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Note

THERMOGRAVIMETRIC, IR SPECTROSCOPIC AND X-RAY DIFFRACTION STUDIES OF BIS-(2,9-DIMETHYL-4,7-DIPHENYL-1,10-PHENANTHROLINE)-COPPER(II) COMPLEX SUPPORTED ON SYNTHETIC ZEOLITE 3A

SATI PRASAD BANERJEE

Department of Chemistry, University of Saugar, Sagar 470003 (India)

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The organic reagent 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproin) has been used as an extracting agent for absorptiometric determination of copper(I) [1]. This organic reagent in ethanol has been interacted with aqueous copper(II) sulphate-pentahydrate using synthetic zeolite 3A in powder form as supporting medium. The interaction results in the formation of a blue sorbed derivative of 3A. The present study is devoted to the investigation of this derivative by thermogravimetric, IR spectroscopic and X-ray diffraction methods.

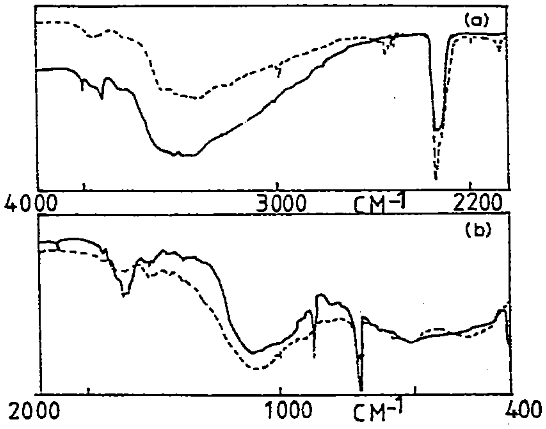

Fig. 1. IR spectra of the bis(bathocuproin)-Cu(II) complex supported on zeolite 3A (a) from 4000 to 2000 cm^{-1} and (b) from 2000 to 400 cm^{-1}. ———, Before TG analysis; - - - - - -, after TG analysis.

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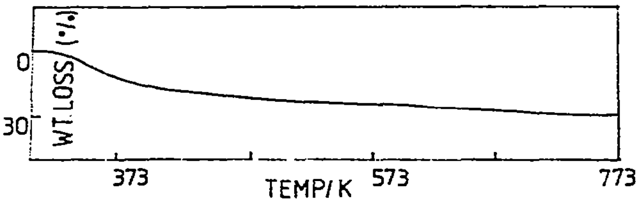

Fig. 2. TG plot of the bis(bathocuproin)-Cu(II) complex supported on zeolite 3A.

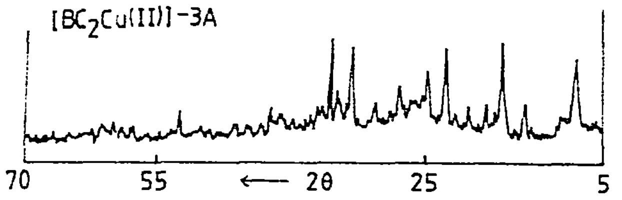

Fig. 3. X-Ray diffractogram of the bis(bathocuproin)-Cu(II) complex supported on zeolite 3A.

TABLE I

Comparative X-ray data for Cu(II)-exchanged and bis-(bathocuproin)-Cu(II)-sorbed derivatives of zeolite 3A

Data from ref. 6 for Cu(II)-3A			This work	
d(Å)	I/I_{max}	hkl	d(Å)	I[a]
			10.92	s
			9.21	m
6.51	30	111	6.42	m
			5.41	vs
5.12	30	210	5.22	m
3.96	100	220	3.90	vs
			3.62	s
3.22	20	222	3.21	s
2.98	10	321	2.92	m
2.69	10	322	2.69	vs
2.53	80	420	2.52	vs
2.17	5	333	2.19	m
1.97	5	440	1.97	w
1.84	5	610	1.82	w
1.76	10	620	1.74	w

[a] vs = very strong, s = strong, m = medium, w = weak.

EXPERIMENTAL

The details of the method of preparation of a similar complex-sorbed derivative of zeolite 3A have been mentioned in an earlier communication [2]. A portion of the air-dried sample was heated in a nickel crucible for several hours and another portion was extracted a number of times with 5 ml portions of hot (~ 373 K) amyl alcohol. Heating resulted in the formation of a yellowish-green residue while the amyl alcohol extracts gave a yellowish-red colour having $\chi_{\max} = 550$ mμ. Much of the complex, however, remained sorbed in the zeolite medium even after repeated extraction with hot amyl alcohol.

Percentages of copper in the original and preheated sorbed 3A zeolites were determined from their solutions in aqua regia using a Beckman Model 1272 Atomic Absorption Spectrometer and were found to be 3.10 and 2.29, respectively. IR Spectra of the original sorbed derivative and its residue remaining after TG analysis up to 773 K were recorded on a UR-10 Carl Zeiss Jena Spectrophotometer using 2 mg of the samples and 1 g of KBr between 4000 and 400 cm^{-1} frequencies. These spectra are reproduced in Fig. 1(a) (between 4000 and 2000 cm^{-1}) and Fig. 1(b) (between 2000 and 400 cm^{-1}) in which the continuous line represents the original complex-sorbed derivative and the broken line its preheated residue after TG analysis. TG plot (Fig. 2) of the complex supported on zeolite 3A was obtained on a DuPont 900 Thermal Analyzer using 12 mg of the sample at a heating rate of 10°C min^{-1} up to 773 K in air. An X-ray diffractogram of the sorbed derivative, as shown in Fig. 3, was used to evaluate the intensity and '*d*' spacings with respect to CuK_α radiation of 1.5418 Å wavelength for 2θ values from 5 to 70°. The X-ray data are given in Table 1.

RESULTS AND DISCUSSION

The IR spectra of the bis-(bathocuproin)-copper(II) complex supported on zeolite 3A and its residue after TG analysis up to 773 K show identical characteristics. A part from the usual hydrated aluminosilicate structure of the zeolite support represented by IR bands around 3600, 3400, 1650 and 1100 cm^{-1}, absorption bands for Cu(II)-Phen$_2$ complex are also found in these spectra [3]. Complete decomposition of the complex does not occur as a result of TG analysis at a slow and regulated rate of heating up to 773 K. Evidence of oxide formation is also not found. The band around 3400 cm^{-1} shows considerable stretching and relates to hydrogen bonding of the complex species.

Result of TG analysis shows that the sorbed zeolite derivative loses weight in three steps. A sharp rate of weight loss, 16%, up to about 393 K can be attributed to desorption of ethanol. Further weight loss steps, between 393 and 453 K and between 453 and 773 K, are due mainly to dehydration. The lower temperature dehydration accounts for 4% loss while at the elevated temperature the loss is 10%. The TG plot exhibits a very slow rate of weight loss beyond 453 K. The average activation energy for the three-step thermal events, evaluated from the TG data for $n = 1$ and 2 comes out to be only 35.2 and 25.9 kJ mole^{-1}, respectively [4]. This establishes the fact that oxidation of copper(II) does not occur up to 773 K. Analytical data for copper corresponds to 0.38 mole of the complex in the original sorbed derivative prior to heating. Strong heating results in a loss of copper as an insoluble residue. The yellowish-green residue formed due to direct heating in a nickel crucible contains partially oxidised copper(II) oxide to the extent of about 26% of the copper initially present as the complex. X-Ray diffractograms of a sample of Cu(I)Y zeolite, measured at different temperatures in air, showed the clear presence of CuO as a separate crystalline phase at about 603 K [5]. In the case of the preheated sorbed derivative of zeolite 3A a new inclusion complex is formed with the remaining copper.

X-Ray diffraction powder patterns of synthetic zeolite 3A and its Cu(II)-exchanged form have been reported earlier [6]. In case of the Cu(II)-exchanged derivative (1,0,0) and (1,1,0) reflections become completely diffused and indistinct. A comparison of structure of the cation-exchanged and the complex-sorbed derivatives of zeolite 3A can be made from the differences noted in the '*d*' spacings and nature of sorption established.

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