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SPECTRAL AND THERMAL STUDIES OF COPPER(II) COMPLEXES OF 3- AND 4-PYRIDINEALDOXIME

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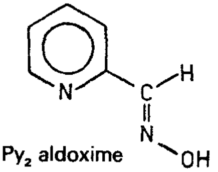
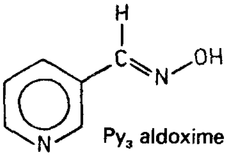
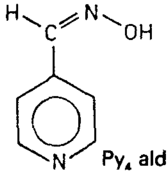
Copper(II) complexes of 3- and 4-pyridinealdoxime have been prepared and analyzed by spectroscopic (ir and diffuse reflectance) and thermoanalytical (TG, DTG and DTA) techniques. For both these systems, only species with metal : organic ligand : chloride ratio of 1 : 2 : 2 were found, and the organic ligand appears as a neutral molecule. The spectral data suggest a polymeric structure where the copper(II) ions are in a distorted octahedral environment.

The thermal decompositions occur through the reduction of copper(II) to copper(I) and the conversion of the residual organic ligand into acid amide, as found for dihydrogenbis(pyridine-2-aldoxime)copper(II) chloride, but the initial decomposition temperatures are slightly increased, giving rise to the thermal stability sequence:

$$[Cu(Py_4—CHNOH)_2Cl_2] \geq [Cu(Py_3—CHNOH)_2Cl_2] > [Cu(Py_2—CHNOH)_2]Cl_2$$


Py₂ aldoxime


Py₃ aldoxime


Py₄ aldoxime

In a recent paper [1] we reported in detail the thermal decompositions of three bis(pyridine-2-aldoxime)copper(II) complexes of the type $[Cu(Py_2—CHNO)_2H_n]Cl_n$ (where $n = 0$, 1 or 2). In order to investigate the effects of the position of the ligand substituent on the structure and thermal stability, the study is now extended to the copper(II) complexes of 3- and 4-pyridinealdoxime, the results being compared with those of the analogous complex of pyridine-2-aldoxime. With this view, the above-mentioned complexes have been prepared and analyzed by spectroscopic (ir and diffuse reflectance) and thermoanalytical (TG, DTG and DTA) techniques.

Experimental

Apparatus

The thermal measurements were carried out with a Perkin–Elmer TGS–2 thermal analyser and a DTA 1700. TG runs were made in vacuo or dynamic nitrogen or

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oxygen gas atmospheres with a flow rate of about 50 ml $\min^{-1}$; DTA runs were made in dynamic nitrogen or oxygen gas atmospheres. The heating rate was 0.5 or 10 deg.$\min^{-1}$, with samples of 4–6 mg.

Infrared (conventional and far-infrared) spectra were recorded with a Perkin–Elmer 983 spectrophotometer.

Diffuse reflectance and UV measurements were made using a Beckman DBG spectroreflectometer and a Perkin–Elmer 320 UV-Visible spectrophotometer.

Compounds

Dichlorodihydrogenbis(pyridine-3-aldoxime)copper(II) ([Cu(Py_3—CHNOH$)_2Cl_2$] and dichlorodihydrogenbis(pyridine-4-aldoxime)copper(II) ([Cu(Py_4—CHNOH$)_2Cl_2$] were prepared by the slow addition of a solution of organic ligand (0.01 mol in about 50 ml 95% ethanol) to a solution of copper(II) chloride dihydrate (0.0025 mol in about 40 ml distilled water). The pale yellow-green or pale blue-green complexes were filtered off, washed several times with water, then with ethanol, and finally, dried in vacuo over silica gel for about 48 h.

The results of chemical and spectroscopic analyses were in agreement with the proposed formulas. The slight solubility in water and the hydrolysis of both complexes at about pH 6 [2], however, prevented determination of the ionizaion constants and the synthesis of monohydrogen- and bis(pyridinealdoxime)copper(II) complexes, as occurs with pyridine-2-aldoxime as ligand [1].

Results and discussion

Spectral studies

3- and 4-pyridinealdoxime can act only as monodentate ligands, so that they cannot give rise to chelated complexes with metal ions as found in the case of pyridine-2-aldoxime.

The conventional and far-infrared spectra (Fig. 1) support this hypothesis. In fact, the shifts of the ring stretching vibration bands (ca. 1600–1400 cm^{-1}) to higher wavenumbers, the "in" and "out-of-plane" ring deformation vibration bands at ca. 659–456 cm^{-1} for the Py_3—CHNOH complex and at 670–456 cm^{-1} for the Py_4—CHNOH complex, ν_{M-Py} at ca. 265–260 cm^{-1} and the strong ν_{OH} bands in the region 3380–3320 cm^{-1} suggest the coordination of the neutral ligand molecules through the pyridine nitrogen [3, 4]. The absence of significant bands in the range 400–300 cm^{-1} suggests that the nitrogen atoms of the oxime group are not coordinated and excludes the presence of terminal Cu—Cl bonds, supporting the hypothesis of bridging metal-halogen bonds: halogens tend to form bridges between two metal atoms and the MX stretching frequences ($\nu_b(MX)$) are lower (ca. 290, 240 cm^{-1}) than in the terminal case (ν_t (MX)) [5]. The complexes exist in distorted octahedral polymeric form, as found by Clark and Williams [4] for the complex [$CuPy_2Cl_2$].

This last hypothesis is also proved by the diffuse reflectance spectra, which are similar to that reported by Holmes et al. [6] for [$Cu(Py_2$—$CHNOH)Cl_2$]. Each compound exhibits a single band (of weaker intensity than that of the corresponding Py_2—CHNOH complex) at about 15,000 cm^{-1} (Fig. 2), which proves that the copper(II) ions are in a tetragonally distorted octahedral environment, with four short metal-ligand bonds in the XY plane and two longer metal-ligand bonds lying along the Z axis above and below this plane [7].

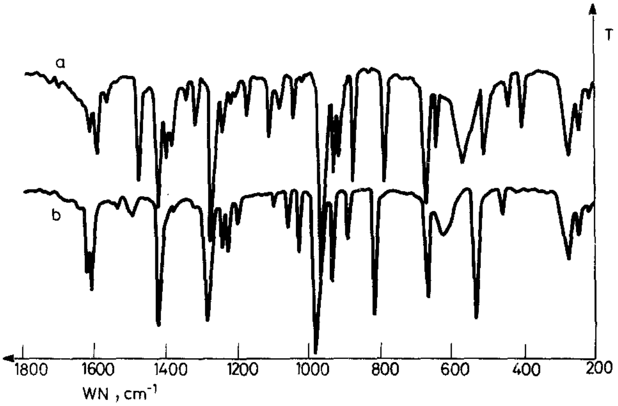

Fig. 1 Infared spectra for: (a) [$Cu(Py$—$CHNOH)_2Cl_2$]; (b) [$Cu(Py_4$—$CHNOH)_2Cl_2$]

Thermal studies

The two complexes exhibit almost the same decomposition behaviour.

Thermogravimetry in vacuo (Fig. 3) shows that the complexes are stable up to about 155° (Py_3—CHNOH) and 160° (Py_4—CHNOH) and then decompose in separate steps, the first of which corresponds to a loss of about 1.5 mole of organic ligand and 1 mole of chloride per mole of complex (ca. 58% mass loss). The chemical and spectroscopic analyses of the intermediates obtained by interruption of the heating of the samples at ca. 220° reveal that the first step of decomposition occurs with a rearrangement of the ligand as found for [$Cu(Py_2$—$CHNOH)_2]Cl_2$ [1]. In fact, the decomposition proceeds through the copper(II) to copper(I) reduction (iodometric analysis) and pyridinealdoxime rearrangement into the corresponding acid amide (UV and ir spectra).

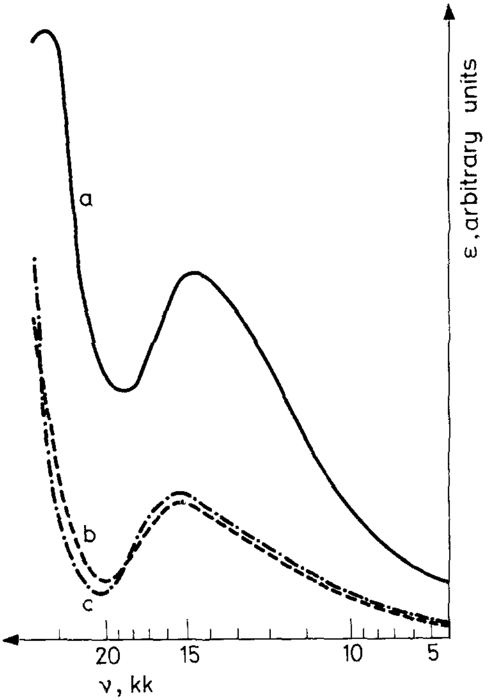

Fig. 2 Diffuse reflectance spectra for: (a) [Cu(Py$_2$—CHNOH)$_2$]Cl$_2$; (b) [Cu(Py$_3$—CHNOH)$_2$Cl$_2$]; (c) [Cu(Py$_4$—CHNOH)$_2$Cl$_2$]

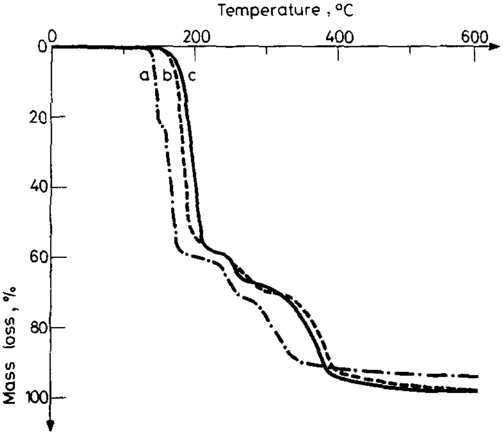

Fig. 3 TG curves in vacuo for: (a) [Cu(Py$_2$—CHNOH)$_2$]Cl$_2$; (b) [Cu(Py$_3$—CHNOH)$_2$Cl$_2$]; (c) [Cu(Py$_4$—CHNOH)$_2$Cl$_2$]

The successive thermal decomposition processes lead to a very slight residue of metallic copper, at ca. 400–500°, because of the sublimation of copper chloride.

In a dynamic nitrogen atmosphere the initial decomposition temperature is slightly increased (about 5°), while in oxygen a larger temperature increase occurs (about 10–15°). The decomposition again occurs through the copper(II) to copper(I) reduction and organic ligand rearrangement, but the intermediates at about 220° are probably a mixture of two or more compounds (mass loss ca. 30–40%). The successive thermal decomposition processes involve two steps, at ca. 225–275° and 275–475° in oxygen (residue 21.0%, calcd. for CuO 21.00%), and 225–275° and 275° →in nitrogen atmosphere.

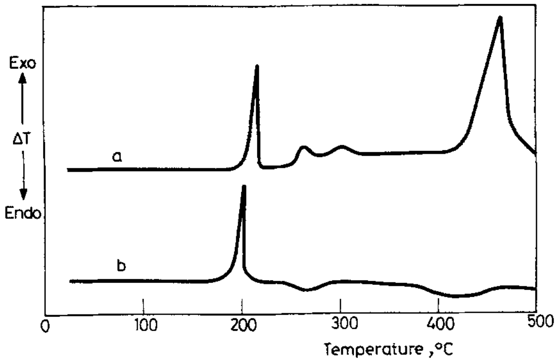

Fig. 4 DTA curves for [Cu(Py_3—CHNOH$)_2$Cl]: (a) in an oxygen atmosphere; (b) in a nitrogen atmosphere

The DTA curves (Fig. 4) in oxygen atmosphere show an exothermic peak corresponding to the first decomposition process of the complexes: the absence of the initial endothermic process found for [Cu(Py_2—CHNOH$)_2$]Cl_2 and assigned to the initial chloride loss [1] suggests that, for Py_3—CHNOH and Py_4—CHNOH, the decomposition process begins with the loss of organic ligand. The oxidative decomposition of the intermediates produces some large unresolved exothermic peaks. In dynamic nitrogen atmosphere the first exothermic decomposition process is not modified, proving the initial non-oxidative transformation of the complexes into the stable intermediates, while the oxidative decomposition of the intermediates occurs to the accompaniment of small endothermic peaks.

Conclusion

The spectral data suggest the proposed polymeric structure for [Cu(Py$_3$—CHNOH)$_2$Cl$_2$] and [Cu(Py$_4$—CHNOH)$_2$Cl$_2$] (Fig. 5), where the copper(II) ions are in a distorted octahedral environment. The polymeric form contains chloride bridging, whereas in [Cu(Py$_2$—CHNOH)$_2$]Cl$_2$ only terminal chlorides are involved (monomeric form). The proposed structure agrees with the very slight solubility and the lower stability in water than that of the chelate obtained with pyridine-2-aldoxime.

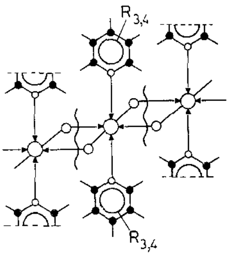

Fig. 5 The proposed structure for the [Cu(Py$_3$—CHNOH)$_2$Cl$_2$] and [Cu(Py$_4$—CHNOH)$_2$Cl$_2$] complexes

The thermal decomposition of these complexes occurs through analogous mechanisms as described for [Cu(Py$_2$—CHNOH)$_2$]Cl$_2$, but the initial decomposition temperature is shifted, giving rise to the thermal stability sequence (in vacuo):

$$[\mathrm{Cu(Py_4{-}CHNOH)_2Cl_2}] \geqslant [\mathrm{Cu(Py_3{-}CHNOH)_2Cl_2}] > [\mathrm{Cu(Py_2{-}CHNOH)_2}]\mathrm{Cl_2}$$

The higher thermal stability, the influence of the atmosphere in the furnace chamber and the absence of the initial endothermic process from the DTA curves suggest that the decomposition process begins with partial organic ligand decomposition, while the loss of the chloride occurs almost simultaneously, not as for [Cu(Py$_2$—CHNOH)$_2$]Cl$_2$.

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Zusammenfassung — Kupfer(II)-Komplexe von 3- und 4-Pyridinaldoxim wurden hergestellt und spektroskopisch (IR und diffuse Reflexion) sowie thermoanalytisch (TG, DTG und DTA) analysiert. Für beide Systeme wurden nur Species mit einem Metall : Ligand : Chlorid-Verhältnis von 1 : 2 : 2 gefunden. Der organische Ligand liegt als neutrales Molekül vor. Die Spektren deuten auf eine polymere Struktur hin, in der die Kupfer(II)-Ionen in einer verzerrten oktaedrischen Koordination vorliegen. Die thermischen Zersetzungen verlaufen über die Reduktion von Cu(II) zu Cu(I) und die Umwandlung des verbleibenden organischen Liganden in Säureamid, wie für Dihydrogen-bis(pyridin-2-aldoxim)-kupfer(II)-chlorid gefunden wurde, aber die Temperaturen des Beginns der Zersetzung und damit die thermische Stabilität steigen in der Reihenfolge $[Cu(Py_4—CHNOH)_2Cl_2] \geqslant [Cu(Py_3—CHNOH)_2Cl_2] > [Cu(Py_2—CHNOH)_2]Cl_2$ etwas an.

Резюме — Получены и изучены термоаналитическими методами (ТГ, ДТГ и ДТА) и спектроскопическими методами (ИК спектроскопия и спектроскопия диффузного отражения) комплексы двухвалентной меди с 3- и 4-пиридинальдоксимами. В обоих комплексах молярное соотношение металл : органический лиганд : хлорид составляло 1 : 2 : 2, а органический лиганд находился как нейтральная молекула. На основе спектральных данных для комплексов предложена полимерная структура, где ионы двухвалентной меди находятся в нарушенном октаэдрическом окружении. Термическое разложение происходит через стадию восстановления двухвалентной меди до одновалентной и превращением оставшегося органического лиганда до амида в случае дигидрогенбис-(пиридин-2-альдоксим)-хлорида меди. Вместе с тем, начальные температуры разложения слегка завышены, располагаясь в следующей последовательности:

$Cu(4\text{-}Py\text{-}CHNOH)_2Cl_2 \geqslant Cu(3\text{-}Py\text{-}CHNOH)_2Cl_2 > Cu(2\text{-}Py\text{-}CHNOH)_2Cl_2$;