Manifestation of electron-nuclear dynamics in ^{59}Co NQR spectra of a series of cobaltocenium derivatives

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A coupling equation relating the quadrupole coupling constant (e^2Qq_{zz}) to the asymmetry parameter (η) of the electric field gradient for a series of cobaltocenium derivatives (^{59}Co NQR) is derived. The estimates of the correlation times of "slow" modulations of electron motions by tunneling processes lie in the range from 10^{-12} to 10^{-14} s. This corresponds to the interval of the characteristic times of nuclear motions.

Key words: ^{59}Co nuclear quadrupole resonance, cobaltocenium, electron-nuclear dynamics, tunneling.

The formation of a chemical bond between a metal atom and cyclopentadienyl rings in metallocene compounds has not been studied in detail so far. It is noteworthy that conventional methods of investigation including structural ones give no answer to the question about the role of dynamic effects in such systems. At the same time if there are two or more orbitally degenerate electronic levels having the same energy, the nuclear configuration can undergo a spontaneous distortion accompanied by considerable reduction of symmetry (Jahn—Teller effect[1]). The distortion can be either static or dynamic.[2] Phenomena similar to the Jahn—Teller effect may also occur in electronically quasi-degenerate systems where one nuclear core configuration corresponds to a number of very closely spaced (but not merged!) electron energy levels (Opic—Pryce effect[3]), which can lead to the dipole instability that is impossible in the case of true Jahn—Teller effect.[1] The Opic—Pryce effect[3] corresponds to all intermediate situations from electronically degenerate systems to nondegenerate ones provided that the electron spin states remain unchanged. Thus, more than one configurational electron density distribution can exist in a molecular electron-nuclear system. Electron-tunneling assisted dynamic transitions between these configurational states give rise to additional splitting of electron energy levels (so-called tunneling or inversion splitting) and to subsequent onset of additional time dependences of the electron distribution configurations. Depending on the ratio of the lifetimes of particular configurational states and on the ratio of the times of complete electron tunneling and the characteristic times of nuclear motions, these differences either may or may not manifest themselves as changes in the configuration of the mutual arrangement of atomic nuclei in the molecular system.

Basic to the model presented in this work is analysis of the changes in the ratio of the characteristic times of nuclear motions and tunneling-assisted "slow" modulation of electron motions.

Usually, the characteristic times of electron motions are assumed to be 5—10 orders of magnitude shorter than those of nuclear motions. This is the case of the well-known Born—Oppenheimer approximation,[4] which ignores the quantum coupling between electrons and atomic nuclei owing to large differences between the characteristic times of corresponding motions (adiabatic approximation).

However, typical electron tunneling probabilities (transparency coefficients) are of the order of 10^{-5}—10^{-10},[5] which causes a significant increase in the correlation time of complete electron transfer from one potential energy minimum to another. The only exception is resonant tunneling provided that the shapes of these energy minima and the positions of the energy levels involved in electron exchange exactly match one another.[5] Similar numerical values of the estimates mentioned above suggest that the times of complete electron tunneling can be similar or equal to the characteristic times of nuclear motions. It follows that in this case the Born—Oppenheimer approximation is not valid and hybrid electron-nuclear states may appear[6] (nonadiabatic approximation).

Theoretical studies of this phenomenon face severe computational problems because the adiabatic approximation conventionally used in quantum chemistry is no longer valid.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1919—1923, October, 2007.

In this connection is it important to find relevant experimental methods of investigation. The main difficulty consists in that the corresponding line broadening in the vibronic spectrum (photoelectron spectroscopy) is of the same order of magnitude or even falls within the limits of experimental error. Structural methods are inappropriate at all due to long exposure times. EPR spectroscopy is also of limited use, because it can be used only when the Jahn—Teller effect did occur and the spin state of corresponding electrons did change and thus gave rise to paramagnetism. Thus, this method can not be used in studies of the Opic—Pryce effect characterized by retention of the electron spin state and diamagnetic properties of the entire systems.

Because of this we carried out our experiments using nuclear quadrupole resonance (NQR) spectroscopy,[7,8] which employs the phenomenon of resonant absorption or emission of a radiofrequency electromagnetic field energy (characteristic times are in the range 10^{-6}—10^{-9} s). This phenomenon is due to the dependence of the energy of electron-nuclear coupling on the mutual orientation of the asymmetrically distributed charges of atomic nuclei, atomic-shell electrons, and the charges beyond the atomic radius. Thus, all changes in the quadrupole coupling constants and NQR frequencies are electrical in nature.

Since the observed NQR frequencies are much lower than the frequencies of nuclear motions, the experimental patterns should correspond to the averaging of NQR frequencies by the mutual electron and nuclear motions.

The key NQR spectral parameters include the quadrupole coupling constant (e^2Qq_{zz}), where e is the charge of electron or proton, eQ is the electric quadrupole moment of atomic nucleus (nuclear constant), eq_{zz} is the maximum diagonal component of the tensor of the electric field gradient (EFG) at the nucleus (eq_{zz} is the second derivative of the electrostatic potential with respect to coordinates; the major contribution to eq_{zz} comes from the valence electrons at the atomic nucleus), and the EFG asymmetry parameter (η) given by

$$\eta = |(q_{xx} - q_{yy})/q_{zz}|. \tag{1}$$

Here q_{xx}, q_{yy}, and q_{zz} are the diagonal components of the EFG tensor. At the nucleus, the Laplace equation holds

$$q_{xx} + q_{yy} + q_{zz} = 0, \tag{2}$$

and the following relation is valid

$$|q_{xx}| < |q_{yy}| < |q_{zz}|. \tag{3}$$

Temperature-induced variations of eq_{zz} and η are due to periodic, rather fast changes in the mutual orientation of the EFG tensor and the nuclear quadrupole moment tensor in the course of molecular librations (the limiting case includes hindered reorientations) and to thermal-induced translational motions of neighboring molecules. Finally, the averaging of the EFG by the "slow" mutual intramolecular electron-nuclear motions, which was not considered earlier, also contributes to this mechanism.

In this work we attempted to allow for the EFG changes due to the configurational instability resulting from interconfigurational electron tunneling at a constant temperature (77 K) taking a series of cobaltocenium derivatives of the general formula $[(\pi\text{-}C_5H_{5-n}R_n)_2Co]^+ \cdot M^-$ as examples. These compounds were chosen because one could expect manifestation of the removal of the orbital degeneration in the NQR spectra of symmetrical compounds (R = H) and thus determine the role of electron dynamics for asymmetrical compounds. ^{59}Co NQR spectroscopy was employed; the NQR-active cobalt atom is located at the center of the positively charged ion. We assumed that the electronic configuration instability should affect this atom to the greatest extent.

Experimental

^{59}Co NQR frequencies of compounds $[(\pi\text{-}C_5H_{5\text{-}n}R_n)_2Co)]^+ \cdot M^-$ (**1—17**) at 77 K were measured on an ISSh-2-13 pulsed NQR spectrometer-relaxometer designed and manufactured at the Special Design Bureau, Institute of Radioengineering and Electronics, USSR Academy of Sciences. They are listed in Table 1.

The ^{59}Co nuclear spin I equals to 7/2 and therefore three frequencies of transitions between corresponding quadrupole energy levels should be observed. The experimental ^{59}Co NQR frequencies (ν_{ij}) at 77 K are shown in Table 1. Once measured the frequencies ν_{ij}, it is possible to determine the e^2Qq_{zz} and η values. In our case one has

$$\nu_{ij} = (e^2Qq_{zz}/28) \cdot \Delta E_{ij}(\eta), \tag{4}$$

where $\Delta E_{ij} = E_i - E_j$ is the difference between the corresponding roots of the secular equation for $I = 7/2$:

$$E^4 - 14(3 + \eta^2)E^2 - 64(1 - \eta^2)E + {} + (35/3)(3 + \eta^2)^2 = 0. \tag{5}$$

Exact solution of this equation gives for the following expressions ΔE_{ij}:

$$\Delta E_{1/2-3/2} = 2\sqrt{(1 + \eta^2/3)}\,(-b_2 + b_3) = \Delta E_1, \tag{6}$$

$$\Delta E_{3/2-5/2} = 2\sqrt{(1 + \eta^2/3)}\,(b_1 - b_3) = \Delta E_2, \tag{6$'$}$$

$$\Delta E_{5/2-7/2} = 2\sqrt{(1 + \eta^2/3)}\,(b_2 + b_3) = \Delta E_3, \tag{6$''$}$$

where

$$b_1 = \sqrt{7 + 2\sqrt{21}\cos(\varphi/3)}, \tag{7}$$

$$b_2 = \sqrt{7 + 2\sqrt{21}\cos(\varphi/3 + 2\pi/3)}, \tag{7$'$}$$

$$b_3 = \sqrt{7 + 2\sqrt{21}\cos(\varphi/3 - 2\pi/3)}. \tag{7$''$}$$

Table 1. ^{59}Co NQR spectral parameters of compounds $[(\pi\text{-}C_5H_{5-n}R_n)_2Co)]^+\cdot M^-$ at 77 K determined in this work and reported earlier[9—11]

Compound	R_n	M^-	Spectral position	ν_{ij}/MHz			e^2Qq_{zz} /MHz	η (%)	δ	$\tau\cdot10^{14}$ /s
				1/2—3/2	3/2—5/2	5/2—7/2				
1 [a]	H	Br_3	*1*	12.031	24.062	36.093	168.434	0	—	—
2 [b]	H	ClO_4	*2*	12.04	24.08	36.12	168.56	0	—	—
3 [c]	H	PF_6	*3*	12.324	24.599	36.907	172.24	2.15	+	89
			4	12.252	24.451	36.686	171.21	2.27	+	53
			5	12.166	24.259	36.400	169.88	2.70	+	24
4	Me	PF_6	*6*	12.365	24.340	36.575	170.75	6.20	–	—
5	Me_2	PF_6	*7*	11.906	23.805	35.708	166.64	0.90	–	—
6	Me_2	I	*8*	12.337	24.138	36.296	169.47	7.30	–	—
7	Me_2	Br	*9*	12.391	24.406	36.671	171.19	6.07	–	—
8 [c]	Me_3	PF_6	*10*	11.950	23.890	35.837	167.24	(–)1.00	–	—
9 [c]	Me_4	PF_6	*11*	12.086	24.018	36.052	168.27	3.90	+	1
			12	12.159	23.922	35.949	167.83	(–)6.30	–	—
10	Me_5	PF_6	*13*	12.113	23.935	35.951	167.82	(–)5.40	–	—
11	Pr^i	PF_6	*14*	12.266	24.247	36.417	169.99	5.30	–	27
			15	12.104	24.088	36.152	168.73	3.45	+	8
12	Bu^t	PF_6	*16*	12.430	24.522	36.838	171.97	5.75	–	78
13	Bu^t	I	*17*	12.190	24.142	36.252	169.22	4.85	–	15
14	Bu^t	Br	*18*	12.442	24.521	36.841	171.99	5.96	–	—
15	$Bu^t{}_2$	PF_6	*19*	12.134	24.175	36.279	169.32	3.04	+	16
16	$Bu^t{}_2$	Br	*20*	12.063	23.950	35.954	167.82	4.20	+	4
17	COOH	PF_6	*21*	11.904	23.460	35.247	164.54	5.96	+	—

[a] See Ref. 9.
[b] See Ref. 10.
[c] See Ref. 11.

Here

$$\varphi/3 = \mathrm{arctg}[\sqrt{3}/(1 + 2a)], \tag{8}$$

where

$$a = \nu_2(\nu_1 + \nu_2 + \nu_3)/(\nu_1\nu_3). \tag{9}$$

In relation (9), $\nu_1 = \nu_{1/2-3/2}$, $\nu_2 = \nu_{3/2-5/2}$, and $\nu_3 = \nu_{5/2-7/2}$.

The asymmetry parameter can be determined from the coupling equation $\eta(\nu_{ij})$

$$(1 - \eta^2)^2/(3 + \eta^2)^3 = (1225/12288)\cdot$$
$$\cdot[(-b_1 + b_2 - b_3)^{-1} + (-b_1 - b_2 + b_3)^{-1} +$$
$$+ (b_1 - b_2 - b_3)^{-1} + (b_1 + b_2 + b_3)^{-1}]^2 = F^2. \tag{10}$$

The solution with respect to η has the form

$$\eta = \pm\left(\frac{1-9F^2}{3F^2} - \frac{2\sqrt{1-24F^2}}{3F^2}\cdot\right.$$
$$\left.\cdot\cos\left\{\frac{1}{3}\arccos\left[\frac{36F^2-(216F^4+1)}{(1-24F^2)^{3/2}}\right]\right\}\right)^{1/2}. \tag{11}$$

The change in sign in expression (11) is due to permulation of q_{xx} and q_{yy} in Eq. (3).

Then, e^2Qq_{zz} can be calculated with ease:

$$e^2Qq_{zz} = 28\Sigma\nu_{ij}/(\Sigma|\Delta E_{ij}|). \tag{12}$$

Results and Discussion

It was established earlier[12] that the changes in the quadrupole coupling constants e^2Qq_{zz} of antimony atoms in the antimony pentachloride complexes with oxygen-containing ligands and the vertical ionization potentials (I) of the ligand oxygen atoms are related by a dispersion equation. However, any changes in the energies of the orbitals involved in the coupling are accompanied by the change in the shape of the electron density distribution for these orbitals. For the NQR-active atoms this means changes in both e^2Qq_{zz} and η.

It is possible to derive the coupling equation relating the e^2Qq_{zz} values to η for relatively narrow series of related compounds.[13—21] For instance, if the total differential is given by

$$d\eta = \frac{\partial\eta}{\partial q_{xx}}dq_{xx} + \frac{\partial\eta}{\partial q_{yy}}dq_{yy} + \frac{\partial\eta}{\partial q_{zz}}dq_{zz}, \tag{13}$$

then substituting the partial derivatives obtained by differentiation of Eq. (1) into expression (13) and introducing an arbitrary origin along the q_{zz} axis followed by performing simple transformations leads to a simple differential equation with separated variables

$$(\eta_0 - \eta)^{-1}\mathrm{d}\eta = (q_{zz} - q_{zz_0})^{-1}\mathrm{d}q_{zz}, \tag{14}$$

where $\eta_0 = \mathrm{d}(q_{xx} - q_{yy})/\mathrm{d}q_{zz} = \mathrm{const}'$ and $q_{zz0} = \mathrm{const}''$ for the given series of compounds. The solution of Eq. (14) obtained after trivial transformations and multiplication of both parts by e^2Q is as follows:

$$e^2Qq_{zz} = e^2Qq_{zz0} + B\delta/(\eta_0 - \eta). \tag{15}$$

Here $\delta = \pm 1$ and $B = \mathrm{const}'''$ for the given series of compounds.

Indeed, the coupling equation (15) correctly describes the dependence of e^2Qq_{zz} on η in the region distant from the origin (e^2Qq_{zz0}, η_0).[15]

Large deviations from the trajectory described by Eq. (15) in the vicinity of the origin can be explained by possible coincidence of the times of "slow" modulations of electron motions and the characteristic times of nuclear motions. In this case one can expect manifestation of the dynamics of these interactions in the NQR spectra.

If the number of interconfigurational tunneling transitions is large, it is appropriate to use the theory of stochastic dynamics of nonlinear oscillation systems.[22] According to this theory, generation of a large number of vibrational degrees of freedom causes the appearance of a spectrum of low-frequency fluctuations characterized by nearly rectangular probability density function.[22] Since the fluctuation frequencies are higher than the experimental NQR frequencies, the observed quadrupole coupling constant e^2Qq_{zz} is averaged. Assuming a rectangular probability density function of width $2\Delta\eta$ for the η fluctuations, one can derive a simple integral averaging of expression (15):

$$e^2Qq_{zz} = \frac{1}{2\Delta\eta}\int\limits_{\eta-\Delta\eta}^{\eta+\Delta\eta}\left(e^2Qq_{zz_0} + \frac{B\delta}{\eta_0 - \eta}\right)\mathrm{d}\eta =$$

$$= e^2Qq_{zz_0} + \frac{B\delta}{2\Delta\eta}\ln\left|\frac{\eta - (\eta_0 + \Delta\eta)}{\eta - (\eta_0 - \Delta\eta)}\right|. \tag{16}$$

Having substituted the e^2Qq_{zz} and η values (see Table 1, spectral positions *3—21*) into expression (16), one gets the following parameters of this equation (number of points is $N = 19$): $e^2Qq_{zz0} = 168.169$ MHz, $B = 3.8697$ MHz $\cdot$ %, $\eta_0 = 3.96345\%$, $\Delta\eta = 1.88765\%$, $\Delta e^2Qq_{zz} = \pm 0.056$ MHz, and $r = 0.9997$ (r is the coefficient of correlation between the experimental e^2Qq_{zz} values and those calculated from Eq. (16)).

Unsubstituted compounds $[(\pi\text{-}C_5H_5)_2Co)]^+ \cdot M^-$ ($M^- = Br_3^-$ and ClO_4^-) do not obey Eq. (16), although the differences between their e^2Qq_{zz} values are noticeable. Probably, this is a result of the Renner effect[23] (loss of a symmetry element by linear electron-nuclear molecular systems). Since here one has $\eta = 0$, the cobalt atom is located exactly on the symmetry axis.

Equation (16) with the parameters listed above describes the interrelation between the experimental e^2Qq_{zz} and η values (see Table 1) with rather high statistical characteristics.

Figure 1 presents the graphical solution of Eq. (16) with the parameters given above.

Analysis of the plot in Fig. 1 and Eq. (16) shows that the $e^2Qq_{zz}(\eta)$ curve is symmetrical with respect to the axes parallel to the axes of coordinates and intersecting at the point (e^2Qq_{zz0}, η_0). At $\eta < \eta_0 - \Delta\eta$, one has $e^2Qq_{zz} > e^2Qq_{zz0}$, which corresponds to $\delta = +1$ in Eq. (16), whereas the case $e^2Qq_{zz} < e^2Qq_{zz0}$ corresponds to $\delta = -1$ in Eq. (16). Thus, the induced EFG and the primary EFG e^2Qq_{zz0} have the same sign at $\delta = +1$ and different signs at $\delta = -1$. At $\eta > \eta_0 + \Delta\eta$, the reverse occurs. Both regions, $\eta < \eta_0 - \Delta\eta$ and $\eta > \eta_0 + \Delta\eta$, formally correspond to the static Opic—Pryce effect.

The interval $\eta_0 - \Delta\eta \le \eta \le \eta_0 + \Delta\eta$ is more interesting. It corresponds to the averaging of the EFG by the "slow" electron-nuclear motions (range of the dynamic Opic—Pryce effect). This interval is characterized by a smooth decrease in the EFG (e^2Qq_{zz}) at $\delta = +1$ and a corresponding smooth increase in the EFG (e^2Qq_{zz}) at $\delta = -1$. At the point (e^2Qq_{zz0}, η_0), both the induced and primary EFG change their signs.

Note that the points in Fig. 1, which correspond to crystallographically inequivalent cobalt atoms (see Table 1, spectral positions *11*, *12* and *14*, *15*), remain on the trajectory described by Eq. (16). It follows that not only intramolecular, but also intermolecular interactions contribute to the formation of the potential energy surface.

Having determined the parameters of Eq. (16), it is possible to estimate the mean correlation time of com-

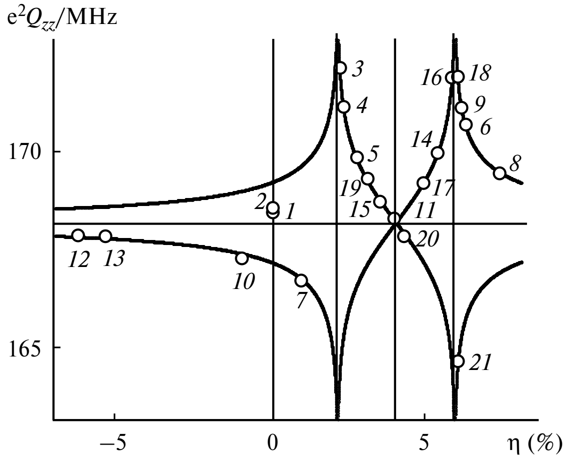

Fig. 1. Quadrupole coupling constants e^2Qq_{zz} plotted *vs.* η for spectral positions *1—21*. Solid lines are drawn using Eq. (16); points denote experimental data.

plete electron tunneling in the region of dispersion of electron-nuclear motions ($\eta_0 \pm \Delta\eta$), *i.e.*, in the region where the EFG is averaged by intramolecular motions. Since for polyatomic molecules the number of the normal modes active in the pseudo-Jahn—Teller effect (so-called Opic—Pryce effect[3]) can be rather large[2] and almost infinite in the case of a crystal, a multimode situation appears, where a number of modes of the same or similar symmetry coexist. The problem of estimating the mean correlation time of complete electron tunneling can be essentially simplified using a distinctive feature of such systems. Namely, if there exists a mode that dominates all other modes, thus "combining" them, it makes the decisive contribution and the problem is reduced to consideration of an ideal single-mode problem.[2] Therefore, the mean correlation time of complete electron tunneling can be estimated using a somewhat rough approximation[15]

$$|(\eta - \eta_0)/\Delta\eta| = (\mathrm{th}x)/x, \qquad (17)$$

where $x = \delta E/(kT)$ and δE is the energy of tunneling (inversion) splitting. Therefore, the mean correlation time of complete electron tunneling in the $\eta_0 \pm \Delta\eta$ region (see Ref. 5) is given by

$$\tau = \pi\hbar/(\delta E) = \pi\hbar/(kTx). \qquad (18)$$

The times τ calculated for compounds $[(\pi\text{-}C_5H_{5-n}R_n)_2Co]^+ \cdot M^-$ are listed in Table 1. They fall in the range 10^{-12}—10^{-14} s, being within the interval of the characteristic times of nuclear motions (10^{-10}—10^{-14} s).

Among the spectra of compounds **1—17**, noteworthy is the spectrum of symmetrical compound $[(\pi\text{-}C_5H_5)_2Co]^+ \cdot PF_6^-$ (see Table 1, compound **3**), which corresponds to a rare case of three inequivalent cobalt atoms. The τ estimates show that all three positions correspond to the dynamic changes in the EFG due to cooperative Opic—Pryce effect. The new superstructure formed in this case is called "incommensurate structure",[24,25] which is similar to helical color symmetry of real spins rather than pseudospins known in theory of magnetism. These structural and dynamic features are usually related to the onset of ferroelectric properties of these crystals.[2]

References

1. H. A. Jahn and E. Teller, *Proc. Roy. Soc. London A*, 1937, **161**, 220.
2. I. B. Bersuker, *Effekt Yana—Tellera i vibronnye vzaimodeistviya v sovremennoi khimii* [*The Yahn—Teller Effect and Vibronic Interactions in Modern Chemistry*], Nauka, Moscow, 1987, p. 84 (in Russian).
3. U. Opic and M. H. L. Pryce, *Proc. Roy. Soc. London A*, 1957, **238**, 425.
4. M. Born and R. Oppenheimer, *Ann. Phys.*, 1927, **84**, 457.
5. E. O. Kane, *Tunneling Phenomena in Solids*, Plenum Press, New York, 1969, p. 19.
6. B. S. Tsukerblat and M. I. Belinskii, *Magnetokhimiya i radiospektroskopiya obmennykh klasterov* [*Magnetochemistry and Radiospectroscopy of Exchange Clusters*], Shtiintsa, Kishinev, 1983, p. 219 (in Russian).
7. V. S. Grechishkin, *Yadernye kvadrupol´nye vzaimodeistviya v tverdykh telakh* [*Nuclear Quadrupole Interactions in Solids*], Nauka, Moscow, 1973, p. 9 (in Russian).
8. G. K. Semin, T. A. Babushkina, and G. G. Yakobson, *Primenenie YaKR v khimii* [*Application of NQR in Chemistry*], Khimiya, Leningrad, 1972 (in Russian).
9. A. N. Nesmeyanov, G. K. Semin, E. V. Bryukhova, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1969, 1936 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1969, **28** (Engl. Transl.)].
10. J. Voitlander and L. Longino, *Naturwis.*, 1959, **46**, 664.
11. G. K. Semin, E. V. Bryukhova, T. L. Khotsyanova, S. I. Kuznetsov, I. R. Lyatifov, and T. M. Dzhafarov, *Metalloorg. Khim.*, 1990, **3**, 391 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
12. G. K. Semin, *Abstrs XI Int. Symp. NQR Spectrosc.*, London, UK, 1991, P. II:32.
13. G. K. Semin, S. I. Kuznetsov, A. M. Raevsky, and E. V. Bryukhova, *Z. Naturforsch. A*, 1994, **49**, 630.
14. G. K. Semin, S. I. Kuznetsov, V. M. Burbelo, E. V. Bryukhova, and R. Sh. Lotfullin, *J. Mol. Struct.*, 1995, **345**, 65.
15. G. K. Semin, S. I. Kuznetsov, E. V. Bryukhova, and T. L. Khotsyanova, *J. Organomet. Chem.*, 1996, **508**, 129.
16. G. K. Semin, L. A. Zemnukhova, and R. Sh. Lotfullin, *Izv. Akad. Nauk. Ser. Khim.*, 1998, 1988 [*Russ. Chem. Bull.*, 1998, **47**, 1933 (Engl. Transl.)].
17. G. K. Semin, S. I. Gushchin, T. L. Khotsyanova, V. V. Saatsazov, and E. V. Bryukhova, *Zh. Fiz. Khim.*, 2000, **74**, 1719 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
18. G. K. Semin, S. I. Gushchin, and E. V. Bryukhova, *Zh. Fiz. Khim.*, 2000, **74**, 1904 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
19. G. K. Semin, *Tez. X Mezhdunar. Konf. "Magnitnyi rezonans v khimii i biologii"* [*Abstrs X Int. Conf. "Magnetic Resonance in Chemistry and Biology"*], Suzdal´, 1998, 37 (in Russian).
20. G. K. Semin, *Tez. V Vseros. soveshch. "Mekhanizmy dvukhelektronnoi dinamiki v neorganicheskikh materialakh"* [*Abstrs V All-Russia Meet. "Mechanisms of Two-Electron Dynamics in Inorganic Materials"*], Chernogolovka, 2002, p. 5 (in Russian).
21. G. K. Semin, S. I. Gushchin, and E. V. Bryukhova, *Abstrs XVII Int. Symp. on Nuclear Quadrupole Interaction*, *(Bonn, Germany, August 2004)*, Bonn, 2004, P-G-18.
22. B. V. Chirikov, *Usp. Fiz. Nauk*, 1971, **105**, 7 [*Sov. Phys.-Usp.*, 1971, **105** (Engl. Transl.)].
23. R. Renner, *Z. Phys.*, 1934, **92**, 172.
24. G. K. Semin, I. M. Alymov, V. M. Burbelo, V. I. Pakhomov, and P. M. Fedorov, *Izv. Akad. Nauk SSSR. Ser. Fiz.*, 1978, **42**, 2095 [*Bull. Acad. Sci. USSR. Phys. Ser.*, 1978, **42** (Engl. Transl.)].
25. S. Kushida, *J. Phys. Soc. Jpn*, 1978, **45**, 414.

Received April 24, 2006;
in revised form July 13, 2007