Monatshefte für Chemie 126, 663–671 (1995)

Monatshefte für Chemie
Chemical Monthly

Electrical Conductivity of Some Phenylthiopyridine Complexes

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Summary. The electrical conductivity of some metal complexes of the composition *LM* and LM_2 (*L*: phenylthiopyridine derivative; *M*: Co(II), Ni(II), or Cu(II)) was measured in the temperature range 298–430 K. The activation energy of the conduction process, charge carrier density and mobility were calculated. The structure of the complexes is discussed on the basis of the results of conductometric titration and electronic and infrared spectra. The formation of four-coordinate complexes is concluded.

Keywords. Four-coordinate complexes; Magnetic susceptibility; Hopping conduction; Resonance effect.

Elektrische Leitfähigkeit einiger Phenylthiopyridinkomplexe

Zusammenfassung. Die elektrische Leitfähigkeit einiger Metallkomplexe der Zusammensetzung *LM* und LM_2 (*L*: Phenylthiopyridinderivat; *M*: Co(II), Ni(II) oder Cu(II)) wurde im Temperaturbereich von 298 bis 430 K gemessen. Die Aktivierungsenergie des Leitungsprozesses, die Ladungsträgerdichte und die Beweglichkeit der Ladungsträger wurden berechnet. Die Struktur der Komplexe wird auf der Grundlage der Ergebnisse von konduktometrischen Titrationen und UV/Vis- und IR-Spektren diskutiert. Es wird auf die Bildung vierfach koordinierter Komplexe geschlossen.

Introduction

Organic semiconductors have been studied for many years mostly in the form of pressed powders. Especially the electrical properties of pyridine derivatives were studied extensively [1–4]. Several charge transfer complexes of pyridine derivatives with *TCNQ* (tetracyanoquinodimethane) salts were prepared reaching electrical conductivities of about $10^{-3}\,\mathrm{ohm^{-1}\,cm^{-1}}$ [5–7]. The effect of complexation with transition metals on the electrical behaviour of pyrazine derivatives has also been investigated [8, 9]. The structure of complexes was explored using magnetic and spectral studies. The room temperature electrical conductivity measurements give 10^{-8} to $10^{-7}\,\mathrm{ohm^{-1}\,cm^{-1}}$ for the prepared compounds. Transition metal and lanthanide cations increase the conductivity of aminohydroxypyridine due to the production of new charge carriers in the conduction band [10].

The synthesis of phenylthiopyridine and its derivatives is of special interest due to their various biological activities (antipyretic and analgesic effects) [11]. However, the chelation of these compounds with transition metals and their electrical properties have not yet been investigated. Therefore, the present study aims to measure the electrical conductivity of 2-amino-4-phenyl-3,5-dicyano-6-phenylthiopyridine (*PTP*) and its complexes with Co(II), Ni(II), and Cu(II). To obtain information about the structure of the complexes, atomic absorption, conductometric titration, and electronic and infrared spectra were used.

Results and Discussion

Conductometric titration is a method of volumetric analysis based on the change in conductance of the solution at the equivalence point. Depending on the nature of the ions, a more or less sharp change in the conductance of the solution occurs. This method was used to determine the stoichiometry of the complexes. At the beginning of the titration, there is a small increment of the conductance where the *PTP* complexes are formed. As soon as the complexes are formed, a common characteristic of the conductometric titration curves is the slight continuous decrease in conductance on successive additions of the ligand *PTP* (basic solution) as shown in Fig. 1. The breaks indicate the formation of 1:1 complexes.

The electronic spectra of the complexes were recorded in acetone as can be seen from Fig. 2. The free ligand does not give any absorption peak in the studied range. However, its complexes with Co(II), Ni(II), or Cu(II) give absorption bands due to d–d transitions. The colour of the cobalt complex changed during the addition of acetone from pink to blue. Whereas most octahedral Co(II) complexes are pink and most tetrahedral Co(II) complexes blue, these colours cannot be taken as infallible

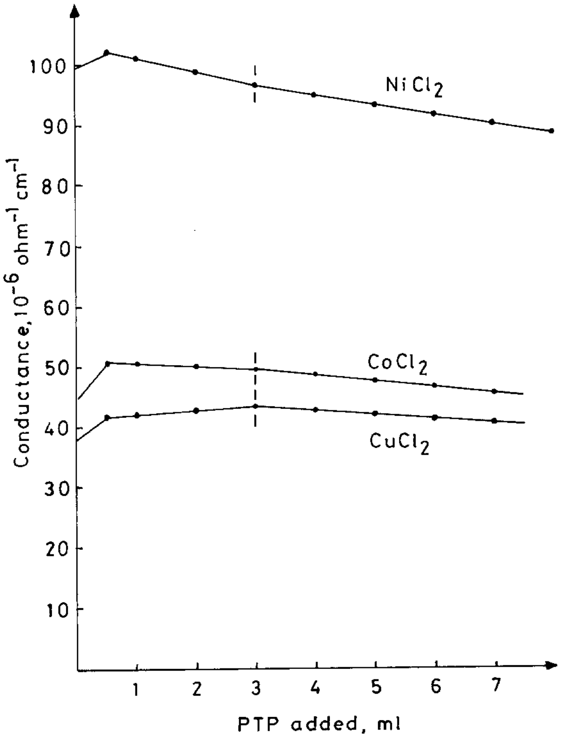


Fig. 1. Conductograms of *PTP* with transition metal ions

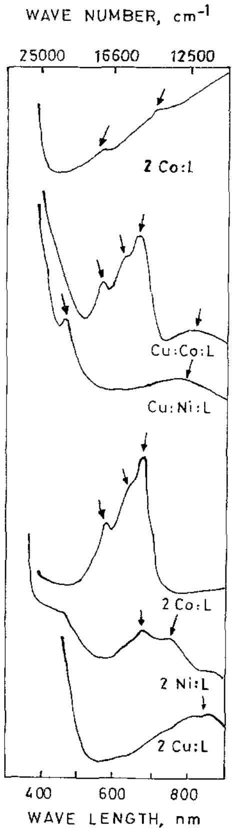


Fig. 2. Electronic spectra of polynuclear complexes; the uppermost one is measured as NaCl disk

guides to stereochemistry [13]. The UV/Vis spectrum of the solid complex (NaCl disk) was recorded and compared with that in soluion. In acetone, the complex exhibits multiple absorption peaks ($^4A_2 \xrightarrow{\nu_3} {}^4T_1(p)$), suggesting that it is tetrahedrally coordinated [14]. In NaCl, two absorption peaks at 692 and 577 nm were observed. These bands were assigned to the ν_3 transition in tetrahedral complexes. The magnetic moment of the cobalt complex is 4.20 BM which is characteristic of high spin tetrahedral Co(II) complexes.

Square planar complexes of Ni(II) are commonly orange or red, but purple and green complexes are also known [14]. The UV/Vis spectrum of the Ni(II) complex exhibits a multiple absorption bands at 732 and 676 nm, assigned to ν_2, and a band at 400 nm, assigned to ν_3. Square complexes of nickel can be distinguished from octahedral or tetrahedral complexes by the fact that no electronic transitions occur below 1000 nm [14]. The observed magnetic moment is 2.95 BM, indicating the presence of two unpaired electrons.

The UV/Vis spectrum of the Cu(II) complex shows one broad absorption band at 900–652 nm corresponding to the transition $^2T_2 \rightarrow {}^2E$. The colour and position of this band may be typical for a square planar complex. The magnetic moment amounts to 1.90 BM, suggesting the presence of a single unpaired electron.

The electronic spectrum of the copper–nickel polynuclear complex shows a broad absorption band at 900–600 nm due to the overlapping of Cu(II) and Ni(II) absorption bands in this region. The same behaviour was observed for Cu(II)–Co(II) polynuclear complex.

The examination of the infrared absorption spectra of *PTP* and its complexes is an important part in the process of identifying the structure of the studied compounds. The IR spectra were recorded in the range of 300–5 000 cm^{-1} as illustrated in Fig. 3. The important bands are given in Table 1.

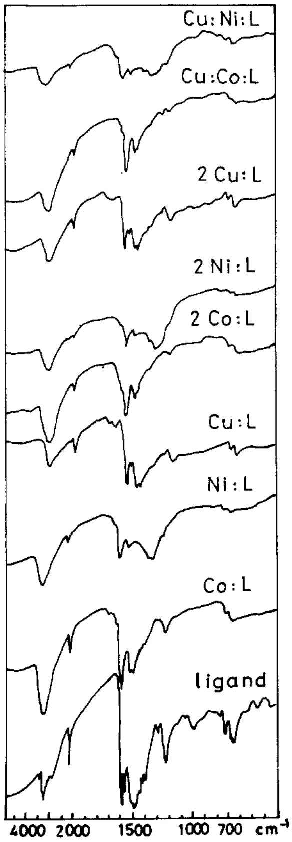


Fig. 3. Infrared spectra of *PTP* and its complexes

Table 1. Main IR absorption bands of *PTP* and its complexes (w = weak, m = medium, s = strong)

Compound	ν(NH$_2$)	ν(OH)	ν(C≡N)	ν(py)	δ(NH$_2$)	ν(C–S)
PTP	3400 m	3250 s	2150 s	1600 s	1540 s	705, 670 640 m
*L*Co	–	3300 s	2150 m	1600 s	–	705 w
*L*Ni	–	3250 s	2160 w	1600 s	–	705 w
*L*Cu	–	3250 s	2150 m	1600 s	–	705 w
*L*Co$_2$·	–	3250 s	2140 w	1600 m	–	–
*L*Ni$_2$	–	3200 s	2150 m	1600 s	–	–
*L*Cu$_2$	–	3250 s	2150 m	1600 s	–	–
*L*CoCu	–	3300 s	2150 w	1600 s	–	–
*L*NiCu	–	3200 s	2150 w	1600 m	–	–

The spectra of all complexes exhibit a strong and broad absorption band at 3 200–3 300 cm^{-1}, suggesting the presence of coordinated water molecules [15].

The spectrum of *PTP* shows a sharp and medium band at 3400 cm^{-1}, corresponding to the stretching vibration of NH_2, and another medium band located at 1 540 cm^{-1}, attributed to the bending vibration of the NH_2 group [16]. These bands disappeared after complexation, indicating that the nitrogen atom of amino group participates in the formation of both mono- and polynuclear complexes. A strong and sharp band located at 2 150 cm^{-1} was assigned to the stretching vibration of the $C{\equiv}N$ group [17]. After complexation, this band is weakened but not shifted, illustrating that the cyano group does not participate in the complex formation. A sharp and strong band at 1 600 cm^{-1}, due to the absorption of pyridine, is present in the spectra of both *PTP* and its complexes, denoting that the nitrogen atom of he pyridine ring does not take part in the complexation process. Finally, the CS frequency was observed at 705–600 cm^{-1}. These bands become weak for mononuclear complexes, but disappear after formation of polynuclear complexes. This means that the sulfur atom of the thiophenyl group can be considered as a second coordination site for the formation of polynuclear complexes.

The electrical conductance of *PTP* and its complexes can be characterized by the determination of three terms: the activation energy of the conduction process (E), the number of charge carriers (n) and the mobility (μ). The conductivity of *PTP* increases with rising temperature, obeying the relation

$$\sigma = \sigma^0 \exp((-E/\mathrm{k}T)$$

The linear behaviour of the temperature dependence of the conductivity of *PTP* is like that of an intrinsic semiconductor.

Fig. 4 shows a plot of the logarithm of the conductivity against the reciprocal of the absolute temperature of he investigated compounds over the temperature range of 294–430 K. It is apparent that the complexing of *PTP* with transition metals results in increased conductivity. In view of the chemical structure, the *PTP* molecule contains various substituents such as NH_2, $S\!\lt$, and $C{\equiv}N$. However, in the case of mononuclear complexes, *PTP* acts as a monodentate ligand where the coordination takes place through the nitrogen atom of the amino group, forming four coordinated complexes as revealed by the spectral measurements. The ligand of this type is classified as a σ-donor ligand, *i.e.* the coordinated bond is formed by overlapping of a filled orbital of the ligand with an empty orbital of the metal ion. Therefore, the conductivity of *PTP* is increased after complexation.

On the other hand, polynuclear complexes show a higher conductivity value than mononuclear complexes, except for Ni compounds. Here, there are two coordination sites: NH_2 and $S\!\lt$. The sulfide can be considered as a σ-donor/π-acceptor because it possesses a partly empty orbital which can overlap with a filled d-orbital on the transition metal cations [18]. The π-acceptor strength is increased by the presence of the CN group. The resulting increase of the electronegativity of the *PTP* molecule can delocalize the negative charge still further. The increase of π-acceptor strength causes to some extent a reduction in the σ-donor strength; it decreases the electron density on the metal and therefore increases the conductivity of the polynuclear complexes [19].

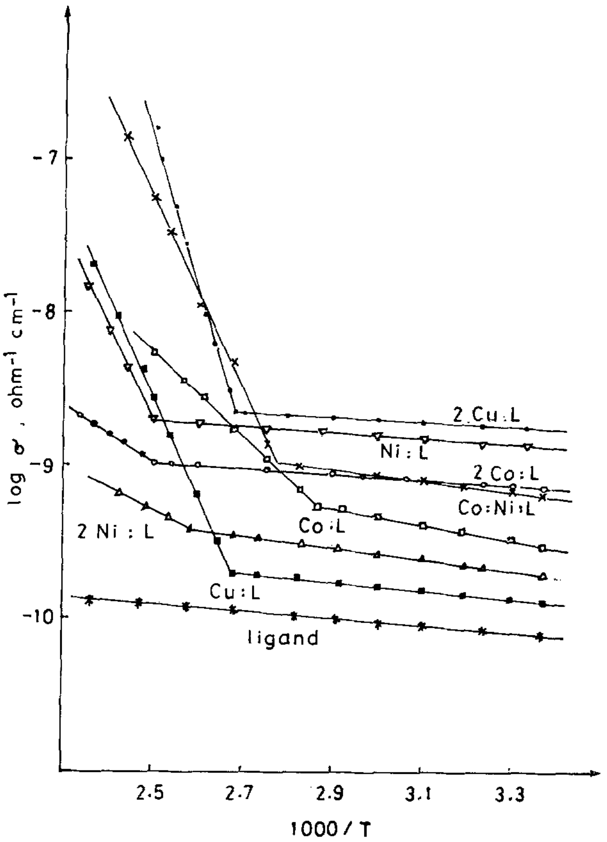
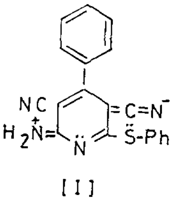
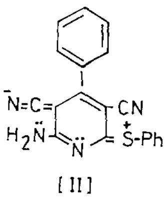


Fig. 4. Electrical conductivity of *PTP* and its complexes

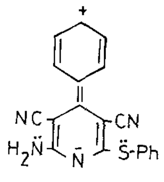
In the light of the resonance effect (the shift of electrons from one part of a molecule to another) of *PTP* molecule, the various possible hybrid structures can be represented as:



[I]



[II]



[III]

The appropriate hybrid structure of the free *PTP* molecule is *I*. After complexation *via* the lone pair of electrons on the nitrogen atom of the amino group (type *LM*) the molecule accepts the hybrid form **II**. For polynuclear complexes, the hybrid structure is **III**. It is clear that structure **III** is more effective than the other ones due to the stability of the heterocyclic nitrogen. Consequently, the conductivity follows the order *PTP* < mononuclear complexes < polynuclear complexes.

To determine the concentration of charge carriers, the following equation can be used ($E > \mathrm{kT}$):

$$n = 2\left(\frac{2\pi m^{+}\mathrm{k}T}{\mathrm{h}^2}\right)^{3/2} \cdot \mathrm{e}^{-E/2\mathrm{k}T}$$

Table 2. Electrical data of *PTP* and its complexes at 298 K

Compound	σ (ohm^{-1} cm^{-1})	E (eV)	n (cm^{-3})	μ (cm^2/V·s)
PTP	7.94×10^{-11}	0.050	9.35×10^{24}	5.31×10^{-17}
*L*Co	3.09×10^{-10}	0.104	3.26×10^{24}	5.92×10^{-16}
*L*Ni	1.38×10^{-9}	0.035	1.25×10^{25}	6.90×10^{-16}
*L*Cu	1.32×10^{-10}	0.050	9.35×10^{24}	8.82×10^{-17}
*L*Co$_2$	7.33×10^{-10}	0.030	1.38×10^{25}	3.32×10^{-16}
*L*Ni$_2$	2.00×10^{-10}	0.076	5.63×10^{24}	2.22×10^{-16}
*L*Cu$_2$	1.78×10^{-9}	0.037	1.21×10^{25}	9.19×10^{-16}
*L*CoNi	6.61×10^{-10}	0.079	5.31×10^{24}	7.78×10^{-16}

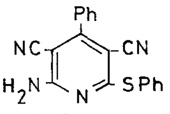
m^+ is the effective mass of the charge carrier (assumed to be equal to the rest mass of the electron). The mobility of the charge carriers was calculated using the relation $\sigma = ne\mu$, where e is the charge of the electron. The electrical data of *PTP* and its complexes are reported in Table 2. However, some of the estimates of n and μ must be regarded as approximate because the expression used for n is valid only for $E \geqslant 3kT$, whereas the low values of E suggest degeneracy [20].

The conduction in solid organic compounds takes place *via* the transport of charges from one molecule to another. This is achieved by the overlapping of molecular orbitals. If the orbital overlap is small, the charge carriers are localized at their atomic centers and a jump of an electron from one atomic site to an equivalent adjacent one can occur. Compounds where electron transport occurs *via* an activated process are known as hopping type compounds [21]. For narrow band compounds, a considerable interaction between charge carriers and the lattice takes place. Here, the electron is neither free nor bound and its mobility becomes very low [22]. This agrees with the obtained μ-values in Table 2 for both *PTP* and its complexes.

If the interaction between charge carriers and lattice is strong, one is dealing with a small polaron consisting of the charge carrier surrounded locally by a strongly deformed lattice. At low temperatures, the small polarons exhibit band-like properties. As the temperature rises, the band narrows until it becomes indistinguishable from the localized levels. According to the *Holstein* model of small polarons [23], a phase transition is observed with rising temperature due to the change of conduction mechanism from band to hopping. All studied complexes exhibit this behavior, suggesting that the conduction process of 2-amino-4-phenyl-3,5-dicyano-6-phenylthiopyridine complexes varies from electronic to ionic mechanism with increasing temperature.

Experimental

The chemicals used were of p.a. grade (Merck). *PTP* was prepared according to Ref. [11].



PTP ($C_{19}H_{12}N_4S$)

Table 3. Analytical data of some *PTP* complexes

Compound	Colour	M.p. (°C)	Co (%)	Ni (%)	Cu (%)
PTP	white	205	–	–	–
*L*Co	pink	205	10.04	–	–
*L*Ni	green	197	–	11.02	–
*L*Cu	yellowish green	204	–	–	11.83
LCo_2	dark pink	204	16.03	–	–
*L*CoNi	pale orange	223	8.00	7.98	–

The solid complexes of composition LM and LM_2 (L: *PTP*; M: Co(II), Ni(II), or Cu(II)) were prepared by mixing the calculated amounts of hydrated metal chloride and ligand, both dissolved in acetone. The reaction mixtures were refluxed on a water bath for 5 hours and then cooled to room temperature. The solid complexes which separated were filtered off, recrystallized from acetone and dried over silica gel. Polynuclear complexes (LM_1M_2) were also prepared by mixing equimolar solution of two different metal ions and the ligand in acetone. The mixtures were refluxed, cooled, filtered, and dried.

To determine the metal content in the different complexes, a Buck Scientific 200 atomic absorption spectrophotometer was used. The analytical data are summarized in Table 3. The melting points were determined using an electrothermal melting point apparatus.

It is known that the complexes lose their water of crystallisation at about 100 °C and their coordinated water molecules at about 200 °C. Therefore, by calculating the weight loss of a certain amount of a solid complex at those two temperatures, the number of crystallized and coordinated water molecules can be determined. The results showed that the mononuclear complexes possess two water molecules of crystallisation and one of coordination. For polynuclear complexes, there are three H_2O molecules of crystallisation and two molecules of coordination.

The stoichiometric ratio of different complexes was determined on the basis of conductometric titrations using a digital conductivity meter 5800-05 solution analyzer, Cole-Parmer Instrument Co. *PTP* was dissolved in acetone and a 0.01 *M* solution was prepared. Similarly, solutions of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$ in acetone (0.001 *M*) were prepared. The *PTP* solution was titrated against transition metal solutions as described previously [12].

The magnetic moment of the powdered complexes was measured by the *Gouy* method [24]. Electronic spectra were recorded on a Perkin Elmer λ-3b spectrophotometer using a 1 cm cell in the range of 300–900 nm. Infrared spectra were measured as KBr discs using a Shimadzu- IR-400 spectrophotometer. The electrical conductivities of the solid complexes were measured by aid of a Schwingkondensator voltameter VA-J-52 (R.F.T. electrometer) using discs of 10 mm diameter and 0.5 mm thickness. The samples were prepared under a pressure of 6000 kg/cm^2. A copper constantan thermocouple was used.

References

[1] Nowakowski T., Mrozinski J. (1989) Mater. Sci. **14**: 19

[2] Reicha F. M., Ahmed M. A., El Nimer M., El Sonbati A. Z., Diab M. A. (1989) Acta Polym. **40**: 653

[3] Allan J. R., Carson B. R., Turvey K., Birnic J., Cerrard D. L. (1991) Eur. Polym. J. **27**: 665

[4] Baek D. J., Choi J. S., Lee Y. K. (1989) Pollimo **13**: 213

[5] Papavassiliou G. G., Yiannopbulos S. Y., Zambaunis J. S. (1986) J. Chem. Soc., Chem. Commun. **23**: 820

[6] Kossmeht G., Kabbeck-Kupijai D., Magonov S. N. (1991) Synth. Met. **42**: 2565

[7] Yu L. J. (1991) Synth. Met. **42**: 175

[8] Allan J. R., Paton A. D., Turvey K. (1991) Thermochim. Acta **186**: 293

[9] Allan J. R., Paton A. D., Turvey K. (1992) Thermochim. Acta **195**: 343

[10] Abd El Wahed M. G., Hassan A. M., Hassan S. A. (1993) J. Mater. Sci. Lett. **12**: 453

[11] El Bahnaswi A., El Mobayed M., Essawy A., Amer A. M. (1993) Bull. Fac. Sci., Zagazig Univ. **15**: 176

[12] Abd El Wahed M. G., Aly S. A., Farouk H. (1994) J. Mater. Sci. Lett. **13**: 1434

[13] Cotton F. A., Soderberg R. H. (1964) Inorg. Chem. **3**: 1

[14] Lever A. B. P. (1968) Inorganic electronic spectroscopy. Elsevier, Amsterdam, pp. 332, 343

[15] Nakamoto K. (1978) Infrared and Raman spectra of inorganic and coordination compounds. Wiley, New York, p. 226

[16] Williams D. H., Fleming I. (1980) Spectroscopic methods in organic chemistry. McGraw Hill, London, p. 51

[17] Bellamy L. J. (1975) The infrared spectra of complex molecules. Chapman and Hall, London, p. 294

[18] Houghton R. P. (1979) Metal complexes in organic chemistry. Cambridge Univ. Press, Cambridge, p. 23

[19] Meier H. (1974) Organic semiconductors. Dark and photoconductivity of organic solids. Verlag Chemie, Weinheim, p. 161

[20] Abd El Wahed M. G., Hassan A. M., Raaft S. (1990) Chemistry & Industry **16**: 263

[21] Honig J. M. (1970) In: Rao C.N.R. (ed.) Modern aspects of solid state chemistry. Plenum Press, New York, p. 519

[22] Seanor D. A. (1982) Electrical properties of polymers. Academic Press, New York, p. 38

[23] Holstein T. (1959) Ann. Phys. **8**: 343

[24] Sharma B. K. (1979) Physical properties and molecular structure. Goel Publishing House, India, p. 51

Received November 3, 1994. Accepted (revised) December 9, 1994