4-bromophenyl)- butane-2,4-dione (H_2L^5).

Table 2 Parameters of IR spectra of copper (II) complex compounds based on benzoylhydrazones of aroyltrifluoroacetylmethanes

Соединение	NH_3	C–H	C=N	N=C–C=N	N=C–O^-	N–N	Cu–O
$CuL^1 \cdot NH_3$	3359	2976	1604	1526	1495	1065	485
$CuL^2 \cdot NH_3$	3362	2973	1605	1528	1497	1072	489
$CuL^3 \cdot NH_3$	3357	2975	1607	1527	1494	1073	486
$CuL^4 \cdot NH_3$	3356	2977	1608	1528	1498	1075	488
$CuL^5 \cdot NH_3$	3357	2976	1607	1529	1496	1078	490

3.2. X-ray diffraction anaysis

Conclusions about the planar structure of the complex with tridentate coordination of the ligand dianion $(L^n)^{2-}$, based on the results of IR spectra and the X-ray diffraction method for the $CuL^5 \cdot NH_3$ complex grown single crystal.

$C_{17}H_{13}BrF_3N_3O_2Cu$ crystals, triclinic, a=9,7929 (13), b = 12,5906 (20), c = 15,6732 (16) Å, α = 86,427 (10)°, β = 84,771 (10)°, γ = 69,602 (13)°, V= 1802,8 $Å^3$, ρ (h) = 1,812 g/sm^3, Z = 4, etc. gr. P-1. The complex molecule contains almost flat articulated five-and six-membered metallocycle (Fig. 3.). The doubly deprotonated residue of the H_2L^5 molecule is coordinated by a copper atom through two oxygen atoms and a nitrogen atom of the hydrazone fragment. The fourth place in the flat square of the trans-N_2O_2 coordination node is occupied by the nitrogen atom of the ammonia molecule [17-19].

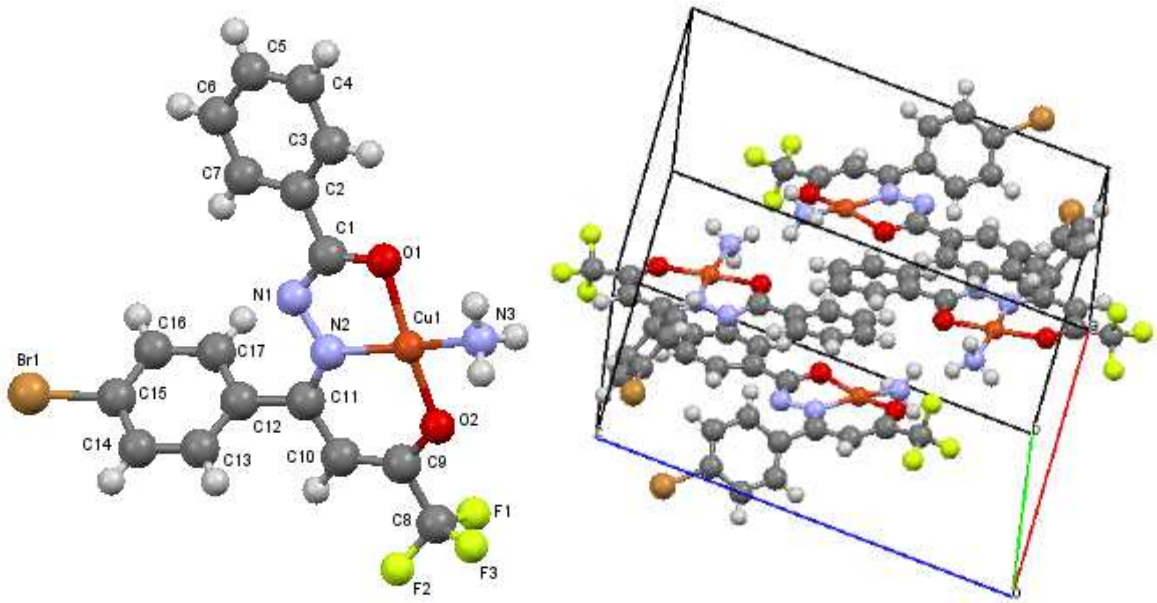


Figure 3 Molecular structure and packaging of $CuL^5 \cdot NH_3$ molecules.

4. Conclusion

Thus, as a result of studies using IR spectroscopy and X - ray diffraction, it was found that the interaction of Cu (II) ions with benzoylhydrazones of aroyltrifluoroacetylmethanes, which exhibit the functions of a tridentate ligand, forms coordination compounds with articulated five - and six-membered metal cycles of a flat-square structure.

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