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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Metal-Containing Polymers Based on Disalicylidenediamines and Their Electrophysical Properties

A. G. Ivanov[a,b], **B. V. Chernitsa**[a], **V. V. Shamanin**[a], **and L. V. Vinogradova**[a]

[a] *Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia*
[b] *St. Petersburg State Technological Institute (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia*
e-mail: alexey.ivanov@bk.ru

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Abstract—Metal-containing poly(disalicylidenediamines) exhibiting semiconductor properties were prepared by polycondensation of salicylidene derivatives of aromatic diamines with metal (Fe, Co, Ni, Cu) acetates. The data obtained confirm that the transfer of charge carriers in these polymers occurs along the chain through "nonclassical" polyconjugation zones formed via multiple intramolecular donor–acceptor interactions of lone electron pairs of the azomethine groups with the unoccupied d orbitals of the metal ions.

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Ample data obtained in the field of catalysis and chemistry of macromolecular, coordination, and organometallic compounds served as the basis for the development of practically important polymer systems containing bound metals [1–6].

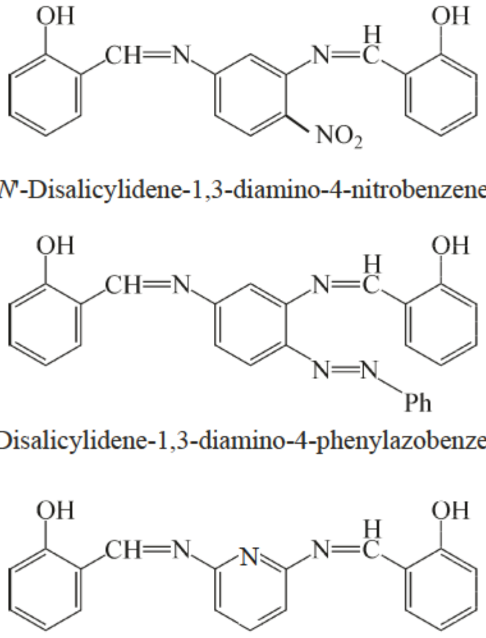
Metal atoms impart to metal-containing polymers a number of new properties, e.g., biological and catalytic activity, redox, photochemical, adsorption, electrophysical, magnetic, and other properties [3–5], which are of much practical interest. Such polymers show promise for the development of organic semiconductor materials for modern nano- and optoelectronics [7], for deposition of coatings preventing biofouling [3], for formation of nanoimprint resists [8], and for use in medicine, e.g., for preparing contrasting substances in tumor diagnostics [9].

For the use of the planar technology in fabrication of electronic devices (organic transistors, photoconverters, light-emitting diodes, displays, solar batteries, gas sensors, electronic optical switches, memory devices, etc.), metal-containing polymers should exhibit, along with electrical conductivity, also good film-forming properties. In turn, to prepare thin-film items by traditional methods (casting, dipping, sputtering, centrifugation, jet printing), the conducting polymers should exhibit good solubility and high adhesion to supports of different types. "Classical" conducting polymers (polyaniline, polypyrrole, polythiophene, polyphenylenevinylenes, etc.) are virtually insoluble in organic solvents. Metal-containing polymers prepared by various methods also seldom exhibit good solubility.

It was shown previously [10–12] that the organometallic polymers, poly(tetrasalicylidenetetramines), prepared by polycondensation are soluble film-forming semiconductors exhibiting photo- and dark conductivity [10–12]. Proceeding with studies in this field, we developed in this work the procedures for preparing new soluble conducting metal-containing polymers.

Salicylidene derivatives of diamines are a specific group of chelating agents capable of readily forming metal-containing complexes [13–17]. This feature was used in our study in developing methods for preparing metal-containing macromolecular compounds derived from disalicylidenediamines. The backbone of such polymers, poly(disalicylidenediamines), incorporates locally conjugated fragments: electron-donor azomethine groups and metal ions with unoccupied d orbitals as electron acceptors. As metal-containing component we

Scheme 1.



N,N′-Disalicylidene-1,3-diamino-4-nitrobenzene (**I**)

N,N′-Disalicylidene-1,3-diamino-4-phenylazobenzene (**II**)

N,N′-Disalicylidene-2,6-diaminopyridine (**III**)

used the Fe, Co, Ni, and Cu ions. We also studied the electrophysical properties of the new metal-containing polymeric structures with the aim of finding correlation between the structure, bond system, and nature of the metal component in the synthesized polymers.

EXPERIMENTAL

Monomers **I**–**III** were prepared by Schiff condensation of salicylaldehyde with 1,3-diamino-4-nitrobenzene, 1,3-diamino-4-phenylazobenzene, and 2,6-diaminopyridine.

Salicylaldehyde was taken in a double molar excess relative to the diamine. Dioxane was used as solvent. The product was purified by recrystallization from toluene. The product purity was checked by thin-layer chromatography (TLC). The yield of the monomers after purification reached 95%. The structure of the monomers was confirmed by spectroscopic methods (IR, ^{1}H NMR, UV spectroscopy) (Table 1). Elemental analysis of the monomers and polymers was performed with a LECO CHNS(O)-932 CHN analyzer (Leco Corporation, the United States). The content of the elements was consistent with the calculated values within the measurement uncertainty.

The polymers were prepared by polycondensation of monomers **I**–**III** (Scheme 1) with metal (Fe, Cu, Ni, Co) acetates taken in equimolar ratios in dimethylformamide (DMF) solution with stirring. The reaction was performed in a dry argon atmosphere for 6 h, after which the reaction mixture was evaporated in a vacuum rotary evaporator, and the dry residue was dissolved in methanol. The polymer was isolated by reprecipitation of the methanol solution of the polymer into diethyl ether. The reprecipitated polymer was washed with water (to remove the unchanged acetate) and dried. The polymer purity was checked by TLC. The yield of the polymers was 85–95%. The structure of the polymers was confirmed by spectroscopic methods (IR, ^{1}H NMR, UV spectroscopy) (Table 2).

The content of metals in the polymers was determined by X-ray fluorescence analysis (XFA, REAN analyzer, Scientific Devices Private Joint-Stock Company, Russia). Measurements were performed under the following conditions: X-ray tube voltage 25 kV, current 100 μA, measurement time 100 s without filtration of primary radiation, molybdenum anode. The X-ray fluorescence spectra of the polymers contained the K_α and K_β lines of cobalt (6.9 and 7.7 keV, respectively), nickel (6.3 and 7.1 keV, respectively), copper (8.1 and 8.8 keV, respectively), and iron (6.4 and 7.2 keV, respectively).

Table 1. Spectroscopic characteristics of monomers **I**–**III**

Monomer	Spectroscopic data
I	^{1}H NMR (DMF, δ, ppm): 13.1 s (2H, OH), 9.2 s (2H, CH=N), 6.9–7.6 m (11H, C_{ar}–H); IR (KBr, ν, cm^{-1}): 3310–2995 (OH); 1614 (C=N); 1584, 1545, 1510 (C=C); UV (methanol, λ, nm): 245 sh, 327 m, 410 w
II	^{1}H NMR (DMF, δ, ppm): 13.0 s (2H, OH), 9.0 s (CH=N), 6.9–7.6 m (16H, C_{ar}–H); IR (KBr, ν, cm^{-1}): 3310–2990 (OH); 1614 (C=N); 1582, 1550, 1510 (C=C); UV (methanol, λ, nm): 205 sh, 235 sh, 355 s
III	^{1}H NMR (DMF, δ, ppm): 12.9 s (2H, OH), 9.0 s (2H, CH=N), 6.9–7.6 (C_{ar}–H); IR (KBr, ν, cm^{-1}): 3250–2994 (OH); 1614 (C=N); 1580, 1550, 1510 (C=C); UV (methanol, λ, nm): 240 sh, 265 m, 330 w, 416 m

Table 2. Spectroscopic characteristics of poly(disalicylidenediamines) **IV–VI**

Polymer	Metal	Spectroscopic data
IV	Fe	^{1}H NMR (DMF, δ, ppm): 9.5 s (2H, CH=N), 6.8–7.8 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2995 (OH); 1604 (C=N); 1574, 1538, 1505 (C=C); UV (methanol, λ, nm): 327 sh, 436 s, 573 w
	Co	^{1}H NMR (DMF, δ, ppm): 9.5 s (2H, CH=N), 6.9–7.7 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2995 (OH); 1607 (C=N); 1588, 1541, 1512 (C=C); UV (methanol, λ, nm): 335 sh, 433 s, 568 w
	Ni	^{1}H NMR (DMF, δ, ppm): 9.7 s (2H, CH=N), 6.8–7.9 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2995 (OH); 1604 (C=N); 1586, 1543, 1518 (C=C); UV (methanol, λ, nm): 330 sh, 431 s, 564 w
	Cu	^{1}H NMR (DMF, δ, ppm): 9.6 s (2H, CH=N), 6.9–7.8 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2995 (OH); 1607 (C=N); 1581, 1543, 1515 (C=C); UV (methanol, λ, nm): 330 sh, 430 s, 569 w
V	Fe	^{1}H NMR (DMF, δ, ppm): 9.8 s (2H, CH=N), 7.1–8.0 m (16H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2990 (OH); 1607 (C=N); 1564, 1558, 1511 (C=C); UV (methanol, λ, nm): 215 sh, 245 sh, 481 w
	Co	^{1}H NMR (DMF, δ, ppm): 9.5 s (2H, CH=N), 7.0–7.9 m (16H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2990 (OH); 1607 (C=N); 1567, 1538, 1505 (C=C); UV (methanol, λ, nm): 217 sh, 258 sh, 445 sh, 515 w
	Ni	^{1}H NMR (DMF, δ, ppm): 9.7 s (2H, CH=N), 7.0–7.9 m (16H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2990 (OH); 1608 (C=N); 1556, 1547, 1515 (C=C); UV (methanol, λ, nm): 205 sh, 235 sh, 264 sh, 535 w
	Cu	^{1}H NMR (DMF, δ, ppm): 9.8 s (2H, CH=N), 6.9–7.9 m (16H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3310–2990 (OH); 1606 (C=N); 1572, 1541, 1519 (C=C); UV (methanol, λ, nm): 225 sh, 260 sh, 343 s, 535 w
VI	Fe	^{1}H NMR (DMF, δ, ppm): 9.7 s (2H, CH=N), 7.0–7.9 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3250–2994 (OH); 1605 (C=N); 1564, 1545, 1504 (C=C); UV (methanol, λ, nm): 262 sh, 345 sh, 414 s, 583 w
	Co	^{1}H NMR (DMF, δ, ppm): 9.7 s (2H, CH=N), 6.9–8.0 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3250–2994 (OH); 1605 (C=N); 1568, 1549, 1510 (C=C); UV (methanol, λ, nm): 273 sh, 336 sh, 414 s, 583 w
	Ni	^{1}H NMR (DMF, δ, ppm): 9.6 s (2H, CH=N), 7.0–8.0 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3250–2994 (OH); 1607 (C=N); 1559, 1543, 1519 (C=C); UV (methanol, λ, nm): 275 sh, 347 sh, 417 s, 589 w
	Cu	^{1}H NMR (DMF, δ, ppm): 9.6 s (2H, CH=N), 6.9–7.9 m (11H, C$_{ar}$–H); IR (KBr, ν, cm^{-1}): 3250–2994 (OH); 1603 (C=N); 1574, 1556, 1512 (C=C); UV (methanol, λ, nm): 265 sh, 342 sh, 410 s, 578 w

The ^1H NMR spectra of the comonomers and polymers as 10^{-1} M solutions in DMF-d_6 were recorded at room temperature with a Bruker Avance 200 DPX high-resolution NMR Fourier spectrometer operating at 200 MHz. The spectra were taken in the range 1–10 ppm.

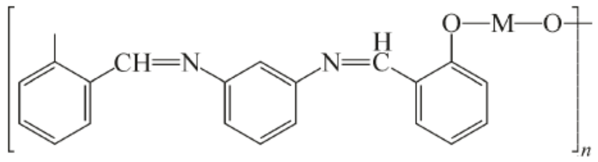
The electronic absorption spectra of the samples as 10^{-5} M methanol solutions were recorded with an SF-2000 spectrophotometer in the wavelength range 200–700 nm.

The vibration spectra of the comonomers and polymers prepared as KBr pellets were recorded with a Vertex Fourier spectrometer (Bruker) in the range 400–4000 cm^{-1}.

The number-average molecular masses M_n and the degrees of polymerization of the polymers were estimated by ^1H NMR spectroscopy from the content of residual terminal hydroxy groups. The values of M_n varied in the interval $(5–12) \times 10^3$, and the intrinsic viscosity of the polymer solutions, in the interval $[\eta] = 0.06–0.1$ dL g^{-1}.

The isothermal volt–ampere characteristics of the polymer samples were determined in the dc mode with the measurement installation of the Ioffe Physicotechnical Institute, Russian Academy of Sciences. From the values obtained, the resistance R and specific electrical conductivity σ were evaluated.

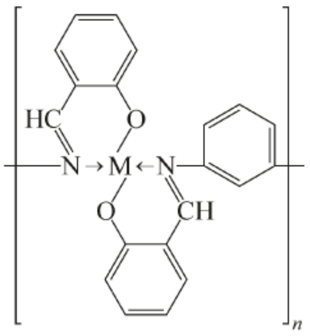
The series of the poly(disalicylidenediamines) differing in the substituent at the central phenylene fragment and in the metal atom in the backbone can be presented by the general structural formula:



where M is the metal atom (Fe, Co, Ni, Cu).

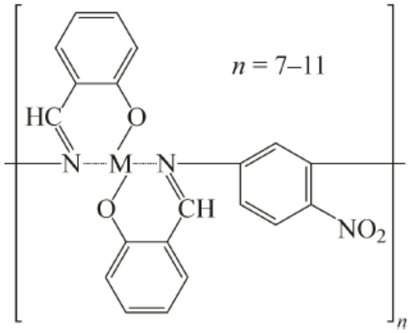
Such a structure does not suggest conducting properties of the material, because in its macromolecules there are no common polyconjugation zones present in “classical” polyconjugated polymers.

Previous studies on synthesis and properties of element-containing (Si, Ge, Sn) poly(tetrasalicylidenetetramines) [10–12] proved the occurrence of intramolecular donor–acceptor interactions of the valence shells of the element atoms with the π or n electrons of the atoms incorporated into the conjugated fragments, with the formation of intramolecular charge-transfer complexes. Therefore, there were good grounds to anticipate similar effects in the metal-containing poly(disalicylidenediamines):

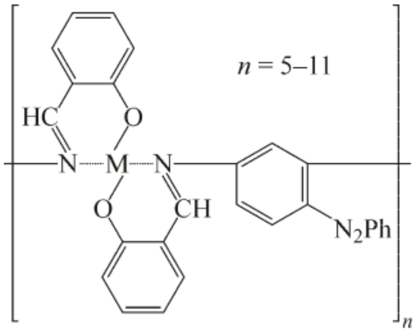


M = Fe, Cu, Ni, Co

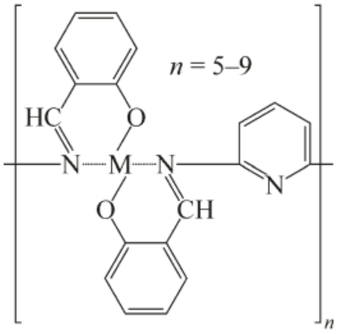
To prepare metal-containing poly(disalicylidenediamines), we synthesized monomers **I–III** containing different substituents in aryl fragments (nitro, phenylazo groups, pyridine nitrogen atom). From these monomers, we were able to prepare a series of polymers readily soluble in the majority of organic solvents: catena-poly[metal(μ-*N*,*N'*-disalicylidene-1,3-diamino-4-nitrobenzene- *O*,*N*;*O'*,*N'*)] (**IV**), catena-poly[metal(μ-*N*,*N'*-disalicylidene-1,3-diamino-4-phenylazobenzene-*O*,*N*;*O'*,*N'*] (**V**), and catena-poly[metal(μ-*N*,*N'*-disalicylidene-2,6-diaminopyridine-*O*,*N*;*O'*,*N'*)] (**VI**), where M = Fe, Co, Ni, and Cu:



IV



V



VI

Table 3. Electrical conductivity of poly(disalicylidenediamines) at $T = 300$ K

Polymer	Metal	Specific conductivity σ	σ_{max} after doping
		S cm^{-1}	
IV	Fe	5.3×10^{-7}	0.6×10^{-2}
	Cu	8.1×10^{-7}	1.3×10^{-3}
	Co	6.5×10^{-7}	1.9×10^{-3}
	Ni	6.9×10^{-7}	2.7×10^{-3}
V	Fe	0.7×10^{-7}	6.4×10^{-2}
	Cu	7.1×10^{-7}	7.6×10^{-2}
	Co	3.2×10^{-7}	5.0×10^{-2}
	Ni	9.2×10^{-8}	3.9×10^{-2}
VI	Fe	6.8×10^{-8}	1.5×10^{-3}
	Cu	5.3×10^{-8}	8.2×10^{-2}
	Co	7.5×10^{-8}	3.9×10^{-2}
	Ni	8.8×10^{-8}	$2.8\cdot \times 10^{-2}$

The choice of transition metal acetates as comonomers is governed by the fact that the acetate substituents are readily leaving groups. The possibility of the metal coordination with the nitrogen atoms of the azomethine group favors the condensation of the phenol group with the metal derivatives.

An IR study of the poly(disalicylidenediamines) containing the Fe, Co, Ni, and Cu atoms reveals certain general trends (Table 2). In going from one metal to another in the same series of the polymers, the intensities of the absorption bands vary similarly. The strongest effect is observed for the stretching vibration bands of the azomethine group ν(C=N). The intensity of the ν(C=N) band varies in the same direction as the acceptor power of the metal. The spectral data obtained allow the relative intensity of the azomethine absorption band, ν(C=N), to be considered as a criterion of the efficiency of the N → M donor–acceptor bonding in the metal-containing polymers obtained.

In the ^{1}H NMR spectra of the polymers, there are a series of signals in the range 7.0–8.0 ppm, corresponding to protons of aromatic rings (C_{ar}–H) and the azomethine proton (CH=N) signal in the range 9.5–9.7 ppm. The azomethine proton signal in the spectra of the polymers is shifted downfield relative to the monomers (Tables 1, 2). Such a shift of the azomethine proton signal in the spectrum of the polymer, as well as the above-given IR data, indirectly confirms the occurrence of nonzero donor–acceptor interaction between the lone electron pairs of the nitrogen atoms and unoccupied *d* orbitals of the metal ions in the polymer. The downfield shift of the azomethine proton signal indicates that the electron density on the azomethine group decreases, which is consistent with its electron-donor behavior in interaction with the metal ion.

In the electronic absorption spectra of the poly(disalicylidenediamines), there are charge-transfer bands in the range 550–650 nm. The main absorption bands at 250–400 nm, corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in aromatic and azomethine fragments (Fig. 1), undergo bathochromic shift (by 50–60 nm) with hyperchromic effect in going from the monomers (Table 1) to the polymers (Table 2), which suggests the formation of more extended conjugation zones in the macromolecules.

For all the polymers obtained, we performed electro-physical measurements. From the isothermal volt–ampere characteristics of the polymeric samples, we estimated their resistance *R* and specific electrical conductivity σ. The σ values at room temperature for all the polymers in the undoped stated appeared to be close: 10^{-7}–10^{-8} S cm^{-1}. On doping the polymer films with iodine, the conductivity σ increased by 5–6 orders of magnitude and reached 10^{-3}–10^{-2} S cm^{-1} (Table 3). Within the first 50 h of keeping the film in iodine vapor, the resistance *R* sharply decreased. Longer keeping of the samples in iodine vapor did not lead to further appreciable changes in their resistance. Similar changes in the conductivity on doping are observed for the majority of polyconjugated polymers exhibiting semiconductor properties. The conductivities of the poly(disalicylidenediamines) obtained allow them to be classed with semiconductor polymers.

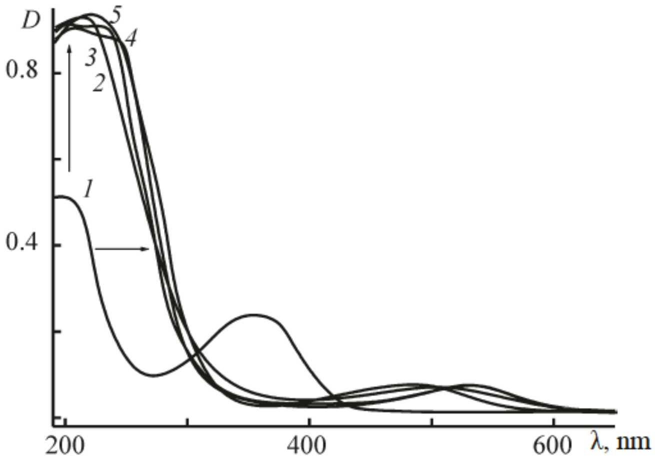
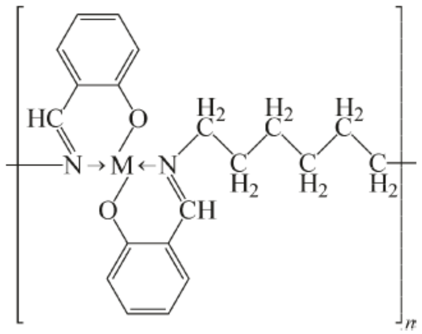


Fig. 1. UV absorption spectra of the (*1*) monomer, *N,N'*-disalicylidene-1,3-diamino-4-phenylazobenzene, and (*2*–*4*) polymers, catena-poly[metal(μ-*N,N'*-disalicylidene-1,3-diamino-4-phenylazobenzene-*O,N;O',N'*)]; M: (*2*) Co, (*3*) Ni, (*4*) Fe, and (*5*) Cu. (*D*) Optical density and (λ) wavelength; the same for Fig. 2. Arrows demonstrate the bathochromic shift of the absorption bands (along the abscissa), accompanied by the hyperchromic effect (along the ordinate).

The results of studying the electrophysical properties do not allow unambiguous conclusions on the mechanism of the electrical conductivity of the poly(disalicylidenediamines) obtained. If we assume that the main limiting mechanism of the charge transfer in the bulk of the polymer is interchain activation or tunnel electron hopping from one local conjugation region to another, then introduction of a short aliphatic spacer into the polymer chain should not significantly affect the electrophysical properties of the polymers. The occurrence of the "nonclassical" polyconjugation in this case would not be the decisive factor responsible for the conductivity. To check this assumption, we synthesized and studied organometallic poly(*N,N'*-disalicylidene-1,6-hexanediamines), catena-poly[metal(μ-*N,N'*-disalicylidiene-1,6-hexanediamine-*O,N;O',N'*)], where M = Cu, Co, or Fe, i.e., the polymers in which there is a relatively long hexamethylene spacer between the locally conjugated fragments:

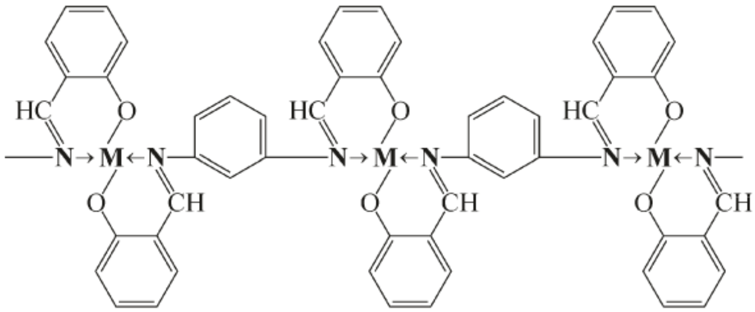


M = Cu, Co, Fe.

As compared to the spectral characteristics of the monomer, *N,N'*-disalilcylidene-1,6-hexanediamine, the UV spectra of the polymers obtained did not exhibit the bathochromic shift of the main absorption bands (Fig. 2), in contrast to the related substances derived from arenediamines. These data show that there are no "nonclassical" polyconjugation zones in the synthesized polymers. Correspondingly, the conductivity of these polymers is considerably lower ($\sigma < 10^{-12}$ S cm^{-1}), and doping with iodine is inefficient. The whole set of these facts indicate once more that specifically intramolecular donor–acceptor interactions are responsible for the electrical conductivity of metal-containing poly(disalicylidenediamines) **IV**–**VI**.

Thus, the results obtained show that the transfer of charge carriers in the synthesized metal-containing poly(disalicylidenediamines) mainly occurs intramolecularly along the polymer chain through "nonclassical"

Scheme 2.



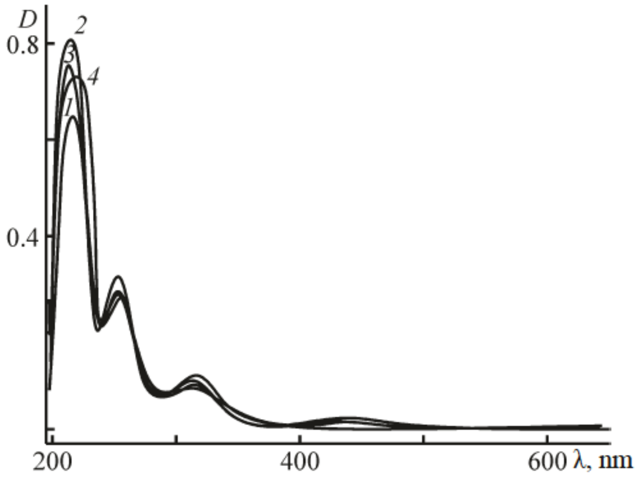


Fig. 2. UV spectra of the (*1*) monomer, *N,N′*-disalicylidene-1,6-diaminohexane, and (*2–4*) polymers, catena-poly[metal(μ-*N,N′*-disalicylidene-1,6-diaminohexane)-*O,N*;*O′*,*N′*)]; M: (*2*) Cu, (*3*) Co, and (*4*) Fe.

polyconjugation zones arising owing to intramolecular donor–acceptor interactions (indicated bold in Scheme 2).

CONCLUSIONS

(1) New soluble poly(disalicylidenediamines) containing Fe, Co, Ni, and Cu atoms in the backbone were prepared by polycondensation of salicylidene derivatives of aromatic diamines with the corresponding metal acetates. The structure of the polymers obtained was confirmed by IR, ^{1}H NMR, and UV spectroscopy.

(2) The polymers obtained exhibit conducting properties. Their conductivity increases by more than 5 orders of magnitude on doping with iodine.

(3) It has been proved experimentally that the electrical conductivity of the metal-containing poly(disalicylidenediamines) is due to the occurrence of nonclassical polyconjugation along the polymer chain due to multiple intramolecular donor–acceptor interactions. Such film-forming polymers with semiconductor properties show promise for nano- and optoelectronics.

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