Reviews

Nuclear magnetic resonance of donor atoms as a tool for determination of the structure of platinum metal complexes in solutions

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Data on the NMR spectroscopy of C, N, O, Si, P, and Sn donor atoms of platinum metal complexes in solutions are surveyed. The chemical shift of a donor atom mainly depends on the ligand in the *trans*-position (due to the trans-effect). The chemical shift of a donor atom on a particular coordinate of the complex (coordinate shift, CSh) is an attribute of this coordinate and can be used to identify such a coordinate in platinum metal complexes and to determine the structures of complexes. Based on the known data, CSh diagrams were composed for ^{1}H, ^{13}C, ^{14}N, ^{17}O, ^{19}F, ^{31}P, and ^{119}Sn. Examples of using the CShs for determining the structures of platinum metal complexes in solutions are presented.

Key words: complexes, structure, platinum metals, NMR of donor atoms, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, ^{14}N NMR spectroscopy, ^{17}O NMR spectroscopy, ^{19}F NMR spectroscopy, ^{31}P NMR spectroscopy, ^{119}Sn NMR spectroscopy.

During the first NMR experiments dealing with the donor oxygen atoms in the Rh^{III}—HCl—H_2O system, we found[1—3] that the ^{17}O NMR chemical shift for coordinated water (H_2O^c) in the $[RhCl_x(H_2O)_{6-x}]^{3-x}$ complexes (x = 1—5) acquires only two values (−99±1 and −141±1 ppm) in eight different aquachloro complexes, which are distinguished in the ^{103}Rh NMR spectra.

Although the shift of the oxygen donor atom signal induced by ligand coordination to the complex was much greater than the shifts for coordinated hydrogen[4,5] and nitrogen[6—8] atoms known at that time, the presence of only two values of chemical shift meant the occurrence of water on two coordinates of the complex: $H_2\underline{O}$—Rh—Cl and $H_2\underline{O}$—Rh—OH_2; the difference in chemical shifts was due to trans-effect inherent in platinum metal complexes. Further studies dealing with the structure of platinum metal complexes with electron-donating O and N atoms in the ligands showed clear-cut specificity of the chemical shifts of donor atoms with respect to the coordinates of these complexes. In what follows the chemical shift of a ligand donor atom on a particular coordinate is referred to as the coordinate shift (CSh).[9,10]

This review summarizes the experimental data on the chemical shifts of N, O, C, F, Si, P, and Sn donor atoms

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on different coordinates of complexes and gives examples of using the CShs for determining the structures of platinum metal complexes.

Chemical shifts of donor atoms of ligands in complex

Nuclear magnetic resonance appears to be the most specific technique in determining the molecular structures of species (molecules, ions, mono- and polynuclear complexes, clusters, adducts, *etc.*) in solutions if for no other reason than because this is a pure-isotopic method whose parameters are highly sensitive to the environment of the atom under interest. The key NMR parameters used to recognize a chemical species in solution and to determine its structure include the position of signals, *i.e.*, the chemical shift with respect to a particular compound (reference), and the spin-spin coupling constants. The chemical shift is measured in the δ scale in which a positive shift corresponds to an increase in the NMR frequency (or a decrease in shielding, or a downfield displacement of lines). This shift is due to different degrees of shielding of the external magnetic field on the nucleus of the same atom on passing from one compound to another and is composed of shieldings by the electrons involved in the chemical bond (valence electrons), as the shielding by electrons of closed shells is the same in all compounds of a given element.

The shielding is described by a known Ramsey equation,[11] which represents the sum of diamagnetic and paramagnetic terms. The shielding of hydrogen nuclei is described by the diamagnetic term; in the case of other nuclei, the paramagnetic term predominates. The Ramsey equation adapted for Period 2 elements, B—F, is given below (Eq. (1)). Splitting of the signal from the metal incorporated in a complex caused by the spin-spin coupling between the metal nucleus and the donor atom nuclei allows one to determine the number of identical ligands in the complex. The spin-spin coupling constant by itself can characterize a complex. In the case of platinum metals, splitting occurs for ^{103}Rh, ^{187}Os, and ^{195}Pt isotopes with the donor atom nuclei having the spin $I = 1/2$. For ligands with the B, C, N, O, and S donor atoms and the natural abundance of magnetic isotopes, splitting caused by spin-spin coupling can be observed in exceptional cases. In some cases, for Ru, Pd, and Ir complexes, the spin-spin coupling constant with a donor atom nucleus can be estimated indirectly.

Study of hydride complexes of platinum metals by ^{1}H NMR revealed unusual (compared to other hydrogen compounds) magnitudes and signs of the chemical shifts of the hydride hydrogen (10—20 ppm upfield shifts relative to tetramethylsilane).[4,5] It was shown theoretically for octahedral hydride complexes[4] and square-planar complexes formed by Group VIII metals with incomplete d-shells[5] that the change in the shielding of hydride hydrogen atoms is largely determined by the paramagnetic component, which gives rise to negative chemical shifts. The coordinates for an octahedral and a square-planar complex are shown in Fig. 1.

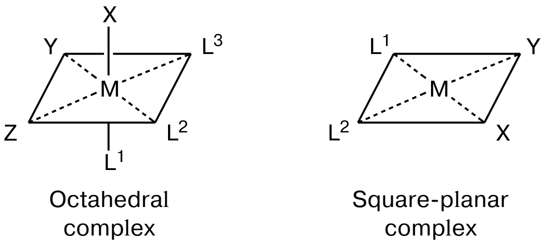

Fig. 1. Coordinates of an octahedral (X—M—L^1, Y—M—L^2, Z—M—L^3) and square-planar (X—M—L^1, Y—M—L^2) complexes.

It was suggested[12] that the chemical shift of the hydride hydrogen atom reflects the influence of the *trans*-ligand. This suggestion was confirmed by different studies including quantum-mechanical calculations.[13]

In the case of other donor atoms, the paramagnetic component of shielding predominates. For Period 2 elements (B—F), in the mean energy approximation, it is given by the relation[14]

$$\delta_p = (\mu_0\mu_B\langle r^{-3}\rangle_{np}\Sigma Q)/(2\pi\Delta E), \quad (1)$$

where $\langle r^{-3}\rangle_{np}$ is the mean value of the function r^{-3}, r is the radius of the p-electrons of the atom in the given environment, ΣQ is the asymmetry factor of the electron cloud, ΔE is the excitation energy of the atom averaged over all levels. Quantum-mechanical calculations of shielding have been successful so far only for relatively small molecules[15,16] and usually they are less accurate than the determination of chemical shifts. However, the validity of relation (1) has been repeatedly confirmed by experimentally measured variation of chemical shifts in a series of compounds selected in such a way that only one parameter in relation (1) is changed. For example, a correlation has been established[17] between $\delta_{^{17}O}$ and $1/(\Delta E)$ in which the excitation energy of the lower level, which makes the major contribution to ΔE, was used in place of the ΔE value. Now the values for shielding of the carbon nucleus in small molecules calculated by various quantum-mechanical methods differ from experimental values by 5—20 ppm. The results of calculations of the shielding of oxygen nuclei in the ozone molecule differ from the experimental value by ~100 ppm.[15] This accuracy is inadequate for elucidating the effects described below. Calculations of shielding of heavy donor atoms in platinum metal complexes are unknown.

The first ^{15}N NMR data obtained showed[6—8] that the nitrogen signals for ammine complexes of platinum met-

Table 1. Shifts of the lines of the donor atoms upon ligand coordination (Δδ)

Ligand	Donor atom	δ[a]	Metal	Δδ
NH_3	N	−383	Co^{III}	−11—−78
			Rh^{III}	−14—−68
			Pt^{II}	−22—−60
NO_2^-	N	234	Co^{III}	−135—−162
			Ru^{II}	−136—−166
			Rh^{III}	−142—−192
			Pd^{II}	−144—−186
			Pt^{II}	−175—−190
			Pt^{IV}	−225—−231
en	N	−357	Rh^{III}	−24—−53
			Pt^{II}	20—−18
NO_3^-	O	412	Rh^{III}	−138[b], 33[c]
H_2O	O	0	Rh^{III}	−70—−144
AcO^-	O	270	Rh^{III}	−71
CO	C	180	Pt^{II}	−18—−21
CN^-	C	169	Pt^{II}	−11—−43
			Pt^{IV}	−35—−83
PMe_3	P	−61	Pd^{II}	+49—+59
$P(OEt)_3$	P	139	Pt^{II}	−70

[a] Chemical shift of the free ligand relative to $[NO_3^-]$ (N), water (^{17}O), Me_4Si (^{13}C), 85% H_3PO_4 (^{31}P).

[b] The donor O atom of nitrate.

[c] The other two O atoms.

als shift upfield from the line for the free ligand. The magnitudes of these shifts (referred to as "coordination shifts" in the literature) are such that the lines of free and complexed ammonia can be distinguished also in the ^{14}N NMR spectra recorded in magnetic fields with $H_0 \geq 4$ T. The lines of other donor atoms undergo similar shifts upon ligand coordination.

The coordination shifts observed in the NMR spectra of ligands are summarized in Table 1. The coordination shifts of the same donor atom in different ligands are appreciably different (*cf.* NH_3 and NO_2^-). The lines of other atoms in polyatomic ligands also shift upon coordination, but these shifts are smaller than those for the donor atoms (see Table 1, ^{17}O NMR data for the nitrate). The downfield shifts of the signals of phosphine ligands do not fit into the general pattern. The scales of the coordination shifts of the same ligand in similar complexes formed by different metals are different (see data for Co^{III}, Ru^{II}, Pt^{II}, Pt^{IV}, and NO_2^-).

Trans-effect and chemical shifts of ligand donor atoms

In the study[1—3] of complexation in the $Rh^{III}—HCl—H_2O$ system, the assignment of the ^{17}O NMR lines for the H_2O^c molecules in the $[RhCl_x(H_2O)_{6-x}]^{3-x}$ complexes to the $H_2O—Rh—Cl$ (δ −99) and $H_2O—Rh—OH_2$ (δ −141) coordinates was based on the order of appearance of these signals during the aquation of the complexes starting from $[RhCl_5H_2O]^{2-}$. The former value (δ −99) was assigned to the $H_2O—Rh—Cl$ coordinate, as this line was the first to appear upon the aquation of $[RhCl_6]^{3-}$. The Cl^- ligand in this coordinate cannot be identified based on the ^{35}Cl NMR spectrum (its NMR line in complexes is too broad to be detected). However, aquation results in an increase in the concentration of the free Cl^- ligand (this concentration can be easily determined using the ^{35}Cl NMR method), and the solution contains no ligands but H_2O and Cl^-. The ^{17}O NMR line for the coordinated water (δ −141) appeared in the spectra of solutions at $x \leq 4$, *i.e.*, in the presence of complexes with the $H_2O—Rh—OH_2$ coordinate. It is evident that the ^{17}O chemical shift for the H_2O^c molecule depends on the ligand that occupies the *trans*-position relative to this molecule.

A relationship between the nitrogen chemical shifts in ammine complexes and the trans-effect was first mentioned by Bramley *et al.*[6] Subsequently, when investigating solutions of nitro complexes of platinum metals[18—31] by ^{14}N NMR, we found that the chemical shift of the nitro group also depends on the ligand that occupies the *trans*-position (in low fields, the lines of coordinated NH_3 occurring different coordinates are not resolved, due to the substantial width of the NMR lines of donor N atoms, and the lines for the NO_2^- ligand were not detected[32]). These findings led to the idea that chemical shifts of donor O and N atoms do not merely reflect the fact of coordination but are also related to particular coordinates in the complex.[33] The chemical shifts of the donor O or N atoms on a definite coordinate for a given metal were found to depend only slightly on the composition of the inner sphere of the complex, but they differ appreciably from the chemical shifts of these atoms on other coordinates. Since the chemical shift of the donor atom for the selected coordinate in a complex is rather specific for related complexes, we have called it the *coordinate shift*. In a study of the composition of complexes or complexation, the ligands present in the system are usually known, and the measured chemical shift of a donor atom allows one to determine the coordinate and thus to identify the ligand in the *trans*-position to this donor atom without resorting to additional investigations.

Since the chemical shifts for the same ligand on different coordinates are dissimilar due to the trans-effect, they can serve as a measure of trans-effect. The contribution of other ligands to the chemical shift (cis-effect) is smaller than the contribution of the *trans*-ligand and is comparable with other types of contribution (caused by the solvent, protonation, *etc.*). The contributions of ligands that occupy the *cis*-position to the donor atom under study determine the scatter of the chemical shifts for the same coordinate in related complexes; however, it is difficult to distinguish the particular contributions.

According to an early definition given by I. I. Chernyaev, "trans-effect consists in weakening of the bond in the *trans*-position".[34] The term trans-effect is used when considering the influence of the *trans*-partner on the strength of the M—L bond on the A—M—L coordinate, whereas the influence of the *trans*-partner A on the reactivity of the substituent L is referred to as kinetic trans-effect.[35]*

In order to make sure that CShs are due to the thermodynamic or kinetic trans-effect, we compared the CShs for a selected coordinate in complexes with the kinetics of the replacement of the ligands located on this coordinate.[33] Convenient objects for comparing the NMR parameters of donor atoms and the kinetic parameters of chemical reactions are pentammine complexes with a definite reactive coordinate and two different donor atoms (O and N) both suitable for NMR detection. The isotope exchange of water oxygen between the complex and the solvent (which does not change the chemical composition of the complex) was chosen as the reaction with known kinetic parameters

$$[M(NH_3)_5OH_2]^{3+} + {}^{18}OH_2 \xrightarrow{k} [M(NH_3)_5{}^{18}OH_2]^{3+} + H_2O.$$

Comparison of the kinetic parameters for oxygen isotope exchange in the H_2O ligand in aqueous solutions of pentammine complexes (Table 2) shows opposite trends of variation of the rates of oxygen isotope exchange between free and complexed H_2O molecules and the activation energy along the series Ir, Co, Rh, namely, as the k value increases, the $\Delta H^{\neq}$ value decreases. Correspondingly, the CShs also decrease in these series both for the N atoms and for the O atoms of the H_2O molecule. This means that the chemical shift of the donor atom in the complex actually does depend on the trans-effect and can serve as a measure of the trans-effect in a series of related complexes.

Table 2. Rate constants (k), activation energies for water exchange ($\Delta H^{\neq}$), and chemical shifts (δ) of the donor atoms on the $H_2O—M—NH_3$ coordinate in pentammino aqua metal complexes[33]

M	$k \cdot 10^7$ * /s^{-1}	$\Delta H^{\neq}$ * /kJ mol^{-1}	$\delta_{^{14}N}$**	$\delta_{^{17}O}$***
Ir^{III}	0.65	121	−459 (−422)	—
Co^{III}	59	112	−441 (−417)	−129
Rh^{III}	107	103	−431 (−412)	−102

* See Ref. 36.

** Relative to NO_3^-; the nitrogen chemical shifts for the N—M—N coordinate are given in parentheses.

*** Relative to H_2O.

The CShs for the same coordinate are different for different metals (Tables 2 and 3). The range of variation of the chemical shifts of the donor atom (shown for the NO_2^- and NH_3 ligands) allows one to distinguish between coordinates with different ligands in the *trans*-position and those with identical ligands but different metals.

The lines in ^{14}N NMR spectra are often poorly resolved; the resolution becomes better for a higher operating frequency of the spectrometer and a lower solution viscosity. An example of the ^{14}N NMR spectrum is shown in Fig. 2.[10] The spectrum shows the lines of all nitrogen-containing ligands. The donor atoms of a bidentate ligand, ethylenediamine (en) have different chemical shifts (−354 and −372 ppm) due to the influence of different *trans*-partners (Cl^- and NH_3). Owing to the unusually small width of the NH_3 line (δ −388.5, upon the coordination of ammonia, the environment of the N atom became more symmetrical), one can observe the complex multiplet resulting from hyperfine splitting of the ^{14}N NMR line of the NH_3 molecule due to ^{195}Pt and ^1H nuclei. Switching to ^{15}N spectra eliminates the problem of resolution of ^{14}N NMR lines but requires ^{15}N-enriched samples.

Chemical shifts of donor N atoms in platinum metal complexes

Complexes with donor N atoms are often encountered in platinum metal compounds. The CShs for some nitrogen ligands are presented below.

The most abundant data have been obtained for coordinated ammonia (NH_3^c). Table 4 presents the chemical shifts of the NH_3^c ligand referred either to the signal of the standard (NO_3^-) or to the signal of the free ligand. Note that the chemical shifts with respect to NO_3^- are CShs, and the chemical shifts with respect to the free ligand show the displacement induced by ligand coordi-

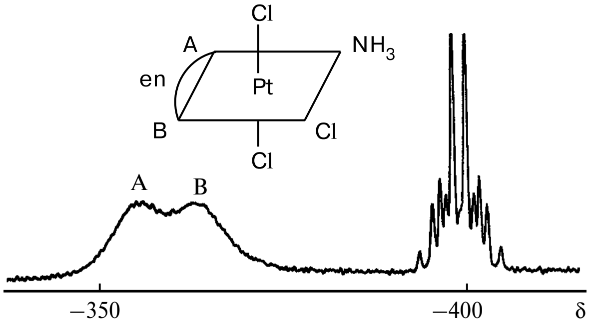

Fig. 2. ^{14}N NMR spectrum of an aqueous solution of $[trans\text{-}Pt(en)ClNH_3Cl_2^*]^+$ at 323 K.

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* In Russian-language literature, the term "trans-effect" is often used to mean the thermodynamic trans-effect and the term trans-effect implies the kinetic trans-effect (*editor's note*).

Table 3. NMR chemical shifts (δ) for the N atoms in nitro and penammine complexes[10] with M = Pd^{II}, Pt^{II}, Co^{III}, Ph^{III}, Ir^{III}, and Pt^{IV}

Coordinate	δ*				
	Pd^{II}	Pt^{II}	Co^{III}	Rh^{III}	Ir^{III}
O_2N—M—NO_2**	87—90	44—51	—	89—91	54—56
Cl—M—NO_2	79—80	55—59	—	65—72	32—40
H_2O—M—NO_2	47	—	—	42—59	13—21
H_3N—M—NH_3	—	—	−412***—−437	−432	−442
Cl—M—NH_3	—	—	−450	−440	−466
H_2O—M—NH_3	—	—	−439***—−461	−451	−479

* Relative to NO_3^-.

** For M = Pt^{IV}, δ = 41.

*** Data for [*cis*-$Co(NH_3)_4(H_2O)_2]^{3+}$.

nation. Table 4 covers most of the published data for various complexes with different metals and different *trans*-partners that contain the selected coordinate. The scatter of CShs for a particular coordinate reflects not only the inaccuracy of measurements but rather the dependence of the CShs on the composition of the coordination sphere of the complex. The data given in the Table were used to construct the CSh diagram for NH_3^c (Fig. 3).

Table 4. Coordinate shifts of the N atoms in ammine complexes measured relative to NO_3^- (I) and free NH_3 ligand (II)

Coordinate	δ*		Ref.
	I**	II	
H_2O—Co—NH_3	−439—−461	−56—−78	23, 33
Cl—Co—NH_3	−427—−450	−44—−57	23, 33
H_3N—Co—NH_3	−415—−437	−33—−44	7, 23, 33, 37, 38
Br—Co—NH_3	−421	−38	33
I—Co—NH_3	−404	−21	38
NC—Co—NH_3	−394	−11	33, 38
O_2N—Co—NH_3	−407	−24	33
NNN—Co—NH_3	−433	−50	38
SCN—Co—NH_3	−435	−52	38
H_2O—Rh—NH_3	−432—−451	−49—−68	23, 38
Cl—Rh—NH_3	−440	−57	33
HO—Rh—NH_3	−423	−40	39
SCN—Rh—NH_3	−421	−38	39
NCS—Rh—NH_3	−407	−24	39
H_3N—Rh—NH_3	−409—−421	−26—−38	33, 39
Br—Rh—NH_3	−415	−32	39
I—Rh—NH_3	−405	−22	39
NC—Rh—NH_3	−397	−14	39
H_2O—Ir—NH_3	−479	−96	33
Cl—Ir—NH_3	−466	−83	33
H_3N—Ir—NH_3	−442	−58	33
H_2O—Pd—NH_3	−412	−29	40
H_3N—Pd—NH_3	−430	−47	40
H_2O—Pt—NH_3	−437—−443	−54—−60	41
HO—Pt—NH_3	−435	−52	42
Cl—Pt—NH_3	−419—−437	−36—−54	8, 41, 42
H_3N—Pt—NH_3	−415—−425	−32—−42	41, 42
Br—Pt—NH_3	−419	−36	42
I—Pt—NH_3	−405	−22	42

* The ranges of the CShs for the specified coordinate in various complexes are given.

** Accuracy ±2 ppm; δ(NH_3^{free}) −383.

The diagram (see Fig. 3) shows the chemical shifts of the N atoms in coordinated ammonia for various *trans*-ligands and metals. This diagram can be used to study ammine complexes if the complex or the system under study contains one of the *trans*-ligands indicated in the diagram. Then the ^{14}N NMR chemical shift would show whether this ligand is in the inner sphere of the complex.

The variation of the CShs for the L—M—X coordinate for various metals with L = NO_2^- and NH_3 is shown in Fig. 4. It can be seen that the CShs for different metals with a hard ligand, NO_2^-, are better resolved than those in the case of the soft NH_3 ligand. The narrow ranges of some CShs are due to the lack of experimental data.

The known CShs of the N atoms in nitro and nitroso complexes are presented in Fig. 5. The large ranges of some CShs for ruthenium and osmium nitroso complexes are related to the fact that the error of measurements of the ^{14}N NMR chemical shifts in low fields is given for each complex rather than to the set of data for these coordinates in different complexes.[32] The error of measurements of the chemical shifts in high fields decreases, so does the range of CShs. It can be seen from Fig. 5 that the CShs for similar coordinates with different metals may coincide but they are clearly distinguished for a particular metal upon variation of the *trans*-partner.

In the case of bidentate ethylenediamine ligand, the chemical shift of the free ligand falls in the range of values typical of the coordinated ligand. Nevertheless, as can be seen from Fig. 6, for a particular metal, the CShs of the N atoms in ethylenediamine with different *trans*-partners are readily discriminated.

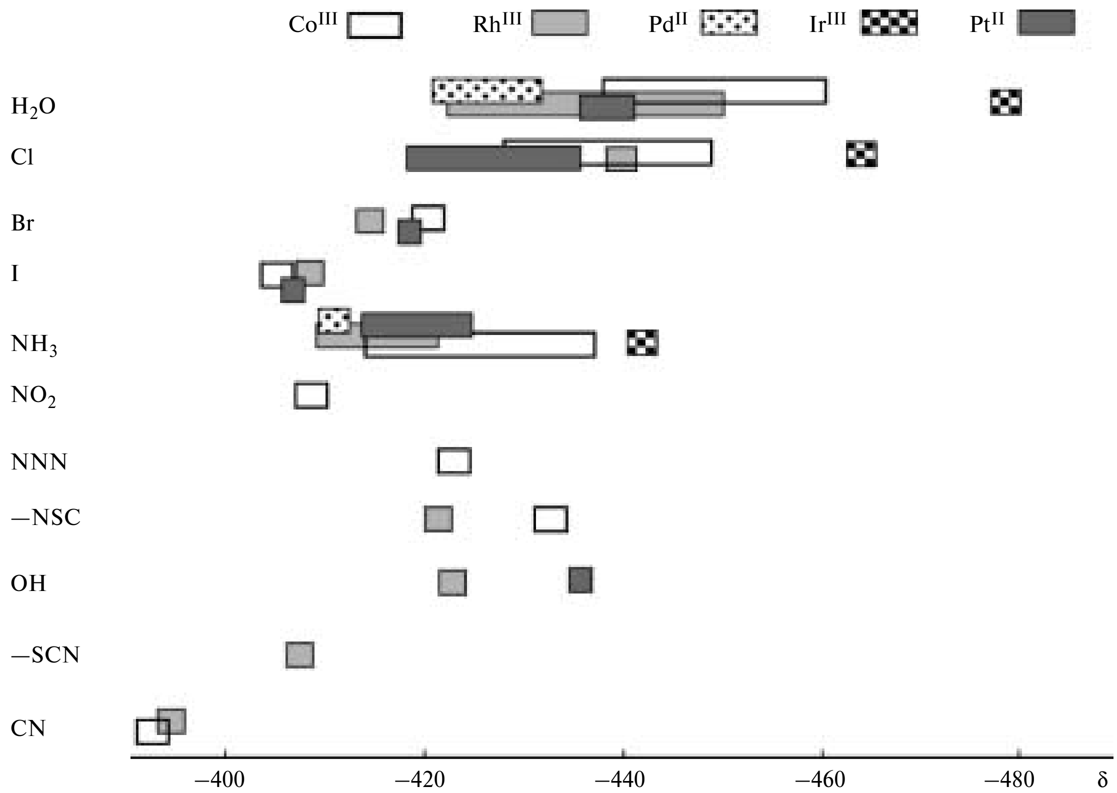

Fig. 3. NMR chemical shifts (δ) of the N atoms of the NH_3 ligand in platinum metal complexes with various ligands in the *trans*-position.

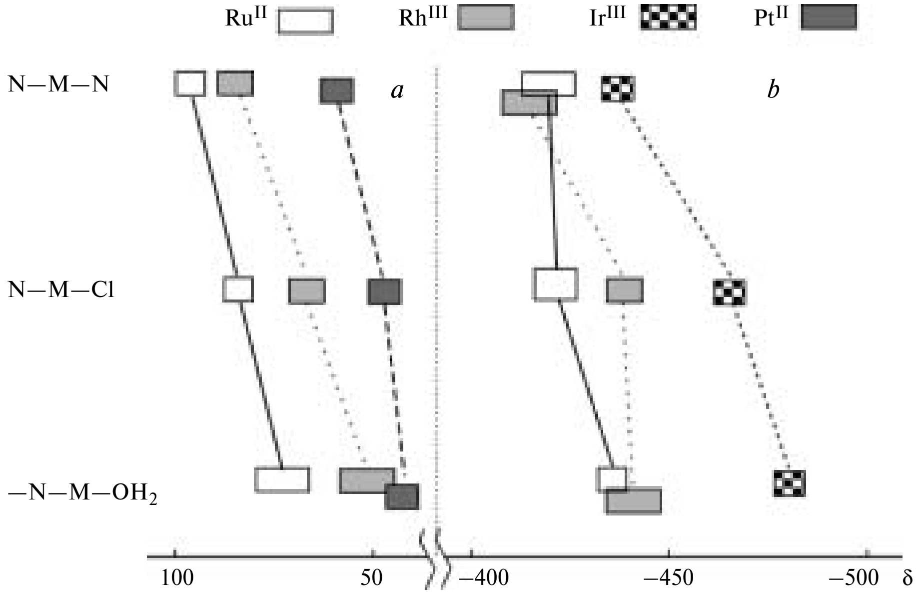

Fig. 4. Coordinate shifts of the N atoms in the NO_2^- (*a*) and NH_3 (*b*) ligands in some platinum metal complexes; the data for Ru^{II} refer to nitro nitroso complexes.

The replacement of the *trans*-ligand by a ligand with a greater trans-effect weakens the bond in the *trans*-position; this results in the change of the CSh toward the chemical shift of the free ligand. In the series of CShs for different *trans*-ligands, smaller (more positive) values correspond to the coordinates with more trans-influencing

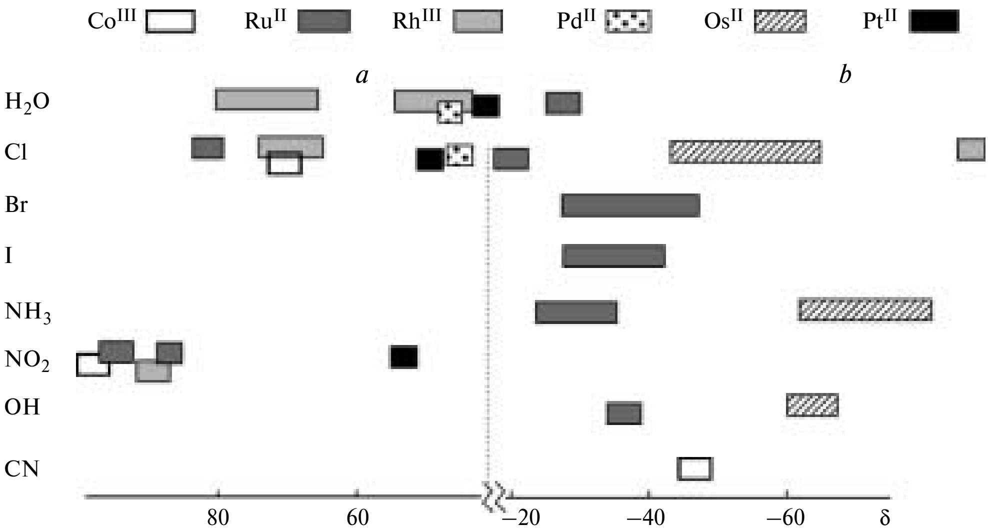

Fig. 5. Coordinate shifts of the N atoms in the NO_2^- (*a*) and NO^+ (*b*) ligands in platinum metal complexes with various ligands in the *trans*-position;[18—32,43,44] for free ligands, $\delta(NO_2^-) = 234$, $\delta(NO^+) = 1$.

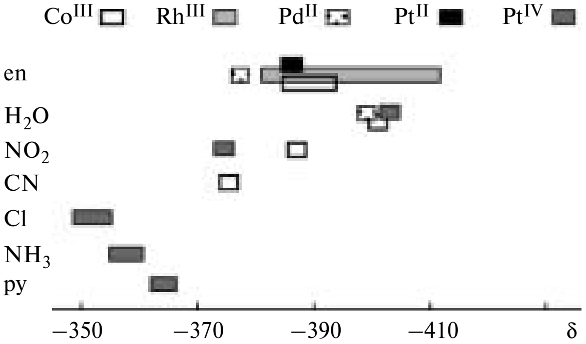

Fig. 6. Coordinate shifts of the N atoms in ethylenediamine in platinum metal complexes with various *trans*-ligands;[10,39,45—49] for the free ligand, δ(en) = −355.

ligands (*vice versa* for phosphines), *i.e.*, the sequence of CShs is opposite to the sequence of trans-effect.

The data of Table 4 allow one to compose the following sequences of trans-effect for different metals:

Co^{III}: $H_2O < NCS^-, Cl^- < NNN^- < NH_3 < Br^- < NO_2^- < I^- < CN^-$;

Rh^{III}: $H_2O < Cl^-, OH^-, NCS^- < NH_3 < Br^- < I^- < CN^-$;

Ir^{III}: $H_2O < Cl^- < NH_3$;

Pd^{II}: $H_2O < NH_3$;

Pt^{II}: $H_2O < Cl^-, OH^- < NH_3 < Br^- < I^-$.

It can be seen that the sequences are almost identical for different platinum metals and the Cl⁻, OH⁻, and NCS⁻ ligands are similar as regards the thermodynamic trans-effect. These sequences can be compared with the previously reported[35] kinetic trans-effect sequences for various reactions with octahedral complexes:

Pt^{IV}: $H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- < NO_2^-$;[50]

Rh^{III}: $H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- < NO_2^- < CN^-$;[51]

Ir^{III}: $NCS^- < Cl^- < Br^- < NO_2^- < I^-$ [52] (out of the sequences given in the original publication, we selected the ligands given in Table 4).

The sequences based on kinetic data[50—52] are somewhat different for different metals (*cf.* the sequences for Rh^{III} and Ir^{III}) but their order as well as the order obtained from NMR data generally coincide with each other. However, neither the known spectrochemical series[53] for the splitting of levels in the ligand field (Δ)

$$I^- < Br^- < Cl^- < F^- < RCOOH < H_2O < C_2O_4^- < Py < NH_3 < NO_2^- < CN^-,$$

nor the nepheloauxetic series[53]

$$F^- < H_2O < NH_3 < C_2O_4^{2-} \approx CN^- < Br^- < I^-$$

correlate with the trans-effect sequences. This means that the CShs can really serve as a measure of the trans-effect, like the parameters obtained by other physical methods.[35]

NMR chemical shifts of the donor oxygen atoms in platinum metal complexes

Although ^{17}O NMR measurements are hampered by the exceptionally low natural abundance of the isotope, donor O atoms can still be detected when the concentration of oxygen incorporated in the complex is at least

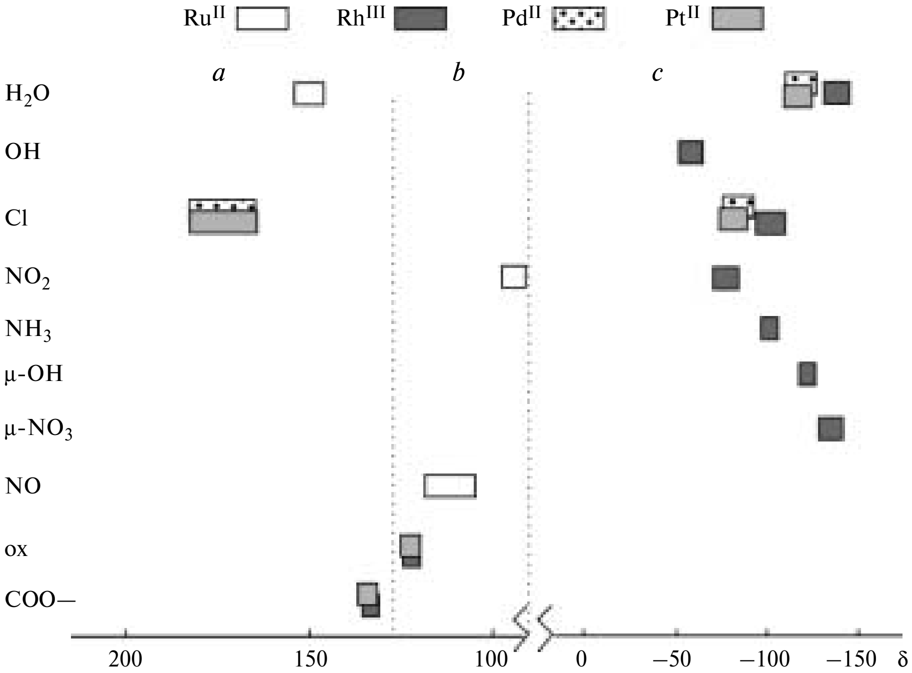

Fig. 7. Coordinate shifts of ^{17}O in the COO^- (*a*), OH^- (*b*), and H_2O (*c*) ligands in platinum metal в complexes with various ligands in the *trans*-position;[1—3,20,22,54—62] for free ligands, $\delta(H_2O) = 0$, $\delta(COO^-) = 257$ for OAc and $\delta(COO^-) = 266—271$ for amino acids; ox is the oxalate anion as ligand.

0.2 mol L^{-1}. For lower concentrations, the ^{17}O enrichment of the ligand is required. The features of variation of the chemical shifts of donor O atoms in complexes with oxygen-containing ligands (Fig. 7) are similar to those for the donor N atoms in both monodentate and bidentate ligands (acetylacetone, oxalate). In aqua complexes, the influence of the composition of the complex coordination sphere on the CSh of the chosen coordinate is much less pronounced than for nitrogen-containing ligands (*cf.* Figs. 3 and 7).

When a monodentately bound ligand contains several potential donor atoms (for example, $RCOO^-$ or NO_3^-), the signal from the donor atom shifts downfield and the signals from other O atoms shift upfield with respect to that of the free ligand.[55,63]

NMR chemical shifts of donor carbon and silicon atoms

Little data on the carbon and silicon CShs in platinum metal complexes have been reported. The specificity of the CShs for C and Si ligands is not much higher than that for O- and N-containing ligands, despite the small width of ^{13}C and ^{29}Si NMR lines. The data on the ^{13}C CShs in cyano complexes are most representative (Fig. 8).

Most often, carbonyl complexes are polynuclear and contain metal—metal bonds; the separation of specific coordinates in such complexes is rather arbitrary. Nevertheless, study of the NMR spectra of the donor atoms in the ligand allows one to identify structurally nonequivalent metal and ligand atoms.

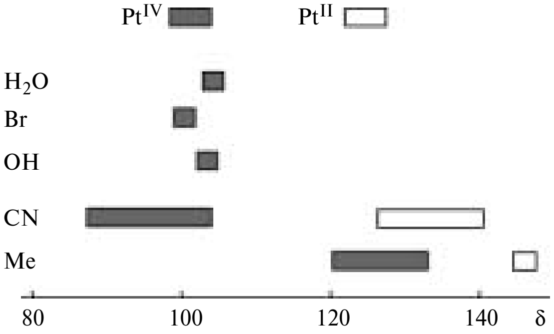

Fig. 8. Coordinate shifts of ^{13}C of the CN^- ligands in platinum complexes with various ligands in the *trans*-position;[64,65] for the free ligand, $\delta(CN^-) = 177$.

For example, in the $Rh_5(CO)_{15}$ cluster built as a trigonal bipyramid (Fig. 9), the ^{13}C chemical shift of the carbonyls[65] in axial positions is 191 ppm, whereas the chemical shift of the carbonyls at the equatorial base of the bipyramid is 209 ppm; finally, the chemical shift of the bridging carbonyls in the equatorial plane is 248 ppm. In this cluster, one can distinguish the $O\underline{C}$—Rh—Rh coordinate for the axial Rh atoms and the $O\underline{C}$—Rh—μ-CO coordinate for the three equatorial Rh atoms having CShs of 191 and 209 ppm, respectively.

The CShs of silicon[66] are known only for Ru^{II} and Os^{II} complexes and for the $SiMe_3$ and $SiCl_3$ ligands. Since

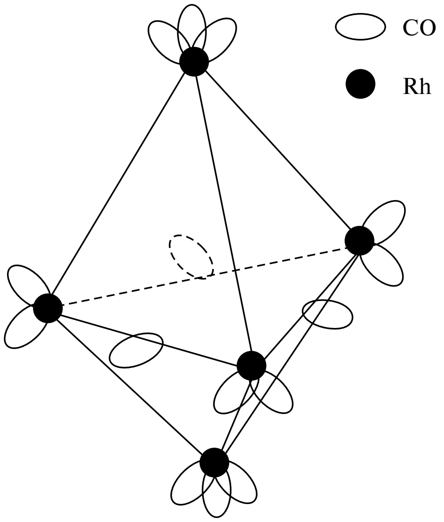

Fig. 9. Structure of the $Rh_5(CO)_{15}$ cluster.

these ligands do not exist in solutions as free species, the shift of their lines induced by coordination cannot be compared with these values for other ligands. In the case of $SiMe_3$, it is possible to compare the CShs for only two coordinates, $Me_3Si—Ru—\underline{Si}Me_3$ and $OC—Ru—\underline{Si}Me_3$.

In the case of ruthenium complexes, the CSh of $SiCl_3$ on the $Me_3Si—Ru—\underline{Si}Cl_3$ coordinate is in the ±10 ppm range, the chemical shifts of silicon on the $Cl_3Si—Ru—\underline{Si}Cl_3$ and $OC—Ru—\underline{Si}Cl_3$ coordinates also fall in this range, and the CShs of this ligand in Os^{II} complexes with *trans*-arranged $\underline{Si}Cl_3$, H, and CO are close to each other (30±2 ppm). The specificity of the CShs for these complexes is relatively low.

^{19}F NMR chemical shifts of fluoro complexes of platinum metals

Data on the CShs of fluoro complexes are few, and they show a record-breaking specificity (Fig. 10). It is of interest that the CShs for the $F—Pt^{IV}—F$ and $F—Pd^{IV}—F$ coordinates are similar. The values for Pd^{IV} are unique because this oxidation state of Pd atoms is stabilized only in the presence of strong oxidants.

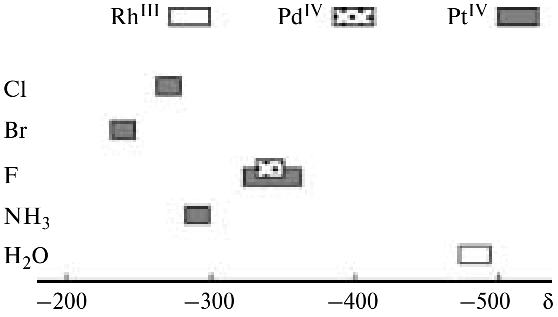

Fig. 10. Coordinate shifts of ^{19}F in Rh^{III}, Pd^{IV}, and Pt^{IV} fluoro complexes with various ligands in the *trans*-position;[67—70] for free fluoride, $\delta(F^-) = -120$.

NMR chemical shifts for donor phosphorus and tin atoms

The diagram of the CShs of phosphorus is shown in Fig. 11 for the PMe_3 and PEt_3 ligands. Although a lot of ^{31}P NMR data for complexes of platinum metals have been reported, they refer to a large number of different phosphorus ligands rather than to different coordinates of the same ligand. The data for complexes with triethylphosphine are most diverse. A peculiar feature of the NMR spectra of platinum metal complexes with phosphines is the fact that the ligand signal shifts downfield upon coordination, unlike the signals of ligands with other donor atoms (see the results for the PMe_3 and PEt_3 ligands). In the case of $P(OR)_3$ ligands, the following general rule holds: the NMR lines of phosphorus shift upfield upon ligand coordination.

The data for the $Et_3P—Pt^{II}—PEt_3$ coordinate can be subdivided into two areas, those for usual complexes and for hydride complexes; the CSh of the latter coincides with that for palladium. Phosphine complexes are often labile at ambient temperature; attaining the temperature where the exchange is completely terminated is limited by freezing of the solvent. Therefore, some data may be inaccurate due to the slow intrasphere ligand exchange.

As expected, an SNSN bidentate ligand with the donor S and N atoms located in the *trans*-position to the phosphine ligands shifts the lines for these atoms in different ways.

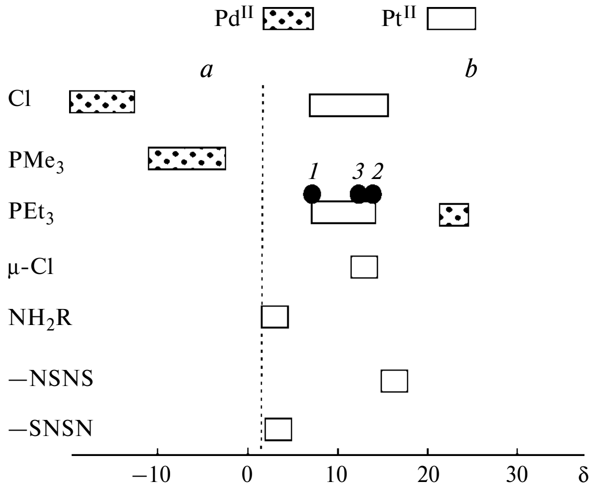

Fig. 11. Coordinate shifts of ^{31}P for the PMe_3 (*a*) and PEt_3 (*b*) ligands in Pd^{II} and Pt^{II} complexes with various ligands in the *trans*-position;[71—78] for free ligands, $\delta(PMe_3) = -61$, $\delta(PEt_3) = -20$; (*1*) *trans*-$Pt(PEt_3)_2(SnCl_3)_2$;[69] (*2*) *trans*-$Pt(PEt_3)_2SnCl_3Cl$;[69] (*3*) *trans*-$PtCl_2(PEt_3)_2$.[72]

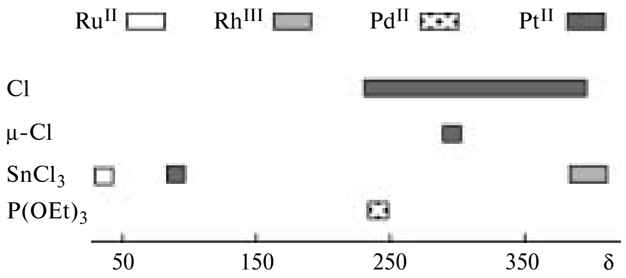

Fig. 12. Tin coordinate shifts[77,79—82] of the $SnCl_3^-$ ligand in platinum metal complexes with various ligands in the *trans*-position.

Figure 12 shows the CSh diagram for complexes with the $SnCl_3^-$ ligand. Precise measurements are hampered by the intrasphere exchange of the Cl^- and $SnCl_3^-$ ligands in mixed-ligand complexes and the exchange of the coordinated $SnCl_3^-$ ligand with the outer-sphere Cl^- ligand. The possibility of retarding the exchange in solution is restricted by freezing of the solution. Apparently, this accounts for the large range of CShs on the $Cl—Pt^{II}—SnCl_3$ coordinate.

^1H NMR chemical shifts for hydride complexes of platinum metals

Although a large number of studies dealing with the ^1H NMR spectra of hydride complexes have been published, only for Pt^{II} was it possible to choose a set of data sufficient for discussing the CSh in these complexes. Among hydride complexes of other metals, there are many five-coordinate complexes in which selection of particular coordinates is not self-evident. The ^1H CShs for octahedral and square-planar complexes are presented in Fig. 13.

Platinum(II) complexes have been described in the literature in most detail. Each point corresponds to a particular complex, therefore, there are no data on the effect of complex composition on the CSh. The scale of this effect can be described only for iridium hydridophosphine complexes. In the case of Pt^{II} complexes, the CShs can be easily differentiated; they can be used to compose the following sequence of trans-effect: $NO_3^- < ONO^- < Cl^- \approx —NCS^- < Br^- < —SCN^- < I^- < CN^- < CO$. This sequence is comparable with the above sequences of trans-effect for ligands with the donor O and N atoms:

Co^{III}: $H_2O < NCS^-, Cl^- < NNN^- < NH_3 < Br^- < NO_2^- < I^- < CN^-$;

Rh^{III}: $H_2O < Cl^-, OH^-, NCS^- < NH_3 < Br^- < I^- < CN^-$;

Pt^{II}: $H_2O < Cl^-, OH^- < NH_3 < Br^- < I^-$.

Comparison of these sequences shows an appreciably different trans-effect of the NO_2^- ligand depending on the way it is attached to the metal, in particular, the trans-effect of the NO_2^- ligand bound through oxygen (nitrito ligand) is much weaker than the trans-effect of the ligand bound through nitrogen (nitro ligand).

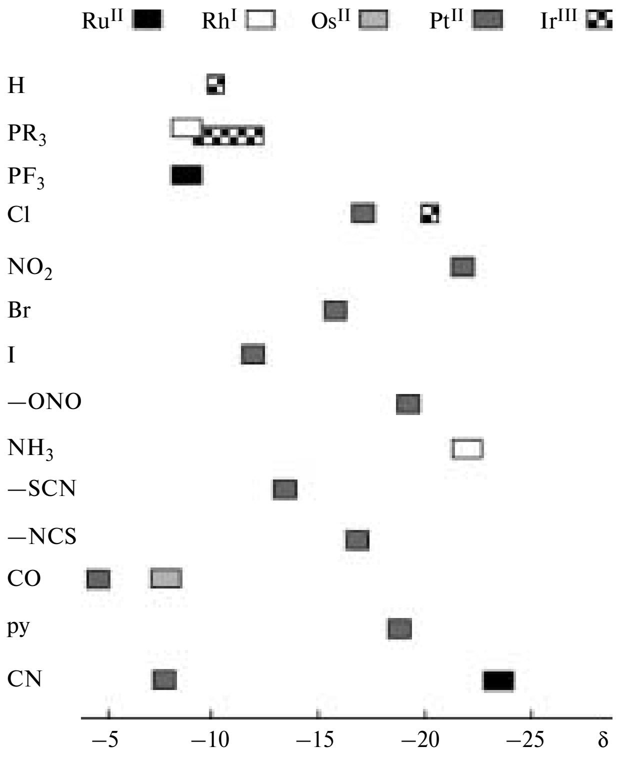

Fig. 13. Coordinate shifts of ^1H for the hydride complexes of platinum metals with various ligands in the *trans*-position.[4,5,13]

The ^1H chemical shift on for H—M—H coordinate is known only for *mer*-$[IrH_3(PEtPh_2)_3]$; it is close to the chemical shift for the $H—Ir—PR_3$ coordinate.

The use of CShs for determination of the structure of complexes

The structures of complexes are usually determined when both the metal and the probable ligands are known but the set of possible coordinates is limited. When no data on the CShs are available, one has to study solutions of reference compounds containing required coordinates. Since complexes of platinum metals are kinetically inert, they are assumed to remain unchanged immediately after dissolution, and the required CShs are measured for them. For instance, the reference complexes $[Rh(NO_2)_6]^{3-}$, *cis*-$[Rh(NO_2)_3Cl_3]^{3-}$, and *cis*-$[Rh(NO_2)_3(H_2O)_3]^0$ were characterized by both rhodium and ligand (^{17}O, ^{14}N) NMR;[23,54] this provided the ^{14}N CShs for the $O_2N—Rh—\underline{N}O_2$, $Cl—Rh—\underline{N}O_2$, and $H_2O—Rh—\underline{N}O_2$ coordinates. The CShs for these coordinates in other nitro complexes are close to those determined above. The CShs found for the reference compounds were used to characterize the nitro complexes listed in Table 5.

Table 5. ^{15}N NMR chemical shifts on different coordinates and ^{103}Rh chemical shifts for Rh^{III} chloronitroaqua complexes[24,54]

Complex	$\delta_{^{15}N}$ (^1J/Hz)*			$\delta_{^{103}Rh}$**
	$O_2N—Rh—NO_2$	$Cl—Rh—NO_2$	$H_2O—Rh—NO_2$	
$[Rh(NO_2)_6]^{3-}$	90.8 (J = 20)	—	—	−2770
trans-$[Rh(NO_2)_4Cl]_2]^{3-}$	89.2 (J = 22)	—	—	—
cis-$[Rh(NO_2)_3(H_2O)_3]$	—	—	50.3 (J = 28)	−1780
cis-$[Rh(NO_2)_3(H_2O)_2Cl]^-$	—	66.0 (J = 23)	53.0 (J = 26)	−1864
cis-$[Rh(NO_2)_3(H_2O)Cl_2]^{2-}$	—	68.6 (J = 23)	55.8 (J = 26)	−1987
cis-$[Rh(NO_2)_3Cl_3]^{3-}$	—	71.8 (J = 23)	—	−2120
cis-$[Rh(NO_2)_2(H_2O)_3Cl]$	—	—	47.5 (J = 24)	—
cis-$[Rh(NO_2)_2(H_2O)_2Cl_2]^-$	—	64.8 (J = 22)	48.3 (J = 24)	—
cis-$[Rh(NO_2)_2(H_2O)_2Cl_2]^-$***	—	—	51.7 (J = 26)	−1630
cis-$[Rh(NO_2)_2(H_2O)Cl_3]^{2-}$	—	68.6 (J = 20)	58.7 (J = 21]	—
cis-$[Rh(NO_2)_2Cl_4]^{3-}$	—	70.6 (J = 22)	—	—
cis-$[Rh(NO_2)_2(H_2O)_4]^+$	—	—	41.7 (J = 22)	—

* The accuracy of determination $\delta_{^{15}N}$ — ±0.3, $^1J_{Rh,N}$ — ±2 Hz.

** Relative to $Rh(acac)_3$, the accuracy of determination is ±5.

*** The Cl atoms are in the *trans*-position.

Now we will follow the procedure of structure determination for some complexes (see Table 5)[24,54] in relation to the spectra presented in Fig. 14. The sample was prepared by dissolving $Na_3[Rh(^{15}NO_2)_6]$ in 3 *M* HCl followed by keeping the solution for 5 h at 343 K. The inner coordination sphere of these complexes contained the Cl^-, NO_2^-, and H_2O ligands, complexes of the RhL_6 type being absent. Since only two complexes predominated in the rhodium NMR spectrum, they were identified without difficulties.

The rhodium NMR spectrum (see Fig. 14, spectrum *2*) exhibits two quartets and a weak unidentified signal. The incomplete resolution of the multiplets is due to the fact that the spectra were recorded in special probes with a magnetic coil in a horizontal (transverse to H_0) position of the sample,[83] which substantially increased the sensitivity with respect to the high-resolution probe (with sample position coaxial to H_0) but gave a poorer resolution. The quartet implies splitting of the rhodium signal ($I = 1/2$) at three ^{15}N nuclei ($I = 1/2$), *i.e.*, the complex contains three nitro groups. During successive elimination of the nitro groups from $[Rh(NO_2)_6]^{3-}$, the facial (*cis*) complexes are the most stable.[22] Judging by the rhodium chemical shift, these complexes are neither *cis*-$[Rh(NO_2)_3Cl_3]^{3-}$ nor *cis*-$[Rh(NO_2)_3(H_2O)_3]^0$ (the positions of rhodium NMR signals for these complexes have already been known, see Table 2). This leaves two options for the composition, either *cis*-$[Rh(NO_2)_3Cl(H_2O)_2]^-$ (**A**)

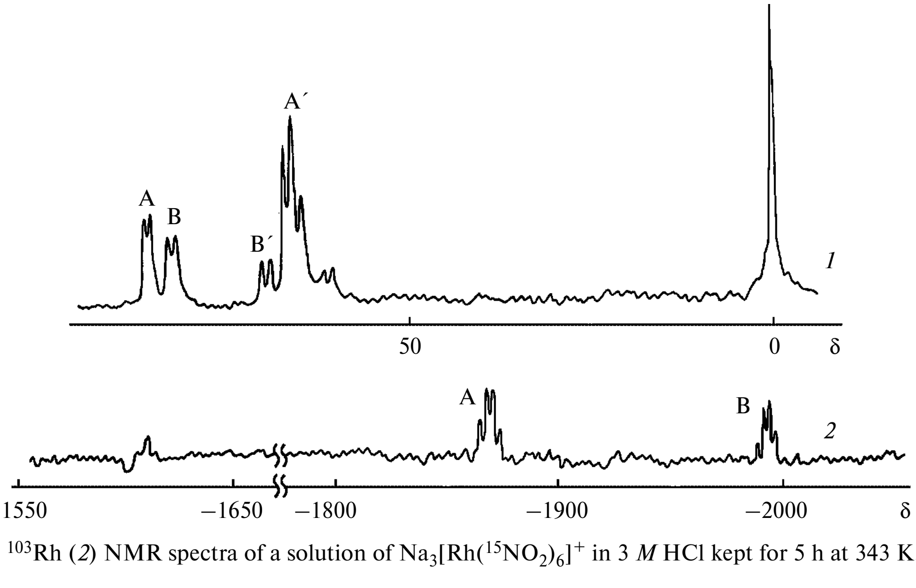

Fig. 14. ^{15}N (*1*) and ^{103}Rh (*2*) NMR spectra of a solution of $Na_3[Rh(^{15}NO_2)_6]^+$ in 3 *M* HCl kept for 5 h at 343 K.

or *cis*-$[Rh(NO_2)_3Cl_2H_2O]^{2-}$ (**B**), which are thus responsible for lines A and B in the rhodium NMR spectrum. The line for complex **A** should be located in lower field, as complex **A** is more aquated than complex **B**, because aquation of both nitro complexes and chloro complexes induces downfield shifts of the NMR lines of rhodium. Therefore, the lower-field (more intense) line in the rhodium NMR spectrum corresponds to complex **A**. The composition of complexes **A** and **B** implies that the signal is actually a doublet of triplets rather than a quartet, because the N atoms are nonequivalent due to different *trans*-partners. The multiplet looks like a quartet because the $^1J_{Rh,N}$ values for the Cl—Rh—$\underline{N}O_2$ and H_2O—Rh—$\underline{N}O_2$ coordinates are similar (see Table 5).

This assignment is confirmed by the ^{15}N NMR spectrum of the solution (see Fig. 14, spectrum *1*). The ^{15}N spectrum exhibits two groups of doublets (due to splitting at the rhodium nucleus, $I = 1/2$), one of them corresponding to the Cl—Rh—$\underline{N}O_2$ coordinate (s, δ >60), and the other being related to the H_2O—Rh—$\underline{N}O_2$ coordinate (s, δ <60). Complex **A** is responsible for the lines of ligands with δ 69 and 53 (A and A´), while complex **B** accounts for the signals with δ 66 and 56 (B and B´). The intensity ratios are 1 : 2 and 2 : 1, respectively, the intensity of the first pair of lines being higher than the intensity of the second pair. This is consistent with the intensities observed in the ^{103}Rh NMR spectrum. The same procedure was employed to assign the NMR lines for the observed coordinates to the complexes shown in Table 5. Most of the identified complexes have not been isolated as a solid phase.

The structures of a number of ethylenediamine complexes were confirmed by ^{14}N and ^{195}Pt NMR spectroscopy.**[10,49]** In these studies, platinum NMR spectra were used to make sure that the specimen is a single complex (after determining the complex composition, the platinum chemical shift becomes specific and can be employed to recognize this complex in a solution).

The composition of the complexes was determined by a procedure similar to that described above for rhodium nitro complexes. Figure 15 shows the structures of four of the twelve complexes studied previously.**[10,49]** The CSh of the ethylenediamine (en) N atoms on the en—Pt—Cl coordinate (−348 ppm) was found from the ^{14}N NMR spectrum of complex **1** (see Fig. 15). This CSh was used to determine the structures of complexes **2** and **3**. After replacement of the first Cl atom by an NH_3 or NO_2^- ligand, whose pattern is obvious (complexes **2** and **3**), the line of ethylenediamine is split into two; from the position of one of them, the CShs for the en—Pt—NH_3 (about −360 ppm) and en—Pt—NO_2 (about −370 ppm) coordinates can be found. The second ^{14}N NMR line for en in these complexes refers to the en—Pt—en coordinate, its chemical shift is about −350 ppm. The replacement occurs in the plane of ligand en, because in the case of replacement in the Cl—Pt—Cl coordinate, the N atoms of the ligand en would remain equivalent and only one line for en would be observed. Now we will consider complex **4** (see Ref. 34). Its ^{14}N NMR spectrum contains line with δ 8, −356, and −375 and a multiplet with δ −389. The lines with δ 8 (NO_2) and δ −375 (en) correspond to the en—Pt—NO_2 coordinate and the line with δ −356 and the multiplet with δ −389 correspond to the en—Pt—NH_3 coordinate.

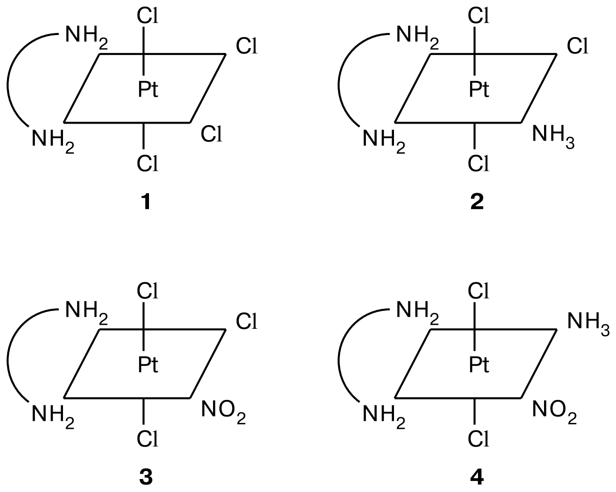

Fig. 15. Structures of Pt^{IV} ethylenediamine complexes **1—4**.

The rhodium NMR lines**[3]** for the Rh—HCl—H_2O system (eight isomers of five $[RhCl_x(H_2O)_{6-x}]^{3-x}$ complexes, where x = 2—6) were assigned taking into account the order in which these complexes appeared during the aquation. However, the assignment of rhodium NMR lines for isomers with the same composition (*cis*- and *trans*-$[RhCl_4(H_2O)_2]^-$, *cis*- and *trans*-$[RhCl_2(H_2O)_4]^+$) was based on a comparison of the intensities of the rhodium line and the ^{17}O NMR line for the H_2O ligand on the appropriate coordinates.

The structures of eight intermediate complexes formed during the transformation of $[Ru(NO_2)_6]^{4-}$ into $[RuNOOH(NO_2)_4]^{2-}$ were determined**[21]** using the CSh of nitrogen in Ru^{II} nitro and nitroso complexes and ^{99}Ru NMR data.

* * *

The use of CShs opens up new opportunities for determination of the composition of complexes in solutions without isolating them in the solid state. Note that NMR of ligand atoms is a more versatile method of investigation of the structures and properties of complexes than NMR of the complex-forming atoms because it is also suitable for those diamagnetic complexes in which metal NMR cannot be detected (for example, Pd^{II}, Ir^{III}, *etc.*) and for paramagnetic complexes.

A limitation of this method is low concentration sensitivity of the NMR method of many atoms, which becomes even lower for quadrupole nuclei due to line broadening caused by ligand coordination. Transition to higher fields (spectrometers operating at 400—500—600 MHz) and the use of special probes[83] markedly extends the scope of determination of the compositions of complexes. For example, the large line width for donor N atoms in the ^{14}N NMR spectra restricts the resolution; the sensitivity also decreases with an increase in the line width, but an increase in the field frequency makes up for these restrictions. The problem of resolution in the nitrogen NMR spectra is eliminated by using the ^{15}N isotope but this requires the use of isotope-enriched specimens. Nevertheless, even with these restrictions, the concept of CShs can be employed efficiently to determine the composition of many complexes. The efficiency will increase with expansion of the data base of the measured chemical shifts of donor atoms in platinum metal complexes.

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