

## COMPLEXES OF COPPER(II) AND NICKEL(II) WITH A SCHIFF BASE BONDED TO A POLYMERIC SUPPORT

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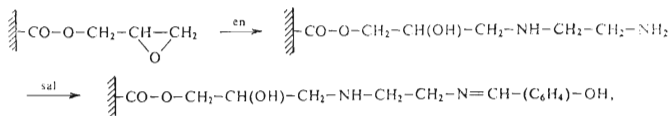
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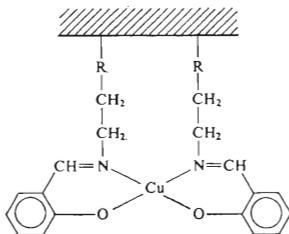
Copper(II) and nickel(II) ions were bonded in complexes of salicylideneimine type on a glycidyl methacrylate-ethylenedimethacrylate copolymer. The geometry of the complexes on the polymer was studied by measuring their magnetic properties, EPR spectra, and ultraviolet-visible spectra. Only paramagnetic complexes possessing a pseudo-tetrahedral configuration were found. The effect of the polymer matrix and of the immobility of the bonded Schiff base on the distortion of the coordination sphere of the central ion is discussed.

The oxiran groups of a macroporous glycidyl methacrylate-ethylenedimethacrylate copolymer can be modified with ethylenediamine (en) and salicylaldehyde (sal) to give the corresponding Schiff base, whereupon a sorbent is obtained capable



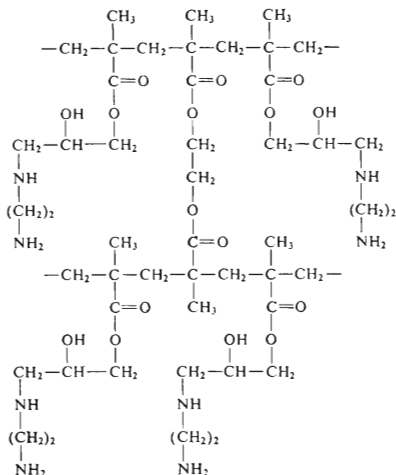
of binding metal cations. The cations only make use of the donor centres at the end of the side branch of the polymer matrix for the bonding, as is seen in the formula of the identified complex<sup>1</sup>.

The additional functional groups, *i.e.* N-alkylimine groups, and also oxygen from the OH groups of the polymeric ligand, remain free, without any bonding interaction with the cations<sup>1,2</sup>. Complexes formed by coordination of N-(*o*-hydroxybenzylidene)-alkylimine functional groups bonded to a polymeric support have been studied particularly for cobalt(II) (ref.<sup>1</sup>) for which the complexes in their low-molecular form are known to be able to reversibly transfer oxygen. It is supposed that the molecules assume a planar structure with free space between the layers and also between



the chelate rings in a plane; as a consequence, the diffusion of oxygen proceeds faster and cobalt atoms can be bonded *via* oxygen bridges<sup>3</sup>. In respect to this fact we concerned ourselves with the geometry of analogous complexes involving ligands from a macromolecular, insoluble support.

For complexes whose ligands are bonded to a polymer, changes in the spatial arrangement resulting from the lengthening and branching of the bridge between the salicylideneimine nitrogen atoms can be expected, analogous distortion of a square planar structure to a tetrahedral arrangement having been observed recently<sup>4-6</sup>.



Really, as will be clear from the schematic of the network of the modified copolymer, the =N—R—N= bridge in the bonded Schiff base extends over the polymeric matrix and is constituted by a long chain ( $R = 21$ ):

The aim of the present work was therefore to examine how the geometry of metal complexes with Schiff bases is affected by the bonding of the ligands to a polymeric matrix. Copper and nickel were used as the metals with regard to the stability of their complexes in air.

## EXPERIMENTAL

A glycidyl methacrylate-ethylenedimethacrylate macroporous copolymer (grain size 125  $\mu\text{m}$ , specific surface area 100  $\text{m}^2 \text{g}^{-1}$ ) was modified chemically with ethylenediamine and, subsequently with salicylaldehyde<sup>1</sup>. A similar procedure was applied to a layer of polyglycidyl methacrylate, deposited on porous Corning glass (content of polymer 16.2%, specific surface area 57  $\text{m}^2 \text{g}^{-1}$ ). The content of the bonded ethylenediamine groups was calculated based on the content of nitrogen in the polymer determined by elemental analysis, the content of bonded salicylaldehyde on the sorbent after the Schiff reaction was determined from the contents of carbon and nitrogen (Table I).

The copper(II) and nickel(II) complexes were prepared by reacting a suspension of the Schiff base-containing sorbent in ethanol (0.5–1 g in 20 ml) with a solution of acetate of the metal of interest, in a stoichiometric amount, in 50% ethanol. The complex was prepared either at room temperature, by shaking the mixture for 30 min, or at 80°C, by heating the mixture on water bath under reflux. The sorbent with the metal-polymeric ligand complex was collected on a glass filter, washed with ethanol to a negative reaction for the metal cation, and dried in air. The model  $N,N'$ -ethylenebis(*o*-hydroxybenzylideneimine) copper(II) and nickel(II) complexes were prepared by the published procedure<sup>7</sup>.

TABLE I

Analysis of the polymer samples with metals bonded in the Schiff base complexes

Modified polymer			Sample after the Schiff reaction			Content of metal after sorption		
C %	N %	ethylenediamine $\text{mmol g}^{-1}$	C %	N %	salicylaldehyde $\text{mmol g}^{-1}$	metal, %	$\text{mmol g}^{-1}$	
51.29	6.47	2.31	56.98	5.18	2.30	Cu	4.07	0.64
						Ni	2.11	0.36
						Ni	2.17	0.37 <sup>a</sup>
11.28	1.96	0.70 <sup>b</sup>	16.00	1.83	0.70	Ni	1.76	0.30
						Ni	1.94	0.33 <sup>a</sup>

<sup>a</sup> Temperature 80°C; <sup>b</sup> polymer layer deposited on glass.

The content of the metal bonded to the polymer was determined spectrophotometrically after elution with  $\text{HNO}_3$  ( $c = 1 \text{ mol l}^{-1}$ ) or after ignition of the sample and elution of the ashes with concentrated  $\text{HNO}_3$ ; nickel was determined with diacetyldioxime, copper with diethyldithiocarbamate<sup>8</sup>. The results are given in Table I.

The electronic reflection spectra of the solid samples were measured in the 200–850 nm region against MgO or the sorbent by means of an integrating sphere on a Perkin–Elmer 340 spectrometer. The EPR spectra were recorded at 20°C in air on a JEOL JES 3BX spectrometer; diphenylpicrylhydrazyl ( $g = 2.0037$ ) and Mn(II)-JEOL served as standards. The magnetic susceptibility of the bonded metal was measured by the Faraday method at room temperature using an apparatus after Vilím<sup>9</sup>. The magnetic moment of copper(II) or nickel(II) in the sample of the sorption material was calculated, based on the additivity rule, as

$$Z_s = x_p Z_p + x_m Z_m, \quad (1)$$

where  $\chi$ 's are the magnetic susceptibilities, the subscripts  $s$ ,  $p$ , and  $m$  refer to the sample in which the metal is bonded in the Schiff base complex, to the polymeric support with the bonded Schiff base, and to the metal, respectively;  $x$ 's are the corresponding mass fractions ( $x_p + x_m = 1$ ). After conversion to the molar susceptibility, correction was made for the diamagnetism of the cation<sup>10</sup>.

## RESULTS AND DISCUSSION

In the electronic spectrum of the square planar crystalline model compound  $[\text{Cu sal}_2 \text{ en}]$ , absorption bands are observed at 285 nm ( $\pi \rightarrow \pi^*$ ), 374 nm ( $\pi \rightarrow \pi^*$  or  $M-L$ ), and broad band at 572 nm ( $d-d$ ) (refs<sup>7,11</sup>). Similarly, the spectrum of the green coloured polymer with copper(II) complexes of the Schiff base exhibits charge transfer bands at 281 and 368 nm and a broad band in the  $d-d$  transition range, shifted towards higher wavelengths, see at 610 nm (Fig. 1). This bathochromic

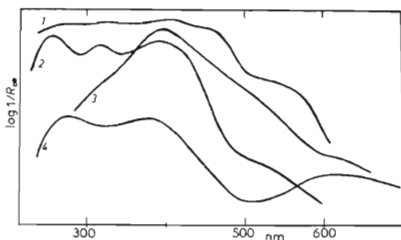


FIG. 1

Reflection spectra of nickel(II) and copper(II) salicylideneimine complexes.  $[\text{Ni sal}_2 \text{ en}]$  1, nickel(II) complex on the polymeric support 2, on the polymeric layer deposited on glass 3, copper(II) complex on the polymer 4

shift, occurring in the spectra of copper(II) complexes of a Schiff base as a result of symmetry change of the square planar molecule due to the lengthening of the carbon chain ( $C > 2$ ) between the two salicylideneimine nitrogen atoms<sup>11</sup>, stems from the higher distortion of the donor atoms from the planar arrangement. The remaining two absorption bands are only slightly shifted ( $\Delta\lambda = -4$  and  $-6$  nm, respectively).

The fact that the square planar geometry of the Schiff base copper(II) complex is distorted to a pseudo-tetrahedral geometry when the complex is bonded to a polymeric support is borne out also by the value of the magnetic moment of copper(II),  $\mu_{\text{eff}} = 2.02$  B.M. While in the square planar N,N'-ethylenebis(*o*-hydroxybenzylideneimine) copper(II) complex the magnetic moment of the metal is  $\mu_{\text{eff}} = 1.84$  B.M., this value increases up to  $\mu_{\text{eff}} = 1.94$  B.M. for the complex in which the ethylenediamine bridge is replaced by the  $=\text{N}-(\text{CH}_2)_4-\text{N}=\text{}$  bridge and the donor atoms are in a pseudo-tetrahedral arrangement<sup>11</sup>. The magnetic moment value is additionally raised owing to the lengthening and branching of the carbon bridge between the nitrogen atoms of the salicylideneimine groups, leading to a tetrahedral arrangement; for this arrangement values of  $\mu_{\text{eff}} = 1.9-2.2$  B.M. have been reported<sup>12</sup>.

An additional evidence of a distorted tetrahedral coordination is provided by the EPR spectrum, which is anisotropic, constituted by two superimposed singlet signals,  $g_{\parallel} = 2.0771$ ,  $\Delta H_{\text{pp}} = 17.6$  mT, and  $g_{\perp} = 2.0103$ ,  $\Delta H_{\text{pp}} = 2.8$  mT (Fig. 2).

Nickel complexes with salicylideneimine ligands exists in two isomeric forms, either in a square planar arrangement (green colour) or in a tetrahedral arrangement (brown colour)<sup>13</sup>. On the polymeric sorbent only the paramagnetic pseudo-tetrahedral form was observed even in conditions that for the low-molecular system favour the formation of the diamagnetic isomer<sup>14</sup>.

In the reflection spectrum of the crystalline model complex  $[\text{Ni sal}_2\text{en}]$ , bands are observed at 326 nm ( $\pi \rightarrow \pi^*$ ), 407 nm (c.t.), and 447 nm (c.t.,  $d \rightarrow \pi^*$ ) as a narrow shoulder, and in the region of  $d-d$  transitions a band is seen at 540 nm in the form

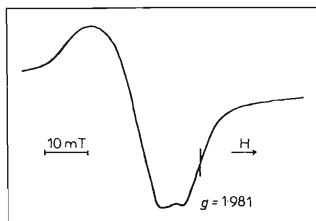


FIG. 2  
EPR spectra of the copper(II) complex of the Schiff base on the polymer

of a broad shoulder (Fig. 1). The brown polymer with the bonded nickel(II) complexes of the Schiff base exhibits bands at 250, 320, 400, and 498 nm. In the spectra of samples prepared by reaction of  $\text{Ni}^{2+}$  with the *N*-(*o*-hydroxybenzylidene) alkylimine functional groups of the polymer layer deposited on glass, the intense charge transfer band lies at 400 nm and the band of the *d*-*d* transitions appears at 600 nm, similarly as in the spectra of the brown nickel complexes with Schiff bases possessing a tetrahedral structure<sup>14,15</sup>.

The magnetic moments calculated for the nickel complexes of the Schiff base formed on the polymeric support at room temperature and at 80°C are  $\mu_{\text{eff}} = 3.2$  and 3.3 B.M., respectively. These values agree with the data reported for Ni(II) complexes of a Schiff base of salicylideneimine type with a pseudo-tetrahedral structure,  $\mu_{\text{eff}} = 3.2-3.3$  B.M. (ref.<sup>15</sup>). For the Ni(II) complexes prepared at room temperature and at 80°C on the polymer layer of the glass coating, the values are 3.8 and 3.9 B.M., respectively, in agreement with the magnetic moment of the tetrahedral nickel(II) complex.

The differences in the geometry of the coordination sphere of the copper(II) or nickel(II) complexes bonded to the two different supports result obviously from the differences in the structure of the polymeric matrix: the thin polymer layer on glass is constituted by polyglycidyl methacrylate with a low degree of cross-linking, and so after the modification the reactants have an easier access, as indicated also by the high degree of coordination saturation of the polymeric ligands. The ligand-to-metal ratio is 2 : 0.9, approaching the theoretical value of 2 : 1 (Table I). In the other sorbent type, the macroporous highly cross-linked copolymer, the mutual distance of the ligands is larger owing to the presence of the cross-linking agent (40%) and the mobility of the chains is also restricted; as a result, the ligands are less easily accessible, the degree of the coordination saturation of the polymeric ligands is lower, and the configuration of the complexes is distorted.

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