Coordination of nitroxyl radical probes to the Lewis acid sites on the surface of gallium oxide: a quantum-chemical analysis

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The results of ESR investigations and quantum-chemical studies on the coordination of 2,2,6,6-tetramethylpiperidine-*N*-oxyl to the Lewis acid sites (LAS) on the surface of gallium oxide are reported and analyzed. The structural, spin, electrostatic, and energy characteristics of the coordination of the simplest nitroxyl radical, $H_2NO^{\cdot}$, to the $Ga(OH)_3$ model cluster-type LAS were calculated by the unrestricted Hartree—Fock method in the 6-31G basis set and using the semiempirical PM3 approximation. The properties of gallium-containing nitroxyl surface complexes and their aluminum-containing analogs are compared. According to the results of cluster quantum-chemical calculations, the LAS on the surface of gallium oxide are stronger than those on the alumina surface.

Key words: quantum-chemical analysis; gallium oxide; nitroxyl radical probes; surface donor-acceptor complexes; structural, magnetic resonance, electrostatic, and energy characteristics of coordination.

Understanding of the mechanisms of heterogeneous catalytic reactions requires studying the nature of the active sites of the surface of catalysts. Comparison of results obtained from quantum-chemical analysis of the interaction of molecules with the surface adsorption sites with experimental data makes it possible to reveal peculiarities of the structure of the surface complexes (SC) and to calculate their energy parameters. Complexes of different compounds with the Lewis acid sites (LAS) of the surface of various solids, including those of nitroxyl radicals with the LAS on the surface of alumina and aluminosilicates, have been extensively studied.[1] These studies can serve as a good example of joint application of experimental and computational methods.

Gallium is the closest analog of aluminum. Related gallium and aluminum compounds are structurally similar and possess similar physicochemical properties. In particular, gallium halides, as well as aluminum halides, are Lewis acids. The surface of gallium-containing catalysts also exhibits high Lewis acidity.[2,3] Several complexes of adsorbed probe molecules with this type of LAS have been studied experimentally.[4,5] Complexes of nitroxyl radicals with gallium halides and coordinatively unsaturated Ga^{3+} ions on the surface of gallium oxide and gallium silicates have been studied in detail by ESR spectroscopy.[2]

Electron-acceptor properties of a particular LAS are dependent on the nature of its nearest environment. It was proposed to use the constant of hyperfine coupling with the magnetic nucleus of a metal cation, a_M, for characterization of the accepting ability of a LAS, since the a_M value reflects the degree of transfer of the unpaired electron from the adsorbed radical to the coordinatively unsaturated metal cation.[6] For instance, complexes of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPO) with gallium halides are characterized by the constants of isotropic hyperfine interaction, a_{Ga}, equal to 39, 35, and 24 Oe for $^{71}GaCl_3$, $^{71}GaBr_3$, and $^{71}GaI_3$, respectively.[7] Complexes of the TMPO radical with the LAS on the surface of gallium oxide are characterized by an anisotropic splitting of ~40 Oe on the metal atom nucleus, whereas that of ~49 Oe is typical for gallium cations surrounded by silicate tetrahedra on the surface of amorphous gallium silicates.[2] (These values were obtained for specimens whose isotopic composition corresponded to the natural abundance of gallium isotopes.).

Despite the fact that related coordination compounds of gallium and aluminum possess similar physicochemical properties, their structural and electronic characteristics can differ appreciably. Unlike complexes with aluminum-containing LAS, only a few quantum-chemical studies of donor-acceptor complexes of simple molecules with gallium-containing LAS have been reported.[8] Changes in the geometry and electronic structure of complex nitroxyl radical probes due to the replacement

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of Al^{3+} by Ga^{3+} ions in the surface LAS can be simulated using the cluster-type versions of semiempirical computational schemes. This work is dedicated to solving this problem.

Scheme of cluster-type quantum-chemical analysis

Preparatory to performing quantum-chemical analysis of the coordination of nitroxyl radical probes to the surface of gallium oxide, we will first of all choose an adequate model of its surface LAS. This can be done with ease using the cluster approximation.[9] In this case, a fragment of the structure (a cluster) consisting of a relatively small number of atoms and retaining the chemical nature of the active surface site is "cut" from the crystal. This is accompanied by the appearance of artificial free valences on the cluster boundary. If (most often) it is possible to construct a covalent (built of atoms) cluster-type model, these valences are "forced" to be saturated with H atoms. Otherwise, they are neutralized by constructing a so-called uncharged cluster shareholder, which includes ordinary ions and boundary pseudoions.[9]

Based on the results of radiospectroscopic studies (see above), it is generally accepted that truncated tetrahedra with tricoordinate Ga^{3+} ions are the strongest LAS on the surface of gallium oxide. Predominance of this type of LAS on dehydroxylated surfaces of alumina and gallium oxide is also indicated by the fact that the magnetic resonance parameters (the *g*-factors and HFC constants) of paramagnetic SC formed in this case are virtually identical with those of analogous complexes of nitroxyl radicals with $AlCl_3$ and $GaCl_3$ in nonpolar solvents.[6] Hence, a structural fragment of the surface of gallium oxide, $Ga(OH)_3$, saturated with hydrogen atoms can serve as the simplest covalent cluster-type model of the LAS in question.

It should be kept in mind that an analogous $Al(OH)_3$ cluster has been widely used in quantum-chemical studies of the adsorption of various compounds on the alumina surface. In particular, it has been shown[1,10] that even such a "minimum" cluster-type model of the surface LAS makes it possible to suggest an adequate quantum-chemical interpretation of the whole set of radiospectroscopic and thermochemical data on the coordination of nitroxyl radical probes to the surface of alumina.

In this work, in order to evaluate the semiempirical computational procedure, we performed a comparative quantum-chemical analysis of the structural, spin, charge, and energy characteristics of coordination of the simplest nitroxyl radical, $H_2NO^{\cdot}$, to the covalent cluster-type LAS $Ga(OH)_3$. Then we considered the paramagnetic SC of the TMPO radical with the LAS of the surface of gallium oxide, which has been studied experimentally. Turning ourselves to the $H_2NO^{\cdot}$ prototype was also motivated by the fact that previously[1] the involvement of $H_2NO^{\cdot}$ in the cluster quantum-chemical calculations appeared to be sufficient for a consistent semiquantitative explanation for experimentally established regularities of the adsorption of nitroxyl radical probes on the surface of alumina and that no qualitative changes were observed on going to calculations of more complex nitroxyl radicals used in experimental studies.

Results and Discussion

Coordination of $H_2NO^{\cdot}$ radical. Table 1 lists the results of quantum-chemical calculations of free radical $H_2NO^{\cdot}$ and its paramagnetic SC with a model LAS, $Ga(OH)_3$ or $Al(OH)_3$, obtained in the unrestricted Hartree—Fock approximation (UHF) using the semiempirical PM3 approach and the *ab initio* computational scheme in the 6-31G basis set.[11] This basis set appeared to be well-proven in the quantum-chemical analysis of the coordination of nitroxyl radical probes to the surface LAS of alumina.[1,10] The reason why the PM3 computational procedure was chosen is that it is the only one among the three semiempirical computational procedures (AM1, MNDO, and PM3) that includes parametrization for gallium compounds. The isotropic HFC constants, $a_{iso}{}^{A}$, were assessed conventionally by multiplying the spin population of the valence s-orbital of atom A under consideration by the corresponding Hartree—Fock coefficient of proportionality.

The characteristics of isolated $H_2NO^{\cdot}$ radical calculated using the two above-mentioned methods are listed in Table 1 (columns 2 and 3). As can be seen, the O—N bond lengths, *r*(O—N), are strongly different. However,

Table 1. Structural, magnetic resonance, electrostatic, and energy characteristics of the simplest nitroxyl radical $H_2NO^{\cdot}$ and its donor-acceptor complexes $H_2NO^{\cdot}...MX_3$ (M = Ga, Al; X = OH, Cl) with "frozen" LAS

Parameter	$H_2NO^{\cdot}$ [1]		$H_2NO^{\cdot}...Ga(OH)_3$		$H_2NO^{\cdot}...Al(OH)_3$ [1]		$H_2NO^{\cdot}...GaCl_3$	
	PM3	6-31G	PM3	6-31G	PM3	6-31G	PM3	6-31G
r(M—X)/Å	—	—	1.83	1.83	1.82	1.82	2.09	2.09
r(M...O)/Å	—	—	1.82	1.85	1.86	1.86	1.82	1.85
r(O—N)/Å	1.23	1.30	1.26	1.25	1.26	1.23	1.26	1.24
r(N—H)/Å	0.98	0.99	0.98	1.02	0.98	1.02	0.98	1.02
α/deg	—	—	109	109	109	109	109	109
θ/deg	—	—	72	52	71	50	76	51
$a_{iso}{}^{N}$/Oe	10	17	12	18	13	42	12	25
$\rho_s{}^{M}$	—	—	−0.001	−0.002	−0.001	−0.001	−0.001	−0.002
ρ^{N}	0.64	0.24	0.77	0.64	0.75	0.65	0.78	0.65
ρ^{O}	0.40	0.81	0.26	0.45	0.30	0.46	0.26	0.46
ΔE_c/kcal mol^{-1}	—	—	−59.2	−62.3	−36.3	−41.5	−58.5	−60.2

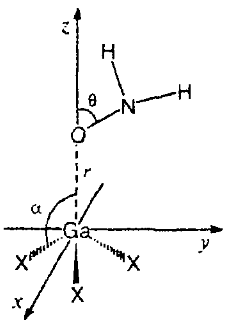
* According to Ref.[1]

both numerical values lie in the range 1.2—1.3 Å, which is in agreement with the results of X-ray diffraction studies of stable nitroxyl radicals.[12] It cannot be ruled out that the N—O bond length in the $H_2NO^\cdot$ radical obtained from PM3 calculations is somewhat underestimated, whereas that calculated using the *ab initio* approach is somewhat overestimated. This can be a reason for either qualitative or quantitative contradiction between the ratio of calculated spin populations ($\rho^O : \rho^N$, see Table 1) and its empirical estimate, $\rho^O : \rho^N \approx 0.6 : 0.4$.[9] At the same time, this ratio is known[1] to be correctly reproduced in the framework of the MNDO approximation. Therefore, this contradiction between experimental data and the results of semiempirical calculations is most likely due to inadequacy of the parametrization of the PM3 method, which was developed in order to describe quantitatively the heats of formation of chemical compounds.

The experimental value of isotropic HFC constant a_{iso}^N of the $H_2NO^\cdot$ radical is -12 Oe.[13,14] The calculated values (see Table 1) are close to the experimental one. It is noteworthy that the PM3 approximation reproduces the numerical value of this constant somewhat better than the UHF/6-31G scheme.

The results of calculations of paramagnetic SC of the simplest nitroxyl radical $H_2NO^\cdot$ with the model system GaX_3 (X = OH, Cl) (Scheme 1) by the UHF/PM3 and UHF/6-31G methods are presented in Table 1 (columns 4, 5, 8, and 9). Following well-reasoned recommendations,[1] the cluster-type LAS $Ga(OH)_3$ was considered to be "frozen" and only the radical fragment geometry was optimized. All bond angles in the cluster were assumed to be equal to the tetrahedral angle and the Ga—O distances, *r*(Ga—O), were assumed to be equal to 1.83 Å (in accord with the data of X-ray diffraction studies of gallium oxide[15]).

Scheme 1



X = OH, Cl

As can be seen in Table 1, the length of the Ga...O coordination bond, *r*(Ga...O), calculated by the UHF/PM3 method is somewhat shorter than that obtained in the UHF/6-31G approximation. According to semiempirical calculations, coordination of the $H_2NO^\cdot$ radical to the LAS of the surface of gallium oxide should cause a lengthening of the N—O bond, whereas the reverse is predicted by *ab initio* calculations. Because of this, both methods give close values for the *r*(O—N) distances in paramagnetic SC $H_2NO^\cdot...Ga(OH)_3$. Upon the coordination, the *r*(N—H) interatomic distance remains unchanged according to semiempirical calculations or is somewhat lengthened according to the *ab initio* calculations. Large angles θ (see Table 1) indicate that both structures of paramagnetic SC $H_2NO^\cdot...Ga(OH)_3$ (see Scheme 1) are highly bent; however, their obvious similarity should be pointed out.

The results obtained using the two quantum-chemical approaches show an increase in the isotropic HFC constant a_{iso}^N of the nitroxyl radical coordinated to the $Ga(OH)_3$ cluster-type LAS. The a_{iso}^N values are close to those of related donor-acceptor complexes measured by ESR spectroscopy.[2] At the same time, the estimates of numerical values of the isotropic HFC constant a_{iso}^{Ga} lie between -2.5 and 5 Oe, which is about an order of magnitude smaller than the experimental values (30 to 40 Oe depending on the type of gallium compound). Previously,[1] such an underestimation of calculated HFC constants a_{iso}^{Al} as compared with their experimental values has also been observed for paramagnetic SC of nitroxyl radicals with the cluster-type LAS of the surface of alumina.

First of all, these large discrepancies are due to the fact that the spin population, ρ_s^M, of the valence s-AO of the Ga atom is very small in absolute value (~0.001; see Table 1) and is therefore extremely sensitive even to small errors of the computational procedure. In these instances, the negligible spin populations of inner s-AO involved in the procedure for assessing the isotropic HFC constants and multiplied by very large coefficients of proportionality begin playing a special role.[16,17] It should be noted that both isotropic HFC constants a_{iso}^{Ga} estimated in the valence approximation have the correct sign.

Both quantum-chemical methods predict that the total spin population on the N atom (ρ^N) increases, whereas that on the O atom (ρ^O) decreases upon coordination of $H_2NO^\cdot$ to $Ga(OH)_3$ (see Table 1). According to calculations, coordination causes an increase in the positive charge on the N atom and in the negative charge on the O atom. By and large, the degree of transfer of the electron density from the coordinated $H_2NO^\cdot$ radical to the $Ga(OH)_3$ cluster-type LAS is rather high. It is also noteworthy that the formation of paramagnetic SC $H_2NO^\cdot...Ga(OH)_3$ is accompanied by a shift of the electron and spin density on the N—O bond in opposite directions.

Among important parameters there are also the complexation energies, ΔE_c, which reflect the character of coordination and make it possible to compare quantitatively the adsorption and catalytic properties of the active sites of the surface of solids. In principle, the ΔE_c values can be determined experimentally; unfortunately, they often are assessed only indirectly. No data on the adsorption of nitroxyl radicals on the surface of gallium oxide are available to date.

As was mentioned above, the parametrization of the PM3 method was developed in order to describe quantitatively the heats of formation of chemical compounds. Therefore, the complexation energies obtained in the framework of this approximation seem to be realistic. In particular, the ΔE_c value for the paramagnetic SC $H_2NO^\cdot...Ga(OH)_3$ obtained from PM3 calculations

(59.2 kcal mol^{-1}) is close to the corresponding value calculated using the *ab initio* UHF/6-31G scheme (62.3 kcal mol^{-1}). This indicates that the PM3 method can be used for obtaining quantitative estimates of the energy characteristics of gallium-containing systems. High complexation energy (~60 kcal mol^{-1}) is unambiguous evidence for the chemisorption character of donor-acceptor interaction between the $H_2NO^{\cdot}$ radical and the $Ga(OH)_3$ cluster-type LAS.

It is also of interest to study how the environment of Ga^{3+} ion affects the properties of the nitroxyl complex. The results of analogous calculations of the coordination of the $H_2NO^{\cdot}$ radical to $GaCl_3$ are presented in Table 1 (columns 8 and 9). As can be seen from comparison of the corresponding columns, the characteristics of the paramagnetic SC $H_2NO^{\cdot}...Ga(OH)_3$ and coordination compound $H_2NO^{\cdot}...GaCl_3$ obtained using the same quantum-chemical method differ only slightly. This is also indicated by the results of experiments with nitroxyl radicals on the surface of gallium oxide and in a $GaCl_3$ solution.[2,7] In addition to confirmation of experimental data, our conclusion that the calculated properties of nitroxyl paramagnetic SC depend only slightly on the type of the environment of the Ga^{3+} ion theoretically substantiates the use of the $GaCl_3$ molecule as a model cluster and indicates that the approach involving the "minimum" cluster-type models is adequate to the problem posed.[18]

On the whole, our comparison of the results obtained using the UHF/PM3 and UHF/6-31G quantum-chemical computational procedures shows their equivalence in the case of assessing the numerical values of physicochemical quantities that have not been measured experimentally. Taking into account that the computational cost of PM3 calculations is much lower, the PM3 method should be preferred for performing the cluster quantum-chemical analysis of structural, radiospectroscopic, and energy parameters of paramagnetic SC of complex nitroxyl radical probes and the LAS on the surface of gallium oxide.

Comparison of acidic and adsorption properties of different oxide catalysts is an important problem which has not been solved even experimentally. Keeping this in mind, it seems quite reasonable to compare gallium oxide and its closest analog, alumina. To this end, in Table 1 (columns 6 and 7) we present the results of analogous calculations of the coordination of the $H_2NO^{\cdot}$ radical to the $Al(OH)_3$ model cluster-type LAS.

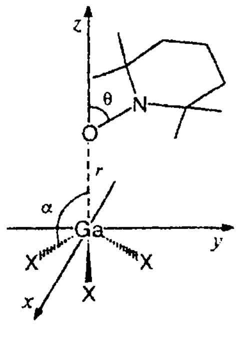
By comparing in pairs columns 4 and 5 with columns 6 and 7 in Table 1 it can be easily seen that the cluster-type paramagnetic SC $H_2NO^{\cdot}...Ga(OH)_3$ and $H_2NO^{\cdot}...Al(OH)_3$ have similar geometry and electronic structure; however, the Al...O coordination bond in the latter is somewhat longer than the Ga...O bond in the former. According to *ab initio* calculations, replacement of Ga^{3+} ion by Al^{3+} ion involves changes only in two values ($a_{iso}{}^{N}$ and ΔE_c), whereas one of them ($a_{iso}{}^{N}$) remains virtually unchanged in the UHF/PM3 approximation.

It should be noted that the constant of isotropic HFC with the nucleus of the N atom in the model paramagnetic SC $H_2NO^{\cdot}...Al(OH)_3$ is strongly overestimated (42 Oe) in the UHF/6-31G approximation and somewhat underestimated (13 Oe) in the UHF/PM3 approximation as compared to the experimental values (19—22 Oe) for several nitroxyl radical probes adsorbed on the surface of alumina.[6] At the same time, the results obtained using both approaches are in quantitative agreement and indicate that the paramagnetic SC $H_2NO^{\cdot}...Al(OH)_3$ is less stable than the $H_2NO^{\cdot}...Ga(OH)_3$ complex (their complexation energies differ by ~20 kcal mol^{-1}). In this connection, it should be emphasized that the calculated absolute values of ΔE_c (~36 and ~42 kcal mol^{-1}, see Table 1, columns 6 and 7) are fairly close to those measured experimentally (32—35 kcal mol^{-1}) in studies on the chemisorption of nitroxyl radicals on the surface of oxide catalysts.[6] This fact is yet another confirmation of the equivalence of the UHF/PM3 and UHF/6-31G approximations used in quantum-chemical studies of thermodynamics of paramagnetic SC of nitroxyl radicals adsorbed on oxides.

Coordination of TMPO radical. Despite the possibility of obtaining important structural-chemical and spectral information using the $H_2NO^{\cdot}$ radical (see above), it is often considered as a "too model" object. Therefore, it is of interest to pass to analogous calculations of nitroxyl radicals and their paramagnetic SC with the oxide LAS used in ESR studies. Among them, we chose the TMPO radical, widely used as a paramagnetic probe.

Calculations of the TMPO radical and its cluster-type paramagnetic SC with the GaX_3 (X = OH, Cl) model LAS (Scheme 2) were carried out using the semiempirical UHF/PM3 method, which was shown to be equivalent to the *ab initio* UHF/6-31G approach (see above). The calculated characteristics of isolated TMPO radical are listed in Table 2 (column 2). Comparison of the corresponding columns in Tables 1 and 2 shows that the TMPO radical is characterized by a somewhat longer O—N bond and substantially larger isotropic HFC constant $a_{iso}{}^{N}$ than that in $H_2NO^{\cdot}$. The $a_{iso}{}^{N}$ value for TMPO is close to those of several stable nitroxyl radicals, measured by ESR spectroscopy (15—19 Oe).[2] On going from $H_2NO^{\cdot}$ to the TMPO radical, the calculated spin populations ρ^{O} and ρ^{N} also become closer to those obtained from the experiment (see above).

Scheme 2



X = OH, Cl

Table 2. Structural, magnetic resonance, electrostatic, and energy characteristics of nitroxyl radical TMPO and its paramagnetic SC TMPO...MX_3 (M = Ga, Al; X = OH, Cl) with model cluster-type LAS calculated by the PM3 semiempirical method

Parameter	TMPO	$Ga(OH)_3$		$Al(OH)_3$		$GaCl_3$
		SC I	SC II	SC I	SC II	SC II
r(M—X)/Å	—	1.78	1.83	1.76	1.82	2.09
r(M...O)/Å	—	1.83	1.81	1.88	1.85	1.80
r(O—N)/Å	1.25	1.27	1.27	1.27	1.27	1.27
r(N—C)/Å	1.53	1.53	1.52	1.54	1.54	1.52
α/deg	—	100	109	102	109	109
θ/deg	—	70	69	61	62	62
a_{iso}^{N}/Oe	18	13	13	23	23	15
ρ^N	0.59	0.70	0.71	0.73	0.76	0.77
ρ^O	0.42	0.32	0.25	0.26	0.23	0.25
Q^M	—	1.30	1.28	0.83	0.81	1.12
Q^N	0.48	0.49	0.56	0.57	0.57	0.56
Q^O	−0.50	−0.48	−0.55	−0.42	−0.43	−0.57
ΔE_c/kcal mol^{-1}	—	−84.5	−76.4	−30.1	−38.3	−78.0

Note. "SC I" and "SC II" denote complexes with LAS with fully optimized geometry and with the geometry considered "frozen" in the form of a regular truncated tetrahedron, respectively.

We studied the effect of fixed geometry of the $Ga(OH)_3$ cluster-type LAS on the results of calculations taking the model paramagnetic SC TMPO...$Ga(OH)_3$ as an example. Calculations using this LAS were performed in two variants, namely, the LAS geometry was either fully optimized (SC I) or considered "frozen" as a regular truncated tetrahedron (SC II). "Freezing" of the $Ga(OH)_3$ cluster corresponds to the presence of a rigid framework in the crystal lattice and is capable of compensating for the drawbacks of the choice of the "minimum" model LAS.[1,18]

The results of calculations of paramagnetic SC TMPO...$Ga(OH)_3$ are listed in Table 2 (columns 3 and 4). Most of the qualitative regularities found for the simplest paramagnetic SC $H_2NO^{\cdot}$...$Ga(OH)_3$ (see Table 1) are also valid in this case; at the same time, some quantitative differences are observed. Compared to the $H_2NO^{\cdot}$...$Ga(OH)_3$ complex, SC II is ~17 kcal mol^{-1} more stable and the N—O bond in SC II is much less polar.

On going from SC II to SC I, optimization of the geometry of the cluster-type LAS leads to appreciable shortening of the intracluster Ga—O bonds and to a slight lengthening of the Ga...O coordination bond. The N—O bond length is insensitive to the geometry optimization procedure, though the angle α (see Scheme 2) becomes appreciably smaller. This means that the model LAS becomes somewhat flattened due to its "dwarf" size and, hence, unjustifiably increased mobility of the nearest environment of the Ga^{3+} ion. In a real Ga_2O_3 crystal, positions of the atoms can be considered rigidly fixed so it is hardly probable that a relatively small radical adsorbed on the surface will cause strong perturbations of the core of the crystal lattice. At the same time, the adsorbed radical used in the model calculations is much larger than the cluster-type LAS, which affects significantly the shape of its optimized structure. It is noteworthy that the use of the "frozen" geometry of the $Ga(OH)_3$ cluster has no effect on the isotropic HFC constant a_{iso}^{N}.

The results of calculations for the complex of the TMPO radical with the $GaCl_3$ molecule with nonoptimized geometry are shown in Table 2 (column 7). Comparison of columns 7 and 4 shows that changes in the composition of the LAS involved in coordination have little effect on the characteristics of complexation. Thus, the conclusion drawn in the studies of the $H_2NO^{\cdot}$ prototype that $Ga(OH)_3$ and $GaCl_3$ are equivalent in the quantum-chemical analysis of the structural, magnetic resonance, and energy parameters of paramagnetic SC of nitroxyl radicals adsorbed on the surface of gallium oxide is also valid for the TMPO radical used in experimental ESR studies.

For comparison, we present the characteristics of coordination of the TMPO radical to the $Al(OH)_3$ model cluster-type LAS calculated analogously (see columns 5 and 6 in Table 2). It should be noted that passage from gallium-containing to aluminum-containing paramagnetic SC with the TMPO radical is characterized by the same regularities as in the case of the $H_2NO^{\cdot}$ prototype. In particular, both the positive charge Q^M on the central metal atom and stability of nitroxyl paramagnetic SC decrease appreciably. Noteworthy is that the ΔE_c values (see Tables 1 and 2) for the paramagnetic SC of $Al(OH)_3$ with the $H_2NO^{\cdot}$ and TMPO radicals are rather close ($\Delta E_c \approx -36$ and -38 kcal mol^{-1}, respectively), whereas they differ appreciably for analogous complexes of $Ga(OH)_3$ ($\Delta E_c \approx -59$ and -76 kcal mol^{-1}, respectively).

By and large, it should be emphasized that the use of the $GaCl_3$ and $Ga(OH)_3$ systems as the model LAS in the cluster-type quantum-chemical studies of the coordination of nitroxyl radical probes on the surface of gallium oxide leads to quantitatively similar structural, electrostatic, radiospectroscopic, and energy parameters of coordination. Complexation of the above-mentioned radicals with the surface LAS containing tricoordinate gallium ions is a chemisorption process. The donor-acceptor complexes formed on the surface of gallium oxide are much more stable than the corresponding complexes formed on the surface of alumina.

Usually, of particular interest is comparison of the acidity of different surface LAS. In this case, either the charge Q^M on the metal atom or the energy ε_v of the lowest vacant MO of the cluster can serve as quantum-chemical characteristics of acidity. Comparison of the $Ga(OH)_3$ and $Al(OH)_3$ model LAS in the framework of the PM3 scheme shows that the gallium-containing LAS is characterized by higher acidity than the aluminum-containing one, because $Q^{Ga} > Q^{Al}$ (1.22 *vs.* 0.89, respectively) and $\varepsilon_v^{Ga} < \varepsilon_v^{Al}$ (−2.5 eV *vs.* −1.6 eV, respectively).

Thus, using cluster-type quantum-chemical calculations we succeeded not only in confirming the experimentally found regularities of coordination of nitroxyl radical probes with the LAS of the surface of gallium oxide, but also in assessing the heat of such a chemisorption process, which has not been measured as yet. To some extent, we approached a solution of the problem of the relative acidity and adsorption capacity of the LAS on the surface of gallium oxide and alumina.

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