Extracoordination sensitivity of tetraphenylporphyrin complexes to gaseous ammonia

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The sensitivity of metal tetraphenylporphyrin complexes MTPP (M = Pt^{II}, $Pt^{IV}Cl_2$, $Re^{IV}O$; TPP is tetraphenylporphyrin) to gaseous ammonia was studied. The gas sensitivity of MTPP is due to the heterogeneous catalytic oxidation of ammonia with the dioxygen ligands in the composition of MTPP. The influence of water vapor on the electrophysical properties of the surface layer of the complexes during adsorption of water and its participation in reactions of the coordinated ammonia and dioxygen were found. Empirical equations relating the conductivity of the MTPP surface layer to the content of water vapor and the concentration of gaseous ammonia were found.

Key words: tetraphenylporphyrin complexes, gas sensitivity of metal porphyrins, coordination of ammonia and dioxygen.

Complexes of porphyrins and related nitrogen-containing macrocyclic ligands with metal ions are characterized by a planar or close to planar structure due to a system of the conjugated π-electron bonds. In these compounds, the central atom retains its capability of additional axial complex formation due to extracoordination of donor ligands, such as NH_3, amines, halides, *etc.* These complexes are also characterized by oxygenation reactions, *i.e.*, addition of O_2 molecules as extra ligands.[1—3] The addition of dioxygen as an axial ligand is due to the cleavage of the $1\pi_g$ level of triplet dioxygen, reorientation of electron spins, and their transition to the first excited (singlet) level with antiparallel spins followed by the formation of a bond between the dioxygen ligand and the d_{z^2} orbital of the central ion. In this case, d_{zx} or d_{zy} electrons of the central ion are transferred, in turn, to one of the split antibonding $1\pi_d$ orbitals of oxygen (dative bond), which is accompanied by enhancement of the charge on the central ion (δ+) and formation of a superoxide radical ion $O^-{}_2$.

The formation of a bond between the O_2 molecule and the central atom of metal porphyrin becomes possible when the latter has a partially occupied d shell, which is especially characteristic of 3d transition metals (Mn, Fe, Co, Ni, Cu).[4,5] The formation of a bond with dioxygen is favored, to a great extent, by the preliminary coordination of donor ligands (for example, NH_3) by the central atom along the remaining axial coordinate of the complex, because an donor ligand can transfer the electron density to the central atom and further to dioxygen, thus facilitating a redox reaction. The involvement of orbitals of the central atom in a system of conjugated π-bonds of the macroligand decreases substantially the activation barrier of possible reactions. Many catalytic processes are known that occur under mild conditions and involve metal porphyrins.[1,6]

Oxidation reactions that do not occur under standard conditions in air (for example, oxidation of NH_3 with air oxygen) can occur, in principle, on the catalyst (metal porphyrin) surface in an air—solid heterogeneous system. Such systems are important from the viewpoint of developing gas-sensitive sensors.

As many chelate metal complexes, metal porphyrins possess semiconducting properties.[7—9] Their electrophysical properties, for instance, conductivity, change significantly during a catalytic process. These changes occur because the dipole moment, polarizability, and other properties of intermediates formed in the surface layer differ from those for the starting metal complexes and can be used as analytical signals of sensors. The process is also accompanied by a change in charges of reactants and the appearance of new charge carriers. For example, the oxygenation of the central atom to form the superoxide radical ion and coordinated extra ligand can be considered as the appearance of a Frenkel exciton, and the catalytic oxidation of an electron-releasing ligand with desorption

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of products can be considered as the decomposition (annihilation) of the exciton. These processes form a physical foundation for functioning of catalytic sensors appropriate for determining the content of electron-donor compounds in air. Complexes of porphyrins and related macroligands can be gas-sensitive materials for these sensors. Sensors for reducing gases based on metal porphyrins,[10—14] phthalocyanines,[13,14] tetraazaannulenes,[15] and similar compounds are known.

The catalytic oxidation of ammonia with dioxygen on the surface of the complex occurs through a step of metal porphyrin activation. This step can be the formation of a molecular compound of ammonia and water $NH_3 \cdot H_2O$, which becomes an efficient generator of active ions OH^-, replacing the acido ligand from the inner sphere of the complex and switching on a catalytic reaction between the ligand O_2 and donor molecule NH_3 in the coordination sphere of the complex. In this case, a change in the electrophysical properties of the surface of porphyrin complexes becomes a function of the ammonia content in the gas phase in the presence of water vapor.[16]

The purpose of this work is to study the gas sensitivity to ammonia of such metal tetraphenylporphyrin complexes (MTPP) in which one (or both) axial coordinates of the complex is occupied by any strongly bonded ligand preventing oxygenation or complexation with gaseous ammonia.

Experimental

Metal complexes (with different fillings of d orbitals) with tetraphenylporphyrin (TPP) containing the oxometallate group $Re^{IV}O$ ($5d^3$), chlorometallate group $Pt^{IV}Cl_2$ ($5d^6$), or (for comparison) Pt^{II} (d^8) were chosen as objects for the study. In the latter case, the complex has no covalently linked ligands in the axial position.

Complexes $Re^{IV}O \cdot TPP$,[17a] $Pt^{II} \cdot TPP$, and $Pt^{IV} \cdot TPP$ [17b,18] were synthesized by previously described procedures. The prepared compounds were purified by column chromatography on silica gel and identified by electronic spectra. The rhenium compounds were additionally identified by mass spectrometry.

Procedures for preparing sensor units on the basis of the indicated complexes and measuring their gas sensitivity have been described previously.[11,12,16] A gas-sensitive unit was placed in a temperature-controlled (5—30 °C) measuring cell containing a dosed ammonia content (0—180 mg m^{-3}). The gas-sensitive unit was a dielectric plate of devitrified glass (such as Pyroceram) with a comb electrodic structure obtained by photolithography. A gas-sensitive layer was supported on the comb structure. The electrophysical properties of the film of a gas-sensitive substance were measured by an E7-8 measuring instrument (immitance meter, Gomel, Belarus).

X-ray photoelectron spectra (XPS) were recorded on an Escalab MK II spectrometer (VG Scientific, Great Britain) in a regime of constant transmission energy of an analyzer (20 eV) using Al-Kα radiation ($h\nu = 1486.6$ eV). Vacuum in a measuring chamber of the spectrometer was maintained at a level $\leq 10^{-8}$ Pa. Sample charging was taken into account by lines 1s of carbon and 2p of silicon on a support. Charge states of elements were estimated from the energy position and shape of lines.[19]

IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer (Germany) for samples contacting with both dry air and an air—ammonia mixture. Samples were supported as thin films on KBr disks or polished silicon plates 300 μm thick.

Mass spectra of the rhenium compounds were obtained on a time-of-flight mass spectrometer (NPO Elektron, Sumy, Ukraine) with ionization by ^{252}Cf fusion fragments.

Electronic absorption spectra of the porphyrins were recorded on a Jasco UV 7800 spectrophotometer (Japan) in $CHCl_3$.

Results and Discussion

The results obtained in this study showed that films of all porphyrin complexes under study changed significantly their electrophysical properties (capacity, conductivity) on exposure to gaseous ammonia, and this change is functionally related to the ammonia concentration. It is most likely that on contact with the film ammonia interacts with active sites of the surface, due to which the number of charge carriers and electric conductivity σ increase substantially (Fig. 1). In the general case, the function $\Delta\sigma = f(C_{NH_3})$ is nonlinear and can be presented by a polynomial of the *n*th power. However, for the compounds under study, the numerical values of the polynomial coefficients, beginning from the second term, are much lower than the experimental error and, hence, $\Delta\sigma = f(C_{NH_3})$ can be considered as a linear function passing through the coordinate origin.

As turned out, the samples have different sensitivities to ammonia. The maximum sensitivity is inherent in films

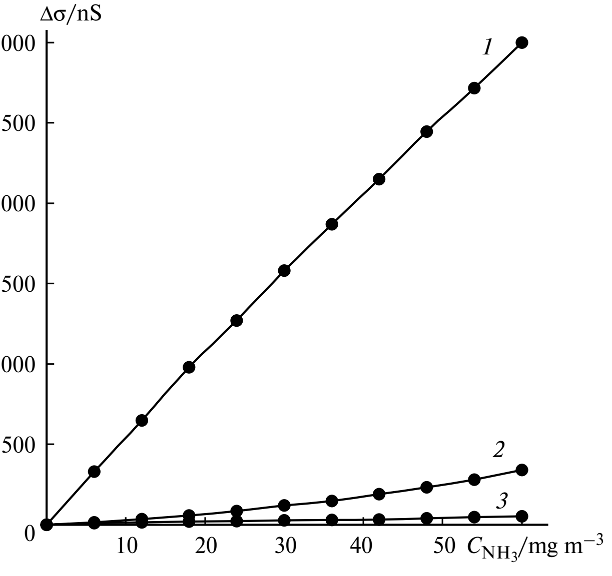


Fig. 1. Change in the conductivity of the metal porphyrin films at different ammonia concentrations (p_{H_2O} = 11 g m^{-3}): $Pt^{II} \cdot TPP$ (*1*); $ReO \cdot TPP$ (*2*); $Pt^{IV}Cl_2 \cdot TPP$ (*3*).

based on the complexes containing no extra ligands, *i.e.*, $\text{Pt}^{\text{II}}\cdot\text{TPP}$; the $\text{Pt}^{\text{IV}}\cdot\text{TPP}$ complexes containing two extra ligands ($\text{Pt}^{\text{IV}}\text{Cl}_2$) have the minimum sensitivity, and the sensitivity of the ReO • TPP complex with one extra ligand is intermediate (closer to that of the $\text{Pt}^{\text{IV}}\cdot\text{TPP}$ complex) (see Fig. 1). It can be assumed that the active site on which ammonia is sorbed is the central atom of the complex: when the central atom is blocked by the extra ligands, ammonia sorption is impeded, and the sensitivity of the complex decreases.

The effect of ammonia on the film surface is reversible: after the film was taken out from an ammonia-containing atmosphere, all its parameters returned to the initial values. This can indicate that the catalytic oxidation of ammonia occurs on the metal porphyrin film surface along with the equilibrium sorption—desorption of NH_3 and O_2 as the first step of process. This assumption can be favored by numerous examples of heterogeneous catalytic reactions of oxidation of various compounds with air oxygen sorbed on the porphyrin and phthalocyanine complexes.[2,3,20]

The electrophysical properties of the films under study change, depending on the content of water vapor and in the absence of ammonia in an air (Fig. 2). These plots are empirically described by exponential functions, which is likely related to the sorption of water vapor on the surface and formation of new conductivity bands. Therefore, we studied the influence of the water vapor content in the gaseous phase on the sensitivity of the complexes to ammonia (Fig. 3). Our experiments showed that an increase in the water vapor content resulted in a substantial increase in the sensitivity for the complexes containing the extra ligands in the axial positions ($\text{Pt}^{\text{IV}}\text{Cl}_2\cdot\text{TPP}$ and ReO • TPP) (see Fig. 3). The latter result indicates obviously that water molecules are directly involved in the catalytic oxidation of ammonia that is incorporated into intermediate complexes or is a participant or the product of some step of the process.

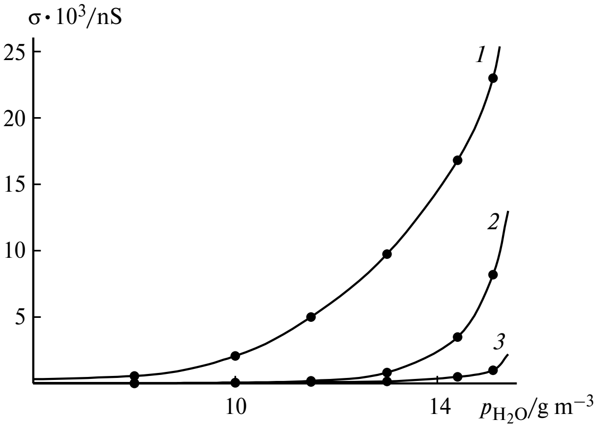


Fig. 2. Conductivity of the metal porphyrin films *vs.* content of water vapor in the absence of ammonia: $\text{Pt}^{\text{II}}\cdot\text{TPP}$ (*1*); ReO • TPP (*2*); $\text{Pt}^{\text{IV}}\text{Cl}_2\cdot\text{TPP}$ (*3*).

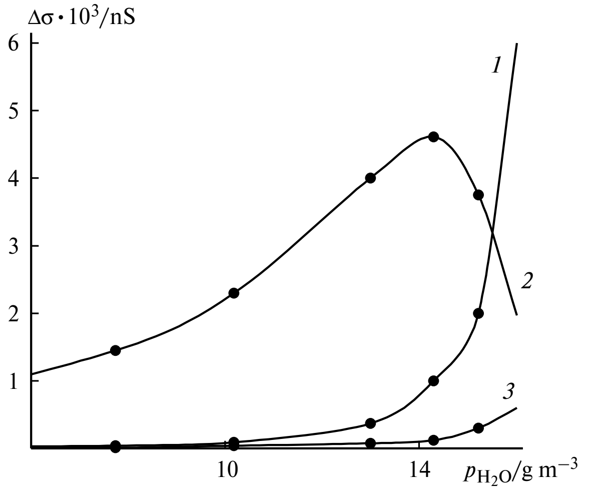


Fig. 3. Change in the conductivity of the metal porphyrin films at different water vapor concentrations at an unchanged ammonia content (48 mg m⁻³): ReO • TPP (*1*); $\text{Pt}^{\text{II}}\cdot\text{TPP}$ (*2*); $\text{Pt}^{\text{IV}}\text{Cl}_2\cdot\text{TPP}$ (*3*).

Processing of the experimental results showed that the plots of the conductivity of the films of the complexes *vs.* content of the water vapor (p) and ammonia (C_{NH_3}) can be approximated by the equations

$$\sigma = k_1 e^{b_1 p} + k_2 e^{b_2 p} C_{NH_3}, \tag{1}$$

$$\sigma = k_1 e^{b_1 p} + k_3 e^{b_3 p} C_{NH_3} \tag{2}$$

with correlation coefficient 0.99—0.97, where k_1, k_2, k_3, b_1, b_2, and b_3 are empirical parameters.

According to these equations, the influence of water vapor is described by exponential functions, and the effect of the ammonia content is described by a function close to linear. It can be assumed that the term $k_1 e^{b1p}$ in Eqs (1) and (2) corresponds to water pre-sorbed on the surface, and the term $k_2 e^{b2p}$ indicates that water is involved in the catalytic reaction. Equation (1) obeys for the complexes $\text{Pt}^{\text{IV}}\text{Cl}_2\cdot\text{TPP}$ and ReO • TPP.

In the case of the complex $\text{Pt}^{\text{II}}\cdot\text{TPP}$ containing no extra ligands, the plot of the sensitivity (conductivity change) to ammonia *vs.* water vapor content is presented by a curve with a maximum (see Fig. 3, curve *2*). This can be due to water adsorption on the film surface in which water forms its conductivity channels due to a specific action. However, water accumulates on the surface and begins to compete with ammonia for the interaction with active sites of the catalyst. In addition, water is one of the products of the catalytic step, shifting the chemical equilibrium of the catalytic step of the process toward the starting compounds. This is why, probably, the empirical plot of the change in the conductivity of the complex *vs.* content of the water vapor and ammonia has a

Table 1. Numerical values of coefficients in Eqs (1) and (2)

Compound	k_1	k_2	k_3	b_1	b_2	b_3
$\mathrm{Pt^{II}\cdot TPP}$	0.03	0.01	4.74	0.43	0.17	−0.28
$\mathrm{Re^{IV}O\cdot TPP}$	0.04	0.01	—	0.76	0.66	—
$\mathrm{Pt^{IV}Cl_2\cdot TPP}$	0.46	0.03	—	0.43	0.34	—

more complicated shape and is described by two equations: Eq. (1), before the maximum at the water content <14 g m^{-3} and Eq. (2), after the maximum at the water content >14 g m^{-3}. The numerical values of the coefficients are presented in Table 1.

The film thickness of the supported substance affects the change in the film conductivity on exposure to NH_3. The plot of the change in the film conductivity *vs.* thickness of the layer of the supported substance is presented by a curve with a maximum. This can be due to the fact that an increase in the thickness of thin films first increases the number of active sites on which the chemical reaction forming charge carriers occurs. In the case of thicker films, the conductivity begins to decrease due to diffusion processes.

To reveal the charge state of elements in gas-sensitive substances before and after exposure to gaseous ammonia, we determined the electron binding energies by XPS (Table 2).

The formal oxidation states of rhenium and platinum are[19] $\mathrm{Re^{IV}}$, $\mathrm{Pt^{II}}$, and $\mathrm{Pt^{IV}}$. In the rhenium complex that was not treated with gaseous ammonia, more oxidized rhenium forms are observed. Oxygen in the $\mathrm{Pt^{II}\cdot TPP}$ sample corresponds to the dioxygen ligand O_2^- adsorbed on the surface of the complex and bonded due to the free $5d_{z^2}$ orbital of platinum. The binding energies for N1s of the N atoms of the pyrrole rings in the platinum complexes indicate that their energy levels become equal due to a conjugation effect in the porphyrin ring. Unlike this, the rhenium complex untreated with ammonia exhibits a small splitting of the O1s levels, probably, due to the shift of the Re atom from the porphyrin ring plane. However, it cannot be excluded that this fact is related to a minor additive of the Re atoms in a higher oxidation state. The binding energy of N1s in the rhenium complex increases after pre-treatment with ammonia, probably, due to the sorption of some amount of the molecular compound $\mathrm{H_2O\cdot NH_3}$ on the surface of the complex. In this case, the charge state of the Re atom rigidly corresponds to 4+. This can be due to the fact that the preliminary ammonia treatment of the complex results in the reduction of Re admixture atoms in higher oxidation states and, as a consequence, the charge state of rhenium equalizes.

Table 2. Binding energies of electrons in the platinum and rhenium metal porphyrins before and after exposure of the surface of the complex to gaseous NH_3

Sample	Binding energy/eV				
	$\mathrm{Re4f_{7/2}}$	$\mathrm{Pt4f_{7/2}}$	N1s	O1s	C1s
ReO·TPP*	43.3	—	398.1	531.6, 530.8 sh	—
ReO·TPP**	43.5	—	398.6	531.6, 532.0	— —
$\mathrm{Pt^{II}\cdot TPP}$*	—	73.3	399.4	532.5	285.6
$\mathrm{Pt^{II}\cdot TPP}$**	—	73.5	399.5	532.9	285.0
$\mathrm{Pt^{IV}Cl_2\cdot TPP}$*	—	74.7	400.1	532.5	286.0
$\mathrm{Pt^{IV}Cl_2\cdot TPP}$**	—	74.5	399.9	532.5	285.0

* After storage in air.

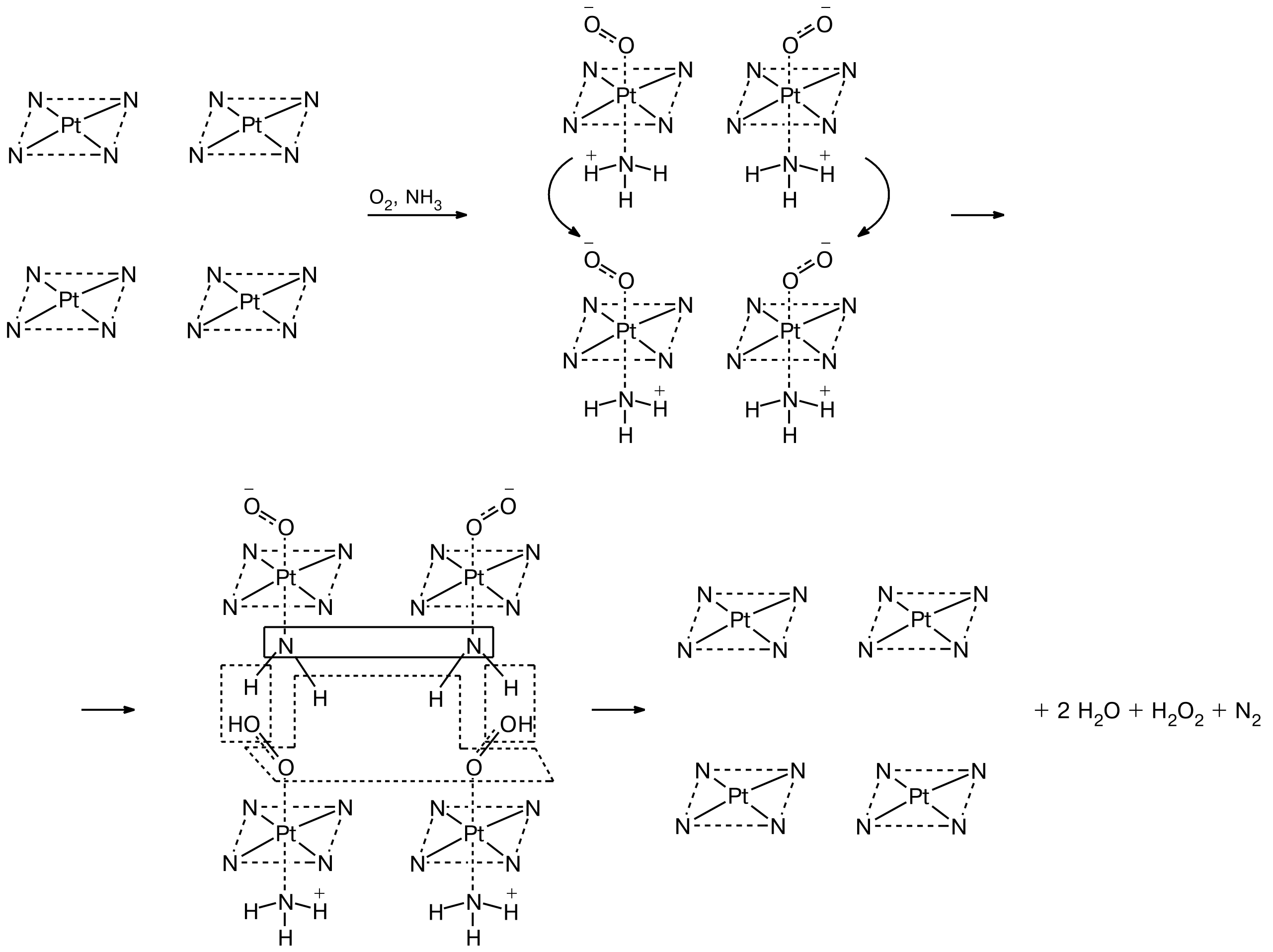
** After storage in air with a high ammonia content.

The data obtained allow one to conclude that the interaction of the ammonia-containing gas with the surface of the MTPP complexes is catalytic and accompanied by the oxidation of ammonia with air oxygen. This reaction is thermodynamically favorable and can afford different products. The formation of molecular nitrogen and water as final products is the most thermodynamically favorable at the molar ratio of the starting reactants $NH_3 : O_2 = 2 : 1.5$. Under real conditions, small amount of ammonia oxidize on the surface of the solid metal porphyrins in high excess oxygen, *i.e.*, the chemosorbed oxygen should not necessarily be reduced to H_2O but H_2O_2 or its mixtures with H_2O can be formed as well. Note that the heats of formation of H_2O (at the ratio $NH_3 : O_2 = 2 : 1.5$) or a mixture of H_2O and H_2O_2 (at the molar ratio of gases 1 : 1) differ insignificantly. However, in the second case, the model of the process of interaction of gases with the metal porphyrins is much simpler. In addition, hydrogen peroxide formation was observed in similar processes of oxygen reduction on the metal phthalocyanine[21,22] and corrin[23] complexes. Therefore, based on our experimental results and published data, we can assume that the $\mathrm{Pt^{II}\cdot TPP}$ and $\mathrm{Pt^{IV}\cdot TPP}$ complexes react with ammonia *via* Schemes 1 and 2, respectively.

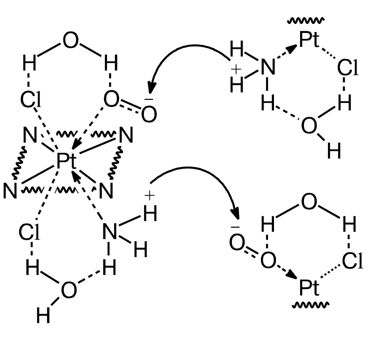
For the metal porphyrins containing no extra ligands (see Scheme 1), the reaction mechanism includes the extra coordination of the O_2 and NH_3 molecules with the metal porphyrin. The electron-releasing character of an NH_3 molecule significantly facilitates the formation of the superioxide radical ion $O_2^{-\bullet}$ followed by proton transfer from the ammonia molecule to the radical ion and desorption of H_2O and H_2O_2. The ammonia molecules lose protons and transform into NH_2 groups, which, being located at different metal porphyrin molecules in a crystal unit cell (according to the X-ray diffraction data,[24,25] the crystal unit cell contains four structural MTPP units), form the nitrogen—nitrogen bond, lose protons that transfer to oxygen, and transform into the N_2 molecule leaving the film surface (see Scheme 1).

For the metal porphyrins with the covalently linked extra ligands (see Scheme 2), interaction includes the

Scheme 1



Scheme 2



sorption of water molecules from the gas phase accompanying by the formation of a hydrogen bond with each extra ligand that interacts with the O_2 or NH_3 molecules. This results in the formation of a transition state with six-membered rings facilitating subsequent transfer of ammonia protons to oxygen atoms.

These schemes make it possible to explain the processes of catalytic ammonia oxidation on the surface of solid metal porphyrins accompanied by the formation of intermediates that differ from the starting complexes by electrophysical characteristics (charges of species, dipole moments, polarizability). These processes change the macrophysical parameters of the solid metal porphyrin film (for example, conductivity) that are functionally related to the ammonia content in air.

The influence of water vapor, which is always present in the atmosphere, produces the following effects: (1) direct involvement of the metal porphyrins with axially linked ligands in ammonia oxidation on the surface; (2) influence on the equilibrium of the process, because H_2O is also one of the reaction products; (3) influence of the surface layer on the conductivity due to intrinsic adsorption on the surface of the sensitive layer.

The proposed model can be used to interpret the interaction of ammonia with dioxygen and changes in the electrophysical properties of the surface and other transition metal complexes with the square plane or octahedral configurations.

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