LONG-WAVELENGTH ABSORPTION SPECTRA OF COMPLEX COMPOUNDS OF ANILINE WITH METALS

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LONG-WAVELENGTH ABSORPTION SPECTRA OF COMPLEX COMPOUNDS OF ANILINE WITH METALS

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Recently synthesized (1) complex compounds of aniline with metals of the type $MeCl_2 \cdot 2PhNH_2$, $Me(NO_3)_2 \cdot 2PhNH_2$, and $MeSO_4 \cdot 2PhNH_2$ ($Me = Cu, Co, Zn$) are of great practical interest, especially for the chemical stabilization of soils (2). However, the structure of these compounds and the mechanism of their action in the hydrophobization of soils have not yet been sufficiently studied.

In (3,4), the infrared absorption spectra of the products of addition of aniline to the nitrate, chloride, bromide, acetate, and sulfate of divalent copper were investigated in the frequency region of the fundamental vibrations of the NH_2 group (3400–2900 cm^{-1}) and in the region 1600–700 cm^{-1}; changes in the frequencies of the stretching vibrations of the N—H and C—N bonds, as well as of the deformation vibrations of the amino group, as a result of complex formation were established and explained.

In the present work, absorption spectra of complex compounds of aniline with chlorides and sulfates of divalent copper, cobalt, and zinc have been obtained in the longer-wavelength region of the infrared spectrum (500–100 cm^{-1}), in which one should expect bands corresponding to stretching and deformation vibrations of metal–halogen, metal–nitrogen bonds, or any other bonds involving the metal.

There is still very little information in the literature on the manifestation of Me—N and Me—Gal bonds in the long-wavelength part of the spectrum. Meanwhile, the nature and properties of these bonds are very important for establishing the structure and properties of the complexes under investigation. In the absorption spectra of the compounds $[Me(NH_3)_6] \cdot Cl_3$ and $[Co(NH_3)_5 \cdot X] \cdot X_2$ (where $X = Cl, Br, J$ and $Me = Co, Ni, Cu, Cr$, and Pt), studied in the region down to 250 cm^{-1} (5), a number of bands were found which were assigned to stretching (bands in the interval 540–330 cm^{-1}) and deformation (330–159 cm^{-1}) vibrations of metal–nitrogen bonds. The manifestation of stretching vibrations of Me—N bonds as separate bands located in the region 530–280 cm^{-1} was also tentatively established in (6), where spectra of complexes of iron, cobalt, nickel, copper, and zinc with 2,2′-bipyridine and 1,10-phenanthroline were studied in the region from 5 to 40 μ.

Fig. 1. Absorption spectra of aniline (A), initial salts—cobalt, copper, and zinc chlorides (curves IIB, V, and G), and the products of aniline addition to these salts (curves IB, V, and G)

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Long-wavelength infrared spectra of metal anilides, as far as we know, have not been studied prior to the present work.

Experimental Part

The complexes $\mathrm{MeCl_2 \cdot 2PhNH_2}$ and $\mathrm{MeSO_4 \cdot 2PhNH_2}$ $(\mathrm{Me = Co, Cu, Zn})$ were synthesized by I. S. Bukhareva using the procedures described in ([3,4]). To obtain spectra in the region 20—100 μ, the substances under study, in the form of powders, were pressed with powdered polyethylene (transparent in the long-wavelength infrared region) in a weight ratio of $1:3$, under a pressure of about 200 $\mathrm{kg/cm}^2$, at room temperature, for a period of 3-5 min. The prepared samples were solid disks 45 mm in diameter and 0.35 mm thick.

The absorption spectra of the samples in the region 20-100 μ were recorded on a small single-beam vacuum spectrometer, described in detail earlier (7). With the filters used (two zero-order echellette gratings with a constant of 0.02 mm, crystalline quartz 2 mm thick, soot-coated polyethylene 2 mm, and a NaCl modulator), the parasitic short-wave radiation outside the blaze of the dispersion echellettes (12 lines/mm for the 20-50 μ region and 6 lines/mm for the 45-100 μ interval) did not exceed 5%. The spectral slit width S in cm^{-1} and the optical equivalent of the time constant of the receiving-recording system $v\tau$ (where v is the scanning rate of the spectrum and τ is the time constant, equal to 20 sec) are given in the upper part of Figs. 1 and 2. The accuracy of determining the positions of the maxima of the absorption bands in the region 400-200 cm^{-1} was ± 2 cm^{-1}, and in the region 200-100 cm^{-1}, ± 3 cm^{-1}. To increase the contrast of the spectra, the compounds studied were cooled to a temperature of $-110°$ with the aid of a special cryostat and liquid nitrogen. However, no significant narrowing of the bands in the spectra of the cooled samples, compared with spectra obtained at room temperature, was observed.

Results and Discussion

Figures 1 and 2 present the absorption spectra of the complexes studied, as well as the spectra of aniline and

Fig. 1. Absorption spectra of aniline (**A**), initial salts—cobalt, copper, and zinc chlorides (curves **IIB**, **V**, and **G**) and the products of addition of aniline

Fig. 2. Absorption spectra of cobalt, copper, and zinc sulfates (curves IIA, B, V) and products of aniline addition to these salts

Figure 2: Fig. 2. Absorption spectra of cobalt, copper, and zinc sulfates (curves IIA, B, V) and products of aniline addition to these salts

to these salts (curves **IB**, **V**, and **G**).

Fig. 2. Absorption spectra of cobalt, copper, and zinc sulfates (curves **IIA, B, V**) and the products of addition of aniline to these salts.

initial salts*. The spectrum of aniline at a layer thickness of 0.02 mm (Fig. 1A), like the spectrum of pure benzene studied by us earlier (^{8,9}), has no intense absorption bands in the region 20-100 μ. The greater, compared with benzene, nonselective absorption of aniline over the entire region investigated is apparently associated with the presence of a large dipole moment in aniline.

The spectra of the salts $MeCl_2$ (curves II in Figs. 1B and 1C) and $MeSO_4$ (curves II in Figs. 2A, B, and C) likewise contain no noticeable absorption bands, except for very weak bands at 326 and 282 cm^{-1} in the spectrum of $CuCl_2$, which in (^{11}) were observed at 329 and 277 cm^{-1} and were assigned to valence vibrations of Cu–Cl in infinite chains and between chains of copper chloride. The difference in the intensity of these bands and of the bands observed by us should apparently be explained by the difference in the crystal structure of the salts. Our samples probably had a simpler structure.

The spectra of the chloride and sulfate complexes of aniline, as was to be expected, are much more complex than the spectra of the initial salts and aniline. They contain a number of fairly intense absorption bands, among which it is not yet possible to isolate the bands corresponding to vibrations of metal–nitrogen bonds. To identify these bands it is necessary to supplement the study with spectra of aniline complexes with heavier metals (for example, Pt, Pb, or Bi), and also to extend the spectral region toward longer wavelengths.

The bands at 300 cm^{-1}, 225-238 cm^{-1}, and at 144 cm^{-1} in the spectra of the chloride complexes of aniline should evidently be assigned to vibrations of the Me–Cl bond. The band at 300 cm^{-1} agrees well with the previously found frequencies of valence vibrations of Me–Cl (312 ± 7 cm^{-1}) in the spectrum of the complex $CuCl_2 \cdot 2$ amin (^{10}) and 297 cm^{-1} in the spectrum of Py_2ZnCl_2 (^{11}). In the spectrum of $CoCl_2 \cdot 2PhNH_2$ (Fig. 1B, dashed curve) this broad band is split into two components, 316 and 301 cm^{-1}, apparently corresponding to symmetric and antisymmetric vibrations of the Co–Cl bond (^{11}). With better resolution such splitting should also be expected in the spectra of the chloride complexes of aniline with zinc and copper.

In conclusion, the authors take the opportunity to express their gratitude to Prof. M. S. Barvinok and I. S. Bukhareva for the synthesis of the complex compounds studied and for discussion of the results obtained.

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* All curves in Figs. 1 and 2 are the result of recalculation of two spectrograms recorded successively by the instrument: the transmittance curve of the sample under study and the transmittance curve of a pure polyethylene sample of the same thickness. To improve the accuracy of the data obtained, the spectra were recorded 3-4 times both at room temperature and at a temperature of −110°, after which the results were averaged. To check the results, spectra were also obtained for some of the salts ($CuCl_2$ and $CuCl_2 \cdot 2PhNH_2$) present as a paste in vaseline oil.

Note: Figure translations are in progress. See original paper for figures.