

Vibrational analysis and thermal stability of Cu and Ni oxamide complexes

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Abstract Studying the coordination nature of oxamide and determining the binding site(s) to metal ions is the key to understand the bioinorganic chemistry of oxamide complexes. Also, this is a possibility to compare the capacity of coordination of some different $3d^8$ and $3d^9$ metal ions with *N, N*-bidentate ligands as oxamide and to characterize thermal and chemical stability for the obtained complexes.

The paper presents a comparative analysis on thermal stability of Cu and Ni oxamide complexes with oxamide in 1:2 molar ratios. The obtained experimental data as elemental analysis, vibrational and crystallographic spectra and decomposition stages show that Cu (II) complex presents a lower stability than Ni (II) complex due to the weaker Cu-N bond in Cu (II) oxamide complex.

Keywords: Ni (II) and Cu (II) square – planar complexes, oxamide, vibrational analysis, TG and DTG analysis.

1. Introduction

Square – planar coordination is found to d^8 or d^9 metal ions which are stabilized by ligand field stabilization energies [1]. According to Pearson classifications, Cu (II) and Ni (II) are acting as borderline acids, but both ions prefer to bond to polarisable ligands and forms square – planar coordination compounds.

Oxamide is acting as a bidentate *N, N*- donor ligand coordinated to the metal ions through both nitrogen atoms. A remarkable characteristic of this ligand is the thermal stability and relatively high sublimation temperature, due to specific role of intermolecular and intra-molecular hydrogen bonding [2].

2. Experimental

The complexes were prepared as described in the literature data [3], using a molar ratio M:L = 1:2 with 10% ligand in excess.

For Ni (II) complex was used $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solved in DMSO and for Cu (II) complex was used $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solved in DMSO. The mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with oxamide and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with oxamide was refluxated and cooled in an alkaline media which has been established by an alcoholic solution of KOH.

The precipitates were washed with ethylic ether and dried.

Ni (II) oxamide complex is presented as dark orange crystals and Cu (II) oxamide complex is presented as yellow-green crystals.

The synthesis methods are based on general reactions of coordination between ligand and metal ions:



All of the chemicals used were extra pure grade.

Chemical composition of the complexes was checked using an EDX spectrometer Philips ESEM XL 30 TMP.

The complexes have been analysed by X ray diffraction using $\text{CuK}\alpha$ $\lambda = 0.15405$ nm wavelength with a Nickel filter. The X ray detector speed was very slow, about 1° min^{-1} , having a real stationary time as long as possible with the powder samples.

FT-IR spectra have been recorded with a FT-IR Spectra – Bruker Vector 22, in KBr pellets on 4000 – 400 cm^{-1} domain.

Thermal analysis data were obtained using a MOM Budapest derivatograph. The weight of the samples were 46.5 mg for Ni (II) complex and 42.0

mg for Cu (II) complex. Both of the complexes have been gradually heated from 50 to 700°C.

3. Results and Discussions

Chemical composition of the complexes:

- For Ni (II) complex compound with oxamide

Experimental: C, 14.51; N, 16.67; O, 23.16; K, 24.08; Ni, 17.72;

Theoretical, considering the formula: $K_2[Ni(NHCOCONH)_2] \cdot H_2O$: C, 14.69; N, 17.13; O, 24.86; K, 23.85; Ni, 17.90.

- For Cu (II) complex compound with oxamide

Experimental: C, 15.49; N, 17.66; O, 20.64; K, 24.57; Cu, 20.31;

Theoretical, considering the formula: $K_2[Cu(NHCOCONH)_2]$: C, 15.30; N, 17.85; O, 20.39; K, 24.85; Cu, 20.24.

X-Ray analysis

The experimental data have been interpreted using CELLREF and DICVOL software on multiphase system program, giving the final volume for cells and the estimated symmetries.

For Ni (II) oxamide complex it has been obtained the X – ray diffraction pattern presented in Fig.1.

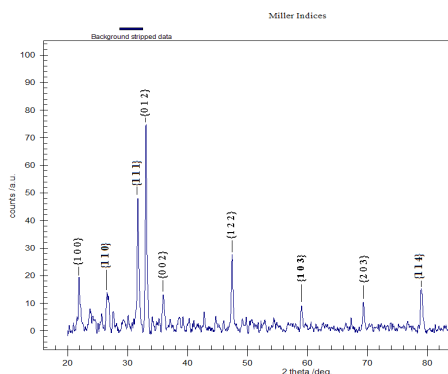


Fig.1. X ray diffraction pattern for Ni (II) complex compound

The volume for elementary cell of Ni (II) complex is 124.5319 Å.

For Cu (II) oxamide complex the X – ray diffraction pattern is presented in Fig. 2.

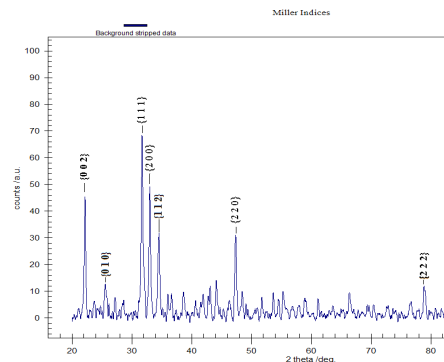


Fig. 2. X ray diffraction pattern for Cu (II) complex compound

The volume for elementary cell is 124.9990 Å for Cu (II) complex.

The relative peak intensities and the position of diffraction peaks in the XRD patterns obtained after coordination conclude that both complexes have the characteristics of a tetrahedral symmetry.

The cell volume increase from Ni (II) to Cu (II), values which are in good agreement with metal ions radii for Ni(II) and Cu(II) when forms square- planar complexes: $r_{Ni^{2+}} = 63\text{pm} < r_{Cu^{2+}} = 71\text{pm}$.

Vibrational analysis

In table 1 are presented the frequencies and proposed assignments for Ni (II) and Cu (II) complexes according to literature data [4].

Table 1 Vibrational analysis for the new complex compounds

Assignment	ν (cm ⁻¹) Ni (II) complex	ν (cm ⁻¹) Cu (II) complex
$\nu_{OH(H_2O)}$	3436.8 (s) 3386.7 (s)	3485.1 – 3318.4 (strong band)
ν_{asNH} ν_sNH	3325.0 (s) 3230.0 (s)	3202.4 -3166.9 (s)
$\nu_{CO(amide I)}$	1664.4 (m) 1640.0 (m)	1674.2 (s) 1668.0 (s)
$\nu_{CN(amide)}$	1422.1 (w) 1410.6 (w)	1478.6 (w) 1403.4 (m)
$\rho(NH_2)$	1105.5 (v w) 1030.4 (w)	1085 (w) 1047 (m)
$\omega(NH_2)$	791.0 (w, sh)	814.4 (w) 770.2 (w)
$\delta(NCO)$	686.6 (m) 632.0 (m)	721.3 (w) 688.9 (w)

The IR spectra for Ni (II) and Cu (II) complexes were comparatively analyzed with other square-planar complexes containing bidentate ligands [5, 6] and with IR spectra for pure oxamide.

The spectra of pure oxamide exhibits a strong band at 3380cm^{-1} (vs) due to NH_2 stretching vibrations, but this band do not exist in IR spectra for Ni (II) and Cu (II) complexes. For the complexes ν_{NH} exhibits at 3325cm^{-1} for Ni (II) complex and at 3202.4cm^{-1} for Cu (II) complex.

Also, in the IR spectra of oxamide exists a strong absorbtion band at 1343cm^{-1} due to C-N stretching vibration, but in IR spectra for the complexes exist two bands, as follows: for Ni(II) complex at 1422.1cm^{-1} (w) and 1410.6cm^{-1} (w) and for Cu (II) complex 1478.6cm^{-1} (w) and 1403.4cm^{-1} (m).

These observations suggests that oxamide is reacting by both N- donor atoms with metal ions, in the anionic form and confirm that the coordination process has been functioned.

Thermal behaviour of the complexes

The experimental data indicates that the decomposition modes of the complexes occur in diferent ways for the complexes.

The TG and DTG curves for Ni (II) complex is presented in Fig.3.

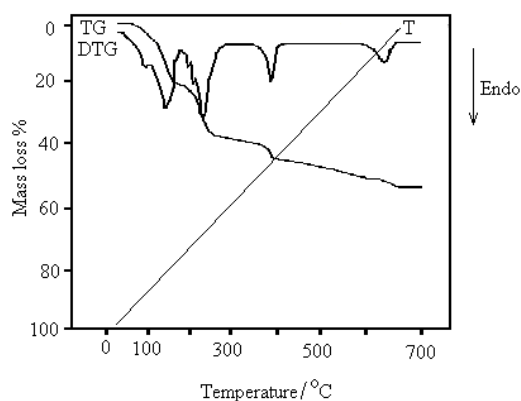


Fig.3. Thermo gravimetric data for Ni(II) oxamide complex compound

For this complex the thermal decomposition in air occurs in five steps, all of them being endothermic processes.

The first step of decomposition occurs in $64 - 97^\circ\text{C}$ temperature range. The observed mass loss is 1.25 mg which corresponds to a half mool of water (calcd: 1,278 mg) this process representing the total dehydration of the complex.

The second step occurs in $97 - 250^\circ\text{C}$ and corresponds to the ligand degradation. This degradation stage flows by forming some instable intermediates, in two steps, which couldn't be isolated.

At the end of decomposition the residue mass is 27.75 mg represented by NiO and K_2CO_3 (1:1), in this case the mass loss calculated is 30.27 mg

The TG and DTG curves for Cu (II) complex is presented in Fig.4.

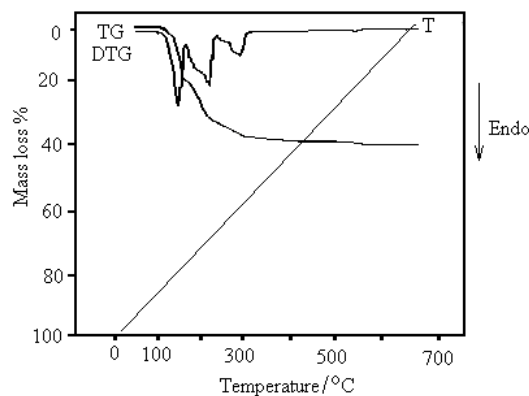


Fig. 4. Thermo gravimetric data for Cu (II) with oxamide complex compound

The complex start to decompose in $106 - 305^\circ\text{C}$ temperature range and the decompositon process include three main steps which are rapidly developing. On this domain of temperature, $(\text{dm}/\text{dt})_{\text{max}}$ are: 146°C , 236°C and 285°C but the intermediates formed couldn't be isolated, the same as Ni - oxamide complex.

The residue left after decompositon of 28.25 mg is represented by CuO and K_2CO_3 (molar ratio 1:1). The calculated mass for residue is 29.14 mg which are in good agrement with the obtained mass for residue at the same molar ratio.

4. Conclusions

The analytical data, crystallographic, IR spectra and thermal analysis confirm that the Ni (II) complex compound with the formula $K_2[Ni(NHCOCONH)_2] \cdot H_2O$ and the Cu (II) complex compound with the formula $K_2[Cu(NHCOCONH)_2]$ have been obtained and the structures of the coordinated complexes are very similar.

The thermal analysis show that Ni (II) complex with oxamide is more stable at higher temperatures than the Cu (II) coordination complex and demonstrate that the Cu-ligand bond is weaker in Cu(II) complex with oxamide. At the Ni (II) complex, the increase strength of the Ni – ligand bond means a lower density on the nitrogen, which results in a decrease of ν NH and ν CN, as obtained in FT-IR spectra.

5. References

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