MIXED COMPLEXES OF CU(II)PAN WITH CHLORIDE AND BROMIDE IONS

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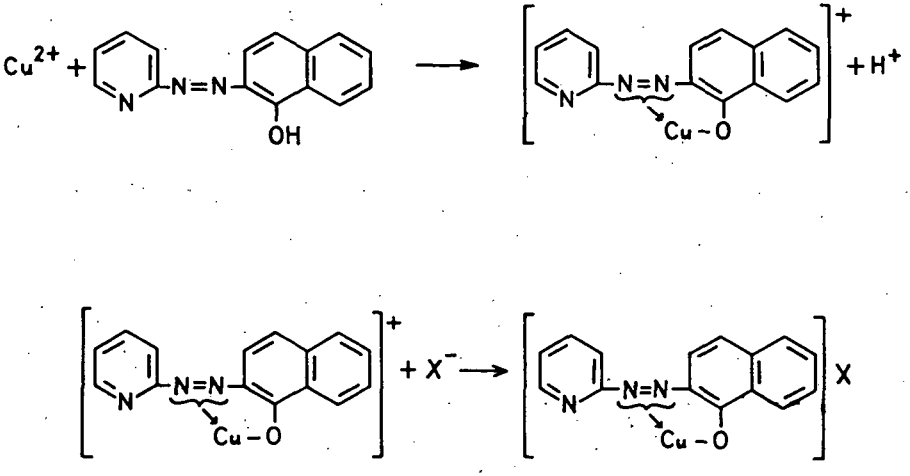
Cu-PAN-Cl and Cu-PAN-Br complexes have been prepared and their structure and composition studied.

Introduction

An orange red dye 1-(2-pyridylazo-)-2-naphtol (PAN) as a valuable indicator has been introduced by CHENG and his co-workers [1—5] in the complexometric titrations of copper, zinc, cadmium and indium solutions with ethylenediaminetetraacetic acid. Recently the stability constants of complexes of Ni, Co, Zn, and Mn ions with PAN in some aqueous-organic mixtures were calculated. The extraction mechanisms of PAN complexes of the metals mentioned above have not been sufficiently studied, but it is evident that in the case of extraction of indium, iron(III), cobalt(III), yttrium, palladium(II), rhodium(III) or iridium with PAN [9—13], mixed complexes are formed with outer anion to produce uncharged complexes. The structures of complexes extractable in chloroform or other organic solutions have not been investigated so far. The aim of the present paper is to study the problem of Cu(II) PAN yielding uncharged mixed complexes with bromide and chloride ions.



$X^- = Cl^-$ or Br^-

Experimental

Materials: $CuSO_4 \cdot 5\,H_2O$ KBr, KCl, p. a. PAN, (REANAL). IR Spectra were taken with an UNICAM SP 200 Spectrometer. Samples were prepared in Merck UVASOL KBr. Preparation of complexes: 2 ml of aqueous 10^{-1} M $CuSO_4 \cdot 5\,H_2O$ was added to 2 ml of ethanolic solution, saturated with PAN, then 2 ml of 5 M aqueous KBr or 2.5 M aqueous KCl was added. Within some minutes a violet red precipitate was formed which after centrifugation was dried over anh. $CaCl_2$ and P_2O_5.

Results

Microanalitical combustion method was used to determine the carbon-, hydrogen, and nitrogen-content. After fuming the complexes with H_2SO_4—$HClO_4$ mixture, copper was determined volumetrically by the iodide-thiosulphate method. Halide was determined gravimetrically as silver halide. The results were as follows:

Cu-PAN-Cl, found: Cu 17.95 C 50.85 N 3.88 H 3.10 Cl 9.76 O 14.44, calc: Cu 18.05 C 51.13 N 3.98 H 3.12 Cl 10.05 O 13.63%.

Cu-PAN-Br, found: Cu 15.95 Br 19.90 O 13.10 N 3.62 H 2.99 C 44.50. calc: Cu 16.04 Br 20.18 O 12.40 N 3.52 H 2.80 C 45.45.

Infrared spectra have been taken. From the curves the following could be established.

In the spectrum of PAN the following peaks appear: 755 cm^{-1} and 841 cm^{-1} aromatic ring, 1215 cm^{-1} (strong) ($\nu C-O$), 1510 cm^{-1} ($\nu N=N$), 1603 cm^{-1} pyridine aromatic ($\nu C{=}{-}C$), further 1563, 1572, 1625 cm^{-1} aromatic ($C{=}{-}C$), 2200 cm^{-1}, 3650 cm^{-1} broad associated OH. In the case of Cu-PAN-Br and Cu-PAN-Cl the OH peak does not appear and the 1510 cm^{-1} strong azo peak can be found at a considerably smaller wave number at 1375 cm^{-1}, in consequence of a metal-ion bond being formed.

No significant change was found with the wave numbers, of the aromatic groups except the peaks appearing about 1600 cm^{-1} which essentially gave two maxima at 1592 cm^{-1} and 1610 cm^{-1}.

Bromide and chloride ions have no influence on infrated spectra in the region measured. According to our assumption the formation of Cu-PAN, Cu(II)PAN-Br and Cu(II)PAN-Cl can be described as follows, Fig. 1. In our opinion the effect of substances accelerating the extraction of Cu(II)PAN into an organic phase can be explained by the formation of a neutral mixed complex.

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СМЕШАННЫЕ КОМПЛЕКСЫ Cu(II) PAN с ИОНАМИ ХЛОРИДА И БРОМИДА

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Авторы готовили комплексы Cu(II) PAN Cl и Cu(II) PAN Br и изучали их строение и содержание.