

COORDINATION OF CU(II) WITH MORPHOLINE DERIVATIVE – STRUCTURAL AND VIBRATIONAL PROPERTIES

Beata Białek¹, Krystyna Gielzak-Koćwin²

¹*Instytut Fizyki, Akademia Jana Długosza, Al. Armii Krajowej 13/15, 42-200 Częstochowa*

²*Instytut Chemii i Ochrony Środowiska, Akademia Jana Długosza, Al. Armii Krajowej 13/15, 42-200 Częstochowa*

ABSTRACT

Two new copper(II) complexes with general formula $[\text{Cu}(\text{etMorph})_2\text{ox}]$ and $[\text{Cu}_2(\text{etMorph})_4\text{ox}](\text{NO}_3)_2$, where etMorph = 4-(2-aminoethyl)morpholine, ox = oxalate, have been prepared by reacting $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and etMorph in an aqueous solution in molar ratio 1 : 2 : 2, respectively.

Solid crystal products were characterised by spectroscopic methods. Their crystal structures have not yet been determined, but on the basis of vibrational (FT-IR) spectral studies as well as quantum-chemical calculations we propose a possible geometry of the complexes.

INTRODUCTION

Polynuclear copper(II) complexes play a significant role in the redox processes in biological systems [1] and exhibit an interesting pattern of magnetic and electronic interactions in the copper-oxygen as well as copper-nitrogen sites. Morpholine is a simple heterocyclic compound with a great industrial importance. It is used as anticorrosive agent and as chemical intermediate: catalyst, solvent, antioxidant, in the production of various pharmaceuticals and pesticides. One of its derivative – 4-phenyl-morpholine were reported to possess antimicrobial [2,3], anti-inflammatory [4–6] and central nervous system activities [6–8]. Schiff bases have been reported to possess antimicrobial properties [9–12] apart from other biological activities.

In this paper we compare theoretically predicted spectra with the experimental ones and discuss the influence of the nature of morpholine moiety on the copper(II) coordination sphere.

SYNTHESIS

4-(2-aminoethyl)morpholine (0,01 mole) was added to a solution of copper(II) nitrate (0,005mole) dissolved in 30 ml of water. To this aqueous solution a potassium oxalate (0,01 mole) in 10 ml of water was added. The resulting deep-blue solution was left standing until crystals were formed. The crystals were then filtered and air dried. We obtained two different sort crystals: blue (1) and deep green (2).

INFRARED SPECTROSCOPY EXPERIMENT

The investigations of vibrational properties of the complexes were carried out on a Nicolet-Nexus FT-IR spectrophotometer within the range of 4000 to 400 cm^{-1} using HeNe laser at 632,8 nm. The compounds were measured as a KBr pellets. Resolution was better than 1 cm^{-1} .

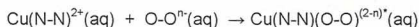
THEORETICAL INVESTIGATIONS

In order to assign the most prominent vibrational modes of the molecule, quantum-chemical calculations have been carried out. An ab initio Hartree-Fock method was applied with an advanced 6-31g(d,p) basis set. At first step, the geometry of morpholine molecule alone was optimised through the total energy minimisation process. When the true minimum was found, which was confirmed by frequency calculations, the molecule was modified to create etMorph. A complex of Cu(II) with two etMorph molecules was built and its geometry was fully optimised. In the last step of our investigations the frequency calculations were done for the optimised $\text{Cu}(\text{etMorph})_2$ structure and the obtained theoretical spectrum was compared with the experimental ones.

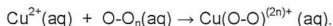
All the calculations were done with the use of Gaussian 03W programme package [13].

RESULTS AND DISCUSSION

The reactions of Cu(II) nitrate trihydrat and 4-(2-aminoethyl)morpholine afforded blue and dark green complexes. Two differently coloured complexes must have different structure. Probably the use of 4-(2-aminoethyl)morpholine as a ligand, which is the chelating agent with two N atoms as donors, causes that the reaction:



is more likely than the reaction:



$\text{Cu}(\text{N-N})^{2+}(\text{aq})$ ion is a harder acid than simple $\text{Cu}^{2+}(\text{aq})$ and hard bases such as oxygen donors prefer the former over the latter. The structure of the complexes might be found in X-ray diffraction analysis, but in the case of the complexes formed with two different ligands, it is desired that a preliminary structure is guessed. Such a preliminary structure may be examined with the calculational method. According to the available data we assumed that the Cu(II) ion is coordinated with etMorph through the nitrogen atoms of the ethylene tail. The preliminary guessed structure of the $\text{Cu}(\text{etMorph})_2$ complex as well as the structure after the full optimisation process is shown in Fig. 1.



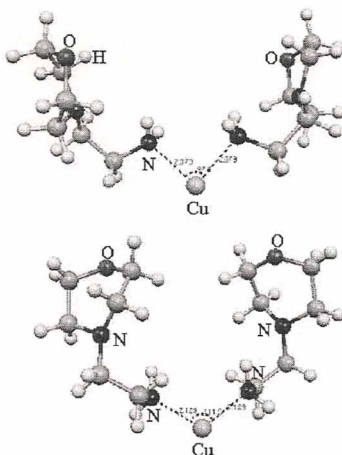


Figure 1. Geometry of $\text{Cu}(\text{etMorph})_2$ complex before (upper picture) and after (lower picture) geometry optimisation; non-described atoms are carbons (dark grey) and hydrogens (light grey)

For the starting geometry we assumed that the Cu-N bond length was not longer than the sum of ionic radii of the two elements, which was estimated as 23.8 nm. The initial N-Cu-N angle was assumed to be 90° . In the result of optimisation the Cu-N bond was shortened by about 10% with the final value of 21.29 nm, and the N-Cu-N angle relaxed to about 112° . As for the ligand, its geometry was hardly altered in comparison with the isolated etMorph molecule.

The experimental FT-IR spectra of the ligand and the obtained compound as well as the respective calculated spectra are presented in Figs 2 and 3.

From the first set of spectra (Fig. 2.) a very good qualitative similarity between the experimental and the calculated data is seen. The broad band seen in the experiment over 3000 cm^{-1} , not present in theoretically derived IR spectrum, reflects probably the presence of water in the investigated sample. The similarity of the etMorph spectra obtained with the two methods let us expect that our theoretical predictions concerning $\text{Cu}(\text{etMorph})_2$ complex should be reliable.

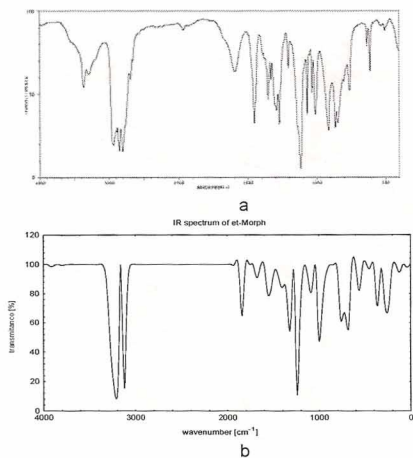


Figure 2. FT-IR (a) [14] and calculated IR (b) spectra of etMorph.

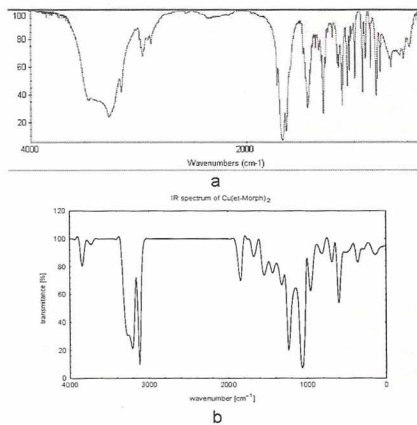


Figure 3. FT-IR (a) and calculated IR (b) spectra of Cu(etMorph)₂ compound.

The FT-IR spectrum of Cu(etMorph)₂ obtained in our laboratory (Fig. 3a) shows number of bands in the region below 2000 cm⁻¹. The theoretically obtained spectrum for the predicted geometry of the complex is not exactly the same. The number of bands below 2000 cm⁻¹ are smaller and their intensities are lower. However, there are still many similarities, which illustrates Table 1.

Table 1. The obtained vibrational frequencies of Cu(etMorph)₂ complex and their interpretation. The values are given in cm⁻¹.

Experimentally derived bands	Theoretically predicted bands	Interpretation
3467,4 ; 3272,8	3430	$\nu_{asym}(N-H)$; $\nu_{sym}(N-H)$
3155;	3342	$\nu(N-H)$
2960,4	2959	$\nu(C-H)$
1449,7	1504	δ -ring
1285,9	1306	$\delta(C-H)$
1106,7	1114	ν -ring
1060	1068	$\nu(C-C) + CH_2def$
988,9	987	ν, δ - ring
794,3	---	$\nu(N-Cu)$
645,8	536	$\nu(N-Cu)$

The morpholine ring has a chair conformation. The IR spectra of the etMorph complexes show a strong bands at ~1700 cm⁻¹ indicating the presence of carbonyl group. The NH₂ scissoring frequencies at 1694 cm⁻¹ on the etMorph spectrum are lowered to 1667 cm⁻¹ by coordination (compare Fig. 2a with Fig. 3a). The reason for this shift is the change on nitrogen orbitals and its effect on the NH₂ force constant because of the change in H-N-H angle [15]. The bands at 654,78 cm⁻¹ in the spectrum of the complex have been ascribed to the NH₂ twisting mode. We have assigned the bands observed at 1294 cm⁻¹ as the $\nu(C-N)$ stretching for the free etMorph. Absorption attributed to this vibration occurs at lower frequencies in the complex at 1286,55 cm⁻¹. Therefore we reassigned the strong bands in the 1069.62 – 1039.7 cm⁻¹ region in the spectra of the complex to the NH₂ wagging mode instead of the assignment at 1070 – 1036 cm⁻¹ in ligand.

The largest divergence between the vibrations found in experiment and those obtained in theory is observed for the bands coming from N-Cu vibrations. In the experiment two bands were found at 794.3 and 645.8 cm⁻¹ while calculations gave only one band at about 536 cm⁻¹. It may suggest that the geometry of the complex obtained through the ab initio calculational method, although very likely, is not exactly the same as in the experimentally investigated sample. Since there are two bands for which N-Cu bond vibrations are responsible, it is very probable that Cu ion is coordinated not only through the ethylene tail nitrogen atoms, but also through the nitrogens of morpholine ring.

CONCLUSIONS

We have applied quantum chemical ab initio method to find the most probable structure of newly synthesised $\text{Cu}(\text{etMorph})_2$ complex. The obtained results were verified through an analysis of experimental FT-IR and theoretically derived IR spectra. The calculational method let us predict a possible structure of $\text{Cu}(\text{etMorph})_2$ complex, in which Cu ion is coordinated to the ligand through N atoms of ethylene tail. The N-Cu bond length was found to be 21.29 nm. The calculated IR spectrum reflects well the observed in experiment vibrational bands as far as it comes to the ligand. As for the bands that involve Cu ion some discrepancy was observed between the experimental and theoretical results. This suggests that some more calculations are needed, with another $\text{Cu}(\text{etMorph})_2$ model structure, in which Cu ion is coordinated also to N atoms of morpholine ring.

REFERENCES

1. M. Erecinska, D.F. Wilson, Arch. Biochem. Biophys., 188 (1978) 1
2. R.S. Varma, R. Prakash, M.M. Khan, A. Ali, Indian Drugs 23 (1986) 345–349.
3. J. B. Hester, E.G. Nidy, S.C. Perricone, T.J. Poel, PCT Int. Appl. (2001) W00144188.
4. V.S. Misra, S. Singh, R. Agarwal, K.C. Chaudhary, J. Chem. Soc. Pak. 3 (1981) 209–213.
5. M.G. Verma, V.R. Sharma, A.K. Saxena, T.N. Bhalla, J.N. Sinha, K.P. Bhargava, Pharmacol. Res. Commun. 16 (1984) 9–20.
6. R. Agarwal, C. Agarwal, S. Singh, V.S. Misra, J. Chem. Soc. Pak. 6 (1984) 84–94.
7. R. Agarwal, K.C. Chaudhary, V.S. Misra, J. Indian, Chem. 22B (1983) 308–310.
8. R.S. Varma, R. Prakash, C.R. Prasad, J. Chem. Soc. Pak. 8 (1986) 117–123.
9. F. Gumus, P. Gurkhan, N. Gunduz, A. Abbasoglu, FABAD Farm. Bilimler Derg. 19 (1994) 5–8.
10. M.D. Deshmukh, A.G. Doshi, J. Orient, Chem. 11 (1995) 85–86.
11. M. Indreen, M. Siddique, S.D. Patil, A.G. Doshi, A.W. Raut, J. Orient, Chem. 17 (2001) 131–133.
12. S.K. Sridhar, M. Saravanan, A. Ramesh, Eur. J. Med. Chem. 36 (2001) 615–625
13. Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, et al., and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
14. SDBSWeb : <http://www.aist.go.jp/RIODB/SDBS/> (National Institute of Advanced Industrial Science and Technology, date of access)
15. M. Kumru, A. Aypar, Spectrochim Acta Part A 47 (1991) 1789