interpret the photoelectron spectra.

CONCLUSIONS

1. Charge-transfer complexes have been prepared from p-chloranil with \(N,N'\)-bis(salicylidene)ethylenediamine chelates of Co(II), Ni(II), Cu(II), and Zn(II).

2. Electronic and x-ray photoelectron spectra indicate the presence of a weak \(\pi-\pi\) interaction between the electronic systems of the chelate ligand as donor and p-chloranil as acceptor, supplemented by a local donor–acceptor interaction between the Cl atoms of p-chloranil as donor and the metal ion as acceptor.

LITERATURE CITED


MOLECULAR COMPLEXES OF CHELATES.

3.* REACTION OF BENZO[b]THIOPHENE-BASED TRANSITION-METAL CHELATES WITH p-CHLORANIL

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In continuation of our investigations [1, 2] into the donor–acceptor interactions between transition-metal chelates as donors and organic electron acceptors, we have prepared charge-transfer complexes (CTC's) of general formula (I)-(III) from benzo[b]thiophene-based transition-metal chelates and p-chloranil, and studied their electronic absorption spectra and x-ray photoelectron spectra

\[
\begin{align*}
\text{(I)-(III)} \\
X=O, \text{R=CH}_2\text{CH}_2\text{(Ia), R=O-C}_6\text{H}_4\text{(Ib); } \\
X=S, \text{R=CH}_2\text{CH}_2\text{(IIa), R=O-C}_6\text{H}_4\text{(IIb); } \\
X=\text{Se, } \text{R=CH}_2\text{CH}_2\text{(IIIa), R=O-C}_6\text{H}_4\text{(IIIb); } \\
\text{M=Gd(II), Ni(II), Cu(II), Zn(II), Cd(II).}
\end{align*}
\]

*See [1] for communication 2.
The starting chelates were synthesized and purified as described in [3-5]. Commercial p-chloranil was recrystallized twice from CH₃COOH. Molecular complexes (I)-(III) were prepared by mixing boiling solutions containing equimolar amounts of the donor and acceptor components in CHCl₃. The precipitates were recrystallized twice from chloroform. The products were colored substances melting with decomposition at >300°C.

The electronic absorption spectra of thin films of the samples deposited on quartz glass by vacuum sublimation were recorded with Unicam 700 and Specord UV-VIS spectrophotometers. The x-ray photoelectron spectra were recorded with an A.E.I. ES-100 spectrometer at -100°C as described in [6]. The spectra were excited by means of Al Kα radiation with an energy of 1486.6 eV. The standard used to determine the binding energies (Eb) was the Cls line hydrocarbons in adsorbed diffusion oil (Eb = 285.0 eV). The Eb values were determined correct to ±0.2 eV.

DISCUSSION OF RESULTS

In the electronic spectra of the chelates (Fig. 1), as in the spectra of transition-metal N,N'-bis(salicylidene)ethylenediamine chelates [1], we can distinguish three basic groups of bands: bands connected with absorption in the peripheral part of the ligand (250-300 nm); bands due to transitions in the coordination center of the chelate (300-400 nm); and intramolecular charge-transfer (IMCT) bands (400-550 nm). As in the case of the N,N'-bis-(salicylidene)ethylenediamine chelates, the bands observed in the 650-780 nm region are evidently due to intermolecular charge transfer between chelates molecules forming a dimer [7].

Comparison of the results obtained with the data in [1] shows that replacement of the benzene fragment by a benzo thiophene fragment in the transition-metal chelates results in a red shift of 20-25 nm in the absorption bands and in the appearance of new bands, connected with the absorption of the thiophene ring, in the ligand absorption region.

As in the case of the transition-metal N,N'-bis(salicylidene)ethylenediamine chelates, the maximum of the intramolecular charge-transfer band is shifted to shorter wavelength as the electronegativity (χ) of the metal atom increases (Table 1), irrespective of the nature of the heteroatom (X). Replacement of X = O by X = S or Se in the chelate of one and the same metal results in a red shift of the intramolecular charge-transfer band in accordance with the decrease in χ: O > S > Se (see Fig. 1 and Table 1).

The electronic spectra of CTC's (I)-(III) are similar to the spectra of the chelates from which they are derived. As in the case of the CTC's of p-chloranil with N,N'-bis(salicylidene)ethylenediamine chelates, the IMCT band undergoes a blue shift (see Table 1), evidently