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CHARACTERIZATION OF COBALT(II) COMPOUND WITH
4-NITROSO-2,5-DIMETHYLRESORCINOL AND
CETYLPYRIDINIUM BROMIDE BY VISIBLE AND
INFRARED SPECTRA

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KOOBALT(II), 4-NITROSO-2,5-DIMETÜÜLRESORTSINOOLI JA TSETÜÜLPÜRIDIINIUMBROMIIDI REAKTSIOONIL TEKKIVA ÜHENDI ISELOOMUSTUS NAHTAVA JA INFRAPUNASE SPEKTRI ABIL. Ille JOHANNES, Jelena SIDORUK, Lilja LAHE

ХАРАКТЕРИСТИКА ПРОДУКТА РЕАКЦИИ КОБАЛЬТА(II) С 4-НИТРОЗО-2,5-ДИМЕТИЛРЕЗОРЦИНОМ И БРОМИДОМ ЦЕТИЛПИРИДИНИЯ СПЕКТРАМИ ВИДИМОГО И ИНФРАКРАСНОГО ИЗЛУЧЕНИЯ. Илле ИУХАНЕС, Елена СИДОРУК, Лилья ЛАХЕ

Key words: nitrosoalkylresorcinols, cobalt complexes, visible and IR-spectra.

In an earlier study [1] it was shown that in slightly acid solutions cobalt(II) and 4-nitroso-2,5-dimethylresorcinol (NR) formed a complex $\text{Co}(\text{NR})_3$, which precipitated as $\text{Co}(\text{NR})_3(\text{Am})_3$ when a cationic surfactant (Am) was added. I. Johannes, L. Mölder, and V. Ahelik [2] have developed a method for extracting or floating cobalt cations from waste water in the form of the complex $\text{Co}(\text{NR})_3(\text{Am})_3$. The reagent NR can easily be synthesized by nitrosing 2,5-dimethylresorcinol (R), a specific phenolic component separated from Estonian oil shale retort water [3]. Moreover, in recent papers [4, 5] Johannes, Mölder, et al. have proposed a new method for the selective colorimetric determination of resorcinol series phenols in total phenols. This method showed all the studied dialkylresorcinols to form complexes analogous with $\text{Co}(\text{NR})_3$.

Information on bondings between cobalt cation, NR and Am, and on structural schemes of $\text{Co}(\text{NR})_3$ and $\text{Co}(\text{NR})_3(\text{Am})_3$ is lacking. The aim of this short communication is to provide a provisional characterization of $\text{Co}(\text{NR})_3$ and $\text{Co}(\text{NR})_3(\text{Am})_3$ by colorimetric and IR-spectroscopic methods.

EXPERIMENTAL

There were five samples under investigation:

R — 2,5-dimethylresorcinol 98%, separated from oil shale phenols [3, 6-8];
NR — 4-nitroso-2,5-dimethylresorcinol, synthesized via the reaction of R with HNO_2 [1];

$\text{Co}(\text{NR})_3$ — a two-component complex, obtained by extracting the reaction product of $2 \cdot 10^{-4}$ M CoSO_4 and $6 \cdot 10^{-4}$ M NR from the water solution (pH 4.5) into butylacetate;

CP — cetylpyridinium bromide, "pure" grade, purchased from CHEMAPOL;
 $\text{Co}(\text{NR})_3(\text{CP})_3$ — a three-component compound, obtained by extracting the reaction product of $2 \cdot 10^{-4}$ M CoSO_4 and $6 \cdot 10^{-4}$ M CP solution in the (1:1)_{mol} mixture of butylacetate and butyl alcohol.

The absorption of water solutions was measured on a SPEKOL 11 spectrophotometer in the wavelength range of 400–600 nm. The IR spectra of dried samples in KBr disks (1–1.5 mg/200 mg) were recorded on a Specord 75 IR spectrometer.

RESULTS AND DISCUSSION

The water solutions of R and CP are uncoloured and show a negligible absorbance in the visible range. The solution of NR is yellow, the solutions of $\text{Co}(\text{NR})_3$ and $\text{Co}(\text{NR})_3(\text{CP})_3$ orange-red. The maximum molar extinction factors of cobalt complexes are about five times higher than that of an equivalent concentration of NR (Fig. 1). The observed bathochromical shift of the maximum absorbance from UV to 420 nm, when CP is added, suggests that a new three-component compound has been formed.

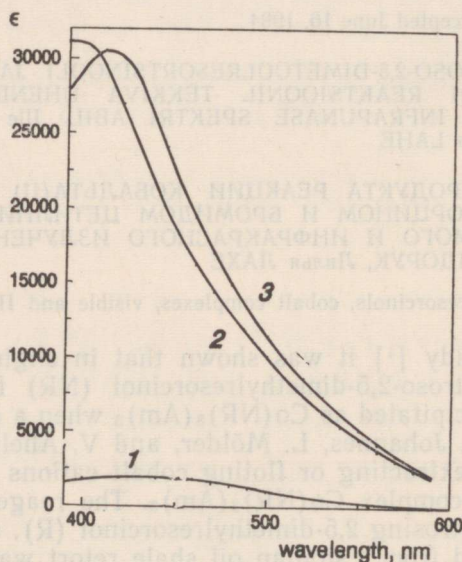


Fig. 1. Molar absorptivity. 1 — NR, 2 — $\text{Co}(\text{NR})_3$, 3 — $\text{Co}(\text{NR})_3(\text{CP})_3$.

The IR spectrum of R (Fig. 2, curve 1) has a characteristic wide absorption band at $3500\text{--}3000\text{ cm}^{-1}$ assigned to the O—H stretching vibration in the polymeric hydrogen bonded hydroxide groups. An intensive band at 820 cm^{-1} is probably due to the out-of-plane C—H deformations in the 1,2,3,5-displaced aromatic ring of R.

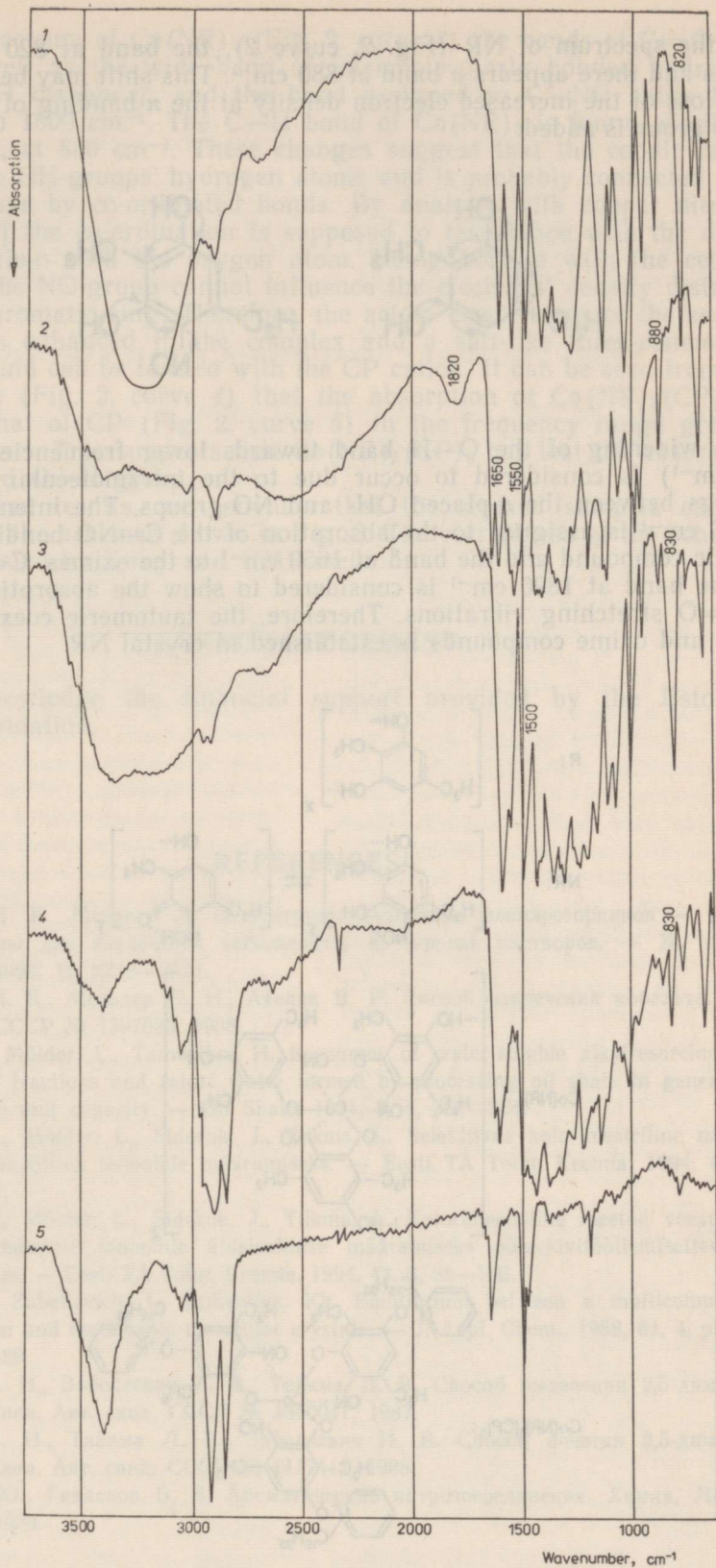
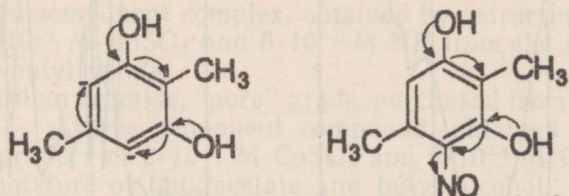


Fig. 2. IR spectra. 1 — R, 2 — NR, 3 — $\text{Co}(\text{NR})_3$, 4 — $\text{Co}(\text{NR})_3(\text{CP})_3$, 5 — CP.

In the spectrum of NR (Fig. 2, curve 2), the band at 820 cm^{-1} disappears and there appears a band at 880 cm^{-1} . This shift may be explained by the loss of the increased electron density at the π -banding of CH when the NO group is added:



The widening of the O—H band towards lower frequencies (2800 — 2300 cm^{-1}) is considered to occur due to the intramolecular hydrogen bondings between the *o*-placed OH- and NO-groups. The intensive band at 1550 cm^{-1} is assigned to the absorption of the C—NO bonding in the aromatic compound and the band at 1650 cm^{-1} to the oximes' C=N bonding. The band at 1820 cm^{-1} is considered to show the absorption due to the C=O stretching vibrations. Therefore, the tautomeric coexistence of nitroso and oxime compounds is established in crystal NR.

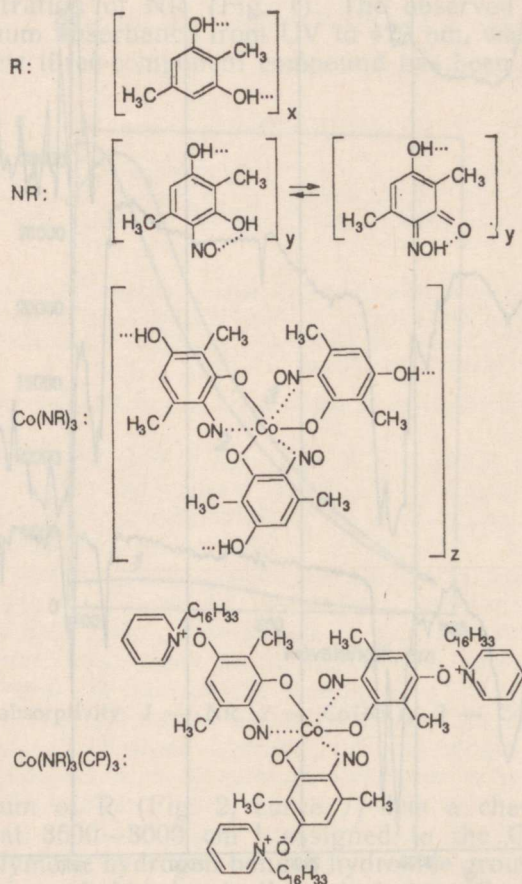


Fig. 3. Molecular schemes of the studied samples.

In the spectrum of $\text{Co}(\text{NR})_3$ (Fig. 2, curve 3) the bands of $\text{C}=\text{O}$ and $\text{C}=\text{N}$, as well as the wide band of intramolecularly bonded hydroxide groups $\text{O}-\text{H}$ disappear, and the band assigned to $\text{C}-\text{NO}$ shifts from 1550 cm^{-1} to 1500 cm^{-1} . The $\text{C}-\text{H}$ band of $\text{Co}(\text{NR})_3$ is found, similarly to that of R , at 830 cm^{-1} . These changes suggest that the cobalt cation displaces the OH -groups' hydrogen atoms and is probably connected with the NO -groups by co-ordinated bonds. By analogy with copper nitroso-phenolate [9] the co-ordination is supposed to take place with the nitrogen rather than with the oxygen atom. Being bonded with the central cobalt ion, the NO -group cannot influence the electrons' density distribution in the aromatic ring. Therefore, the acidic dissociation of the second OH -group is enhanced in the complex and a salt-like three-component ionic compound can be formed with the CP cation. It can be seen from the IR spectrum (Fig. 2, curve 4) that the absorption of $\text{Co}(\text{NR})_3(\text{CP})_3$ is similar to that of CP (Fig. 2, curve 5) in the frequency range greater than 2800 cm^{-1} . This suggests that $\text{Co}(\text{NR})_3(\text{CP})_3$ has lost the absorption of the second $\text{O}-\text{H}$ group.

From these results, we conclude that the studied samples can be described by the schemes shown in Fig. 3. The correctness of the schemes should be tested by X-ray and NMR-methods.

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