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Electrical and Spectral Properties of Manganese Dichloride Complexes with *N*-Oxides of Pyridine Derivatives

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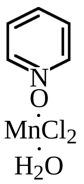
Abstract—Polycrystalline complexes of $MnCl_2$ with *N*-oxides of pyridine, 2-picoline, and 2,6-lutidine contain a molecule of strongly retained crystallization water; two types of the labile networks of hydrogen bonds are formed on the crystal surface. Under solar radiation the long-lived *F*-centers are formed in the crystals, imparting a specific color to the compounds. The thermal motion of $MnCl_2$ complexes with lutidine *N*-oxide in the unit cells can be described as gas-like motion. At low temperatures the electrical conductivity is predominantly maintained by protons, whereas at high temperatures another mechanism of conductivity arises.

Complexes of manganese salts with *N*-oxides of pyridine, 2-, 3-, and 4-methylpyridines, and 2,6-dimethylpyridine exhibit high biological activity [1–4]. Triman-1 (complex of $MnCl_2$ with 2-picoline *N*-oxide) is widely used as a growth regulator of agricultural plants. A detailed analysis using various physicochemical methods is required to elucidate the mechanism of biological activity of this and related compounds. In this work the molecular equilibria, the molecular dynamics, the energy of intermolecular bonds, and the electrical conductivity of Triman and complexes of $MnCl_2$ with *N*-oxides of pyridine and 2,6-lutidine were studied by IR and UV spectroscopy, dielectrometry, and conductivity methods. Taking into account the data of elemental analysis and the results discussed below, the composition of the complexes in question corresponds to structures **I**–**III**.



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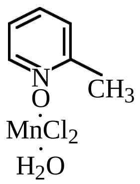

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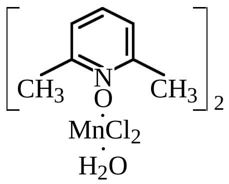

III

The presence of the molecule of crystallization water strongly retained in the complexes even in alcoholic solutions is typical for manganese compounds. Its low mobility is probably due to the formation of additional OH···Cl intracomplex bonds. Based on the data given in [5], the tetrahedral or planar structure of complexes **I** and **II** and octahedral structure of complex **III** can be suggested. Synthesis, purification, and identification of the complexes in question is given elsewhere [1, 2]. The procedures for spectra recording, conductivity measurements, and treatment of experimental data were common [6]. The pellets were pressed at 4400 atm.

The throughly purified Triman powder (particle size several tenth fractions of millimeter) has a light rose color, which significantly intensifies after exposure to bright sunlight. This phenomenon is typical for many ionic crystals [7, 8] and is due to the selective light absorption on so-called *F*-centers, which are the complexes of photoelectrons with positive ions or holes formed after removal of the negative ions from the lattice point. Appearance of such centers causes absorption at ~390 nm in the UV spectrum of Triman (Fig. 1).

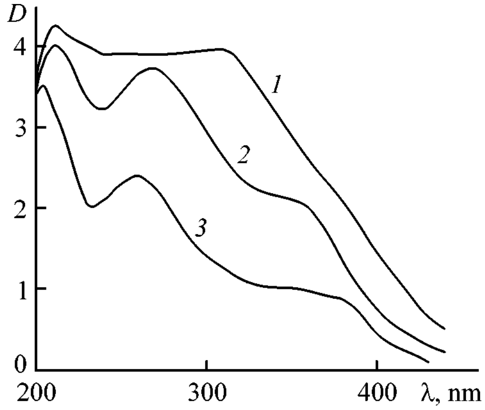

Fig. 1. UV spectra of thin (~0.1 mm) films: (*1*, *2*) complex **III** and (*3*) complex **II**. Spectrum *1* was recorded 1 day after the thermal treatment.

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Table 1. Stretching vibrations of the NO bonds, enthalpy of the NO···Mn bonds, and fractions (*N*) of the base molecules bound in solid complexes **I**–**III** at 19°C

Complex no.	ν(NO) free, cm^{-1}	ν(NO) bound, cm^{-1}	Δν(NO), cm^{-1}	*N*, %	–Δ*H*(NO···Mn), kJ mol^{-1}
I	1250	1218	32	~84	28
II	1256	1206	50	~89	36
III	1273[a]	1206[a]	67	~90	44

[a] Location of the centers of gravity.

Similar spectra are observed for usually yellowish complexes **I** and **III**; $\lambda_{max} \approx 360$ nm for compound **III** (Fig. 1). It should be noted that in the spectra of LiCl and NaCl this band occurs at 380 and 470 nm, respectively [8]. After annealing of complex **III** (heating to 150°C and slow cooling to room temperature) this absorption band disappears. In the other regions the UV spectra of complexes **I**–**III** are similar to that of pyridine.

The IR spectra show that these complexes are appreciably dissociated under the normal conditions. The approximately constant intensity of the absorption band ν(NO) allows quantitative evaluation of the fraction of organic bases bound in the corresponding complexes (Table 1). As seen, the frequency ν(NO) of the free molecules slightly differs from ν(NO) registered in liquid bases: 1240 and 1260 [9] and 1253 cm^{-1} [5]. Using the Δν(NO)–Δ*H* correlation [5], we calculated the enthalpies (–Δ*H*) of the NO···Mn bonds. The enthalpy increases with increasing number of CH_3 groups in the base molecule by nearly 8 kJ mol^{-1} per CH_3 group. The increase in –Δ*H* is probably due to the positive electronic (*I* + *M*) effect of the CH_3 groups, which increases the negative charges on the oxygen atoms and hence the electron-donor power of the base molecules.

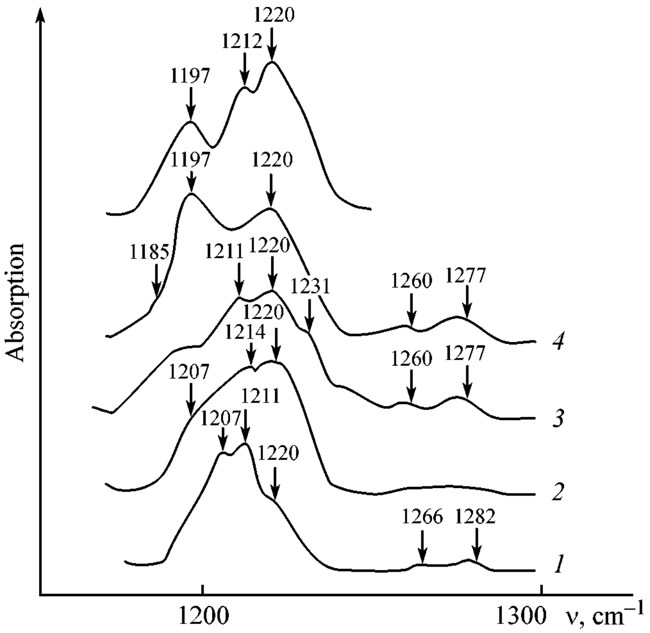

Fig. 2. Absorption band ν(NO) in solid complex **III**, KBr pellets. Registered: (*1*) at 18°C before thermal treatment, (*2*) the same at 84°C, (*3*) the same after cooling to 18°C and 2-h storage, (*4*) at 18°C after triple heating to 150°C and storage for 15 h, and (*5*) at 18–75°C after similar treatment and 8-day storage.

The enthalpy of the H–O···Mn bond can be evaluated from the known proportionality of the energies of coordination and hydrogen bonds [10] and published results [5]. For complex **I** we obtained the value of about 23 kJ mol^{-1}.

The bands ν(NO) of the free and bound molecules of pyridine and 2-picoline *N*-oxides have a simple shape and a half-width of ~10 cm^{-1}. After annealing the shape and position of these bends in the spectra remained virtually unchanged, similarly to the band ν(OH). In the case of complex **II**, the shape of the band ν(NO) did not change even after significant wetting of the sample. This fact suggests that non-crystallization water sorbed by compounds is predominantly localized far from oxygen atoms of the NO group. The most probable centers of its localization are the molecules of crystallization water, where the sorbed molecules can be arranged in several layers.

As compared with compounds **I** and **II**, the IR spectral properties of complex **III** are rather different. The band ν(NO) of the free base molecules, similar to liquid 2,6-lutidine [5], is split in two components in the solid phase (Fig. 2, curve *1*), and the high-frequency component is more intense.

After annealing both components of the ν(NO) band are shifted by nearly 6 cm^{-1} toward the low-frequency region. The band ν(NO) of the bound molecules initially consists of three well-defined components. The storage of the samples at room temperature and their thermal treatment cause appearance of new bands and redistribution of the intensity between the already present components (Fig. 2). The band ν(OH) in the case of complex **III** is also rather complex, it is broad (nearly 500 cm^{-1} half-width) and consists of three ill-resolved components. The spectra of complexes **I** and **II** exhibit two well-resolved components of the ν(OH) band with a half-width of 300 cm^{-1}.

Analogous splitting of the ν(NO) band in the solid phase was observed previously for the complex of 2,6-lutidine *N*-oxide with HCl [11]. This phenomenon can be explained by inertial rotation of complexes in the unit cells. Such a rotation is promoted by nearly spherical shape of the molecules of complex **III**. Certain deviation from classical dependences $\Delta\nu \sim (T, K)^{1/2}$ [12], where $\Delta\nu$ is the difference in the position of the band components, is related either to complex kinematic interaction of the bonds in polyatomic molecules or to changes in the character of the inertial rotation of the molecules in the temperature range studied, similar to the case of liquid 2,6-lutidine *N*-oxide [5]. Gradual variation in the band shape after the heat treatment is probably due to slow attainment of thermal equilibrium in the sample. This is confirmed by the fact that the equilibrium in one of solid pyridine complexes was attained in more than a 2-month period after its heating to 94°C and subsequent cooling to room temperature [5].

The dielectric constant (ε) of the powdered samples (0.08 mm average particle size) and pressed pellets was studied at a 1 kHz frequency similarly to the case of the 2,6-lutidine *N*-oxide complex with succinic acid (Poteitin) [6]. The electrical properties of the powdered samples were predominantly determined by the surface molecules, whereas in the case of the pressed samples the effect of the bulk molecules was decisive. The properties of the powdered sample of complex **I** (bulk density 0.74) in the 18–152°C temperature range were similar to those of Poteitin. Two types of nearly equivalent networks of hydrogen bonds with rather frequent random transitions between them under the action of incident shakes are realized on the particle surface. In both cases the fraction of nonpolar hydrogen-bonded complexes increases with decreasing temperature. The dissociation of crystal lattice providing sharp increase in ε begins at nearly 130°C. The behavior of compound **II** (bulk density 0.67) was similar to that of **I** with the only difference that the transitions between hydrogen bonds are more pronounced and ε in a series of experiments varied within a narrow range. In the case of compound **III** (bulk density 0.45) similar transitions between the hydrogen bonds were observed only in the first test and were absent in the two subsequent tests. The dissociation of the crystal lattice in the first test began at 145°C, whereas in second and third tests it was manifested by a sharp break at 138 and 132°C, respectively. The slope of high-temperature linear section of the dependences with respect to *x*-axis decreases in the series of tests. The equilibrium dielectric constants in these sections were similar after heating of the samples and their cooling. The equilibrium of the rapid processes after gradual heating of the powder sample by several degrees was attained in ~15 min; the transition dependences were described by the zero- and first-order equations, which revealed the sequence of reactions proceeding in the sample. At cooling of the powder with a rate of 0.5 deg min^{-1} nonequilibrium values of ε were obtained. Several experimental dependences are shown in Fig. 3.

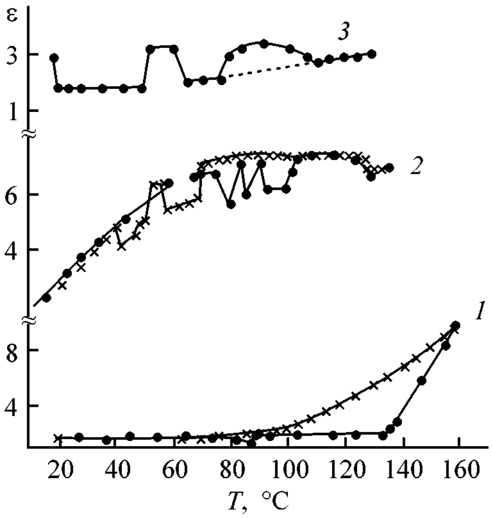

Fig. 3. Temperature dependences of the dielectric constant of the powdered samples (1 kHz): (*1*) Triman **II**, first test; (*2*) the same sample, fourth series of measurements; (*3*) compound **III**, second series of measurements [(*circles*) data registered at heating after the equilibrium attainment and (*crosses*) data registered at cooling with a rate of 0.5 deg min^{-1}].

As for pressed samples of **I**, only irreproducible values of ε were obtained. For example, the temperature dependence of the dielectric constant for the samples studied (ε^{18} 2.60, d^{18} 1.32 g cm^{-3}) exhibited a pronounced maximum of nearly 4.6 at 24°C, and then no rearrangement of the crystal structure was observed up to 150°C. The values of the dielectric constant registered at heating of the sample were by nearly 1 smaller than the values registered at cooling. The half-hour exposure of the samples at each temperature did not affect the pattern. In the case of the second sample, no maximum on the temperature dependence of the dielectric constant was found; the ε values registered at heating and cooling of the sample were similar, and the thermal dissociation of the crystal lattice began above 130°C.

The third sample was prepared after 1 month, its crystal lattice remained unchanged up to 150°C, in the second test the dielectric constant ε passed a maximum (~18) at 27°C and decreased from 2.4 to 1.8 upon cooling from 150 to 40°C; after storage for 17 h

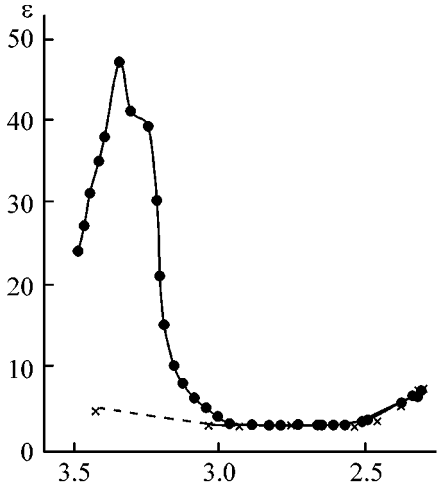

Fig. 4. Temperature dependence of the dielectric constant of a pressed sample of **I** (1 kHz) after attainment of the equilibria of fast relaxation processes [(*circles*, *crosses*) data registered in the course of heating and cooling of the sample, respectively].

the dielectric constant at 17°C was 21. In the course of third heating with a rate of 0.5 deg $\min^{-1}$ ε reached 89 at 40°C and then, after keeping at this temperature for 30 min, it decreased to 2.4. The data registered 4 h after this test are shown in Fig. 4.

At heating of the pressed sample of Triman (d^{19} 1.70 g cm^{-3}) ε passed a maximum (6.3) at 28°C. In the second test after 1 day it comprised 4.6, and in the course of cooling from 130 to 18°C ε was nearly constant (3.2). The dielectric constant of one sample of compound **III** (d^{22} 1.21 g cm^{-3}) passed a maximum at 140°C. The tests using this sample after 1-day storage or another sample showed no maximum on the temperature dependence of ε, and dissociation of the crystal lattice became significant at temperatures higher than 150°C. The dependence of the dielectric constant of the third sample (after 1 month) passed a maximum at 40°C, and dissociation of the crystal lattice began at 130°C. Such a behavior of the samples suggests high lability of the crystal lattices, participation of significant number of bifurcation points in their rearrangement, predominantly antiparallel orientation of molecular dipoles in the crystals, and possible formation of unstable species such as ferroelectric domains. The latter phenomenon is rather typical for hydrogen-bonded crystals [13]. Moreover, ferroelectric domains were registered in solid water [14]. With several samples of compound **I** we revealed oscillation processes in the crystals. In one sample the ε values at 18°C varied from 2.1 to 6 with a period of ~15 min by the harmonic law. In another test ε of the sample at 19°C was 30, it decreased by a factor of 5 in 17 h, and then began to slowly increase.

Table 2. Electrical properties and densities of complexes **I–III** at 19°C

Complex no.	d, g cm^{-3}	ε_∞	P_∞, cm^3	R_D, cm^3	$P_\infty - R_D$, cm^3
I	1.92	3.27	72	68	4
II	1.72	3.17	82	74	8
III	1.50	2.95	132	129	3

The oscillation reactions fairly frequently occur in the nature [15]. Their proceeding is based on at least two conditions: nonlinear dependence of the rate of the direct reaction on the corresponding parameters and the presence of a feedback system. We determined variations in the density of Triman **II** upon transition from the crystalline to the liquid state. In aqueous solutions d^{19} was 1.86 g cm^{-3}, whereas in the solid state it was 1.72 g cm^{-3}; the refractive index n_D^{19} was 1.76, and the Batcher-Kirkwood refraction (R_D) was 74 cm^3. The refractions of compounds **I** and **III** calculated by the additive procedure are listed in Table 2. Using the above data we determined the values of the limiting dielectric constant (ε_∞) and limiting electrical polarization (P_∞).

The differences $P_\infty - R_D$ are relatively small in all the cases studied. This suggests that the crystal lattices of the compounds studied are only slightly deformed in the applied electric field, despite their high thermal lability.

Along with dielectric constant we measured the specific dc conductivity (æ) of the pressed samples. At 25–40°C we obtained the temperature dependences with poorly reproducible peaks corresponding to the maxima in the temperature dependences of the dielectric constant. In many cases the breaks in the æ values were registered, which is typical for the proton conductivity of compounds containing crystallization water. In the case of Triman **II** we found that the high-temperature linear section of the dependence registered upon cooling of the sample is well reproduced, which allowed evaluation of the energy (W_i) of thermal generation of the protons under the given conditions using the standard equation:

$$W_i,\ \text{eV} = 1.98 \times 10^{-4} \tan \alpha,$$

where α is the slope of the diagram with respect to the x-axis (Fig. 5).

The obtained values, $\tan\alpha$ 4.3×10^3 and W_i 0.85 eV, agree well with the energy of generation of the ionic conductivity in solid 3-cyanopyridine and *N*-oxides of pyridine and alkylpyridines (0.8 eV [9]), which are also proton semiconductors. In the case of compound **I** the reproducibility of the linear section was worse, the average value of $\tan\alpha$ was 5.3×10^3, and the corresponding W_i was 1.05 eV. As for compound **III**, in a series of successive tests the high-temperature linear sections were more pronounced, similar to **I**. In some tests $\tan\alpha$ was nearly 5×10^3, and the corresponding W_i was 1.0 eV. But in most cases $\tan\alpha$ was close to 1.2×10^4. The results of one test are shown in Fig. 5, where the first slope is realized at cooling of the sample and the second slope, at its heating. The above value of $\tan\alpha$ gives W_i of 2.4 eV, which is close to the values of high-temperature halogen conductivity and is far from the energies typical for proton conductivity. The energy of thermal generation (W_e) of the electron-hole pares was calculated from the following equation assuming the ionic mechanism of high-temperature conductivity.

$$W_e,\ \text{eV} = 3.97 \times 10^{-4} \tan\alpha.$$

The resulting W_e was 4.8 eV. To evaluate the reliability of this value, we analyzed the electronic spectrum of the compound (Fig. 1); similar to [16], we studied the rapid transition processes under the electric field and determined the increase in the electrical conductivity due to the dissociation of the crystal lattice. In the case of electronic conductivity W_e should correspond to the low-frequency edge of one of two bands in the absorption spectrum. The edge of the high-frequency band (~450 nm) corresponds to W_e 2.8 eV, whereas the edge of the low-frequency band (≥260 nm) corresponds to $W_e \leq 4.8$ eV. Thus, our spectral data do not contradict the possible electronic conductivity mechanism for the compounds in question. Our study of the transition processes did not reveal formation of polarons typical for such conductivity mechanism. Treatment of the experimental results using the procedure given in [17] showed that the increase in the dielectric constant due to the lattice dissociation should cause the increase in log æ by 1.2. The real increase in log æ was 1.1. These results also agree with the possible electronic mechanism of high-temperature conductivity. However, the detailed analysis of this phenomenon requires further investigations.

We compared the specific electrical conductivities of 0.1 M aqueous solutions of Triman **II** ($0.3\ \text{S m}^{-1}$) and $MnCl_2 \cdot 4H_2O$ ($0.65\ \text{S m}^{-1}$) at 18°C. The results suggest certain decrease in the mobility of Cl^- ions in the Triman molecule as compared with the second molecule. The absolute electrical conductivity corresponds to the release of nearly 10–15% of these ions from the Triman molecule.

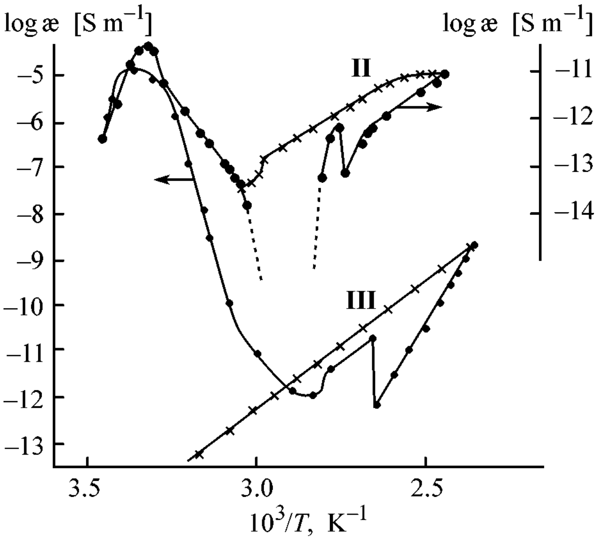

Fig. 5. Temperature dependence of specific dc conductivity of compounds **II** and **III** after attainment of the equilibria of the fast relaxation processes [(*circles*, *crosses*) data registered in the course of heating and cooling of the samples, respectively].

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