^{79}Br NQR Spectra of the Impurity Molecules of Tetrabromides of Group IV Elements in the Matrix Crystals of Group IV Element Halides *

G. K. Semin, A. M. Raevsky, S. I. Kuznetsov, T. L. Khotsyanova, and S. I. Gushchin
Institute of Organo-Element Compounds, Academy of Sciences of Russia, Moscow

Z. Naturforsch. **47a,** 111–116 (1992); received December 18, 1991

Changes in ^{79}Br NQR spectra of the impurity molecules EBr_4 (2–5% mol) (E = C, Si, Ti, Ge, Sn) in the matrix crystals of group IV element tetrahalides $EHal_4$ (E = Si. Ti, Ge, Sn; Hal = Cl, Br) were studied at 77 K. The mixtures of these components are substitution solid solutions (SS), which was proved by the appearance of characteristic satellites in the NQR spectra of the matrix crystals. Changes in the ^{79}Br NQR spectra of the impurity molecules were analyzed from the viewpoint of packing factors and the type of nearest environment.

In the temperature range 77–270 K an abnormal temperature dependence of the ^{79}Br NQR frequencies of $TiBr_4$ impurity in $SiBr_4$ matrix was observed for both lines of the cubic phase. The temperature dependence of the ^{79}Br NQR frequencies of SiBr impurity in $TiBr_4$ matrix is normal.

Key words: ^{79,81}Br NQR, Solid solutions, Group IV element tetrahalides, Temperature dependence of NQR frequencies.

Introduction

We have studied during several years molecular crystals of model solid solutions as to changes in the NQR spectra of the atoms of matrix crystals [1–4] and changes in the NQR spectra of impurity molecules [5].

A special study was dedicated to a continuous series of solid solutions forming isomorphous crystals.

The interaction of the impurity molecules with the molecules of the matrix lattice allows to "unify" the crystal lattice effect on the impurity spectrum [6] and to study fine differences of the crystal field by introducing small amounts of impurities as probes.

In the present work we deal with the latter problem using solid solutions of tetrahalides of group IV elements.

A comparative study of the ^{35}Cl and ^{79}Br NQR spectra of the component substances was carried out previously [7].

The matrix tetrachlorides crystallize in the structure type (ST) of the monoclinic modification of $SnBr_4$ (space group $P2_1/c$, $Z=4$)[1]. The molecules occupy positions which correspond to the quadruplet NQR spectrum (see Table 1).

The matrix of tetrabromides crystallize both in the monoclinic (ST $SnBr_4$) and cubic modification (ST SnI_4, space group Pa3, $Z=8$)[2]. In the cubic modification the molecules are on the symmetry axes 3 which corresponds to the doublet NQR spectrum with the line intensity ratio 1:3.

Tetrabromides of the group IV elements C, Si, Ge, Sn, and Ti were used as impurities (see Tables 1–3). Titanium tetrahalides were chosen to compare them with tetrahalides of the nontransitional elements. The impurity amounts in the matrix were 2–5%.

It was of interest to study:

1. Changes in the NQR spectrum of the impurity on introducing it in an alien lattice.
2. NQR frequency shifts depending on the type of the matrix lattice.
3. Character of the mutual positions of spectral lines due to changes in the local symmetry.

Additionally, we tried to clear up how well-reasoned was our assumption concerning the existence of a weak intermolecular coordination element-halogen in the structure of $SnBr_4$ type and to determine the ratio of the volume- and intramolecular factors in the abnormal temperature dependence of the bromine NQR frequencies in $TiBr_4$.

---

* Presented at the XIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, U.K., July 15–19, 1991.

[1] Type II according to [7].

[2] Type III according to [7].

Reprint requests to Mr. A. M. Raevsky, Institute of Organo-Element Compounds, Academy of Sciences of the Russia, 28 Vavilov St., Moscow 117813, Russia.

0932-0784 / 92 / 0100-0111 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. ^{79}Br NQR spectrum of CBr_4 and ^{35}Cl NQR spectra of matrix crystals of group IV element tetrachlorides with $SnBr_4$ type structure (77 K, frequencies in MHz).

CBr_4				$SiCl_4$	$GeCl_4$	$TiCl_4$	$SnCl_4$
318.01	319.41	320.83	322.38	20.273	25.450	5.980	23.720
318.33	319.46	320.91	322.59	20.408	25.715	6.038	24.140
319.14	319.96	321.14	322.59	20.415	25.735	6.081	24.226
319.33	320.83	321.36	322.81	20.464	25.745	6.112	24.296

Table 2. ^{79}Br NQR spectra of the impurity molecules of group IV element tetrabromides with $SnBr_4$ type structure (77 K, frequencies in MHz).

Lattice	Impurity				
	CBr_4 (I)	$SiBr_4$ (II)	$GeBr_4$ (III)	$TiBr_4$ (IV)	$SnBr_4$ (V)
$SiCl_4$ (1)	323.09	175.526	209.47	46.62	194.12
	323.89	176.628	210.96	47.02	196.34
	324.40	176.807	211.15	47.02	198.02
	324.60	176.915	211.22	47.87	198.16
$GeCl_4$ (2)	322.61	175.538	209.27	46.58	
	324.02	177.214	211.39	47.17	
	324.48	177.214	211.39	47.17	
	324.68	177.250	211.60	48.14	
$TiCl_4$ (3)	322.61	176.029	209.55		
	324.26	177.274	211.60		
	324.32	177.525	211.92		
	324.93	177.621	212.14		
$SnCl_4$ (4)	322.02	176.137	209.37		
	324.90	178.160	212.34		
	325.09	178.328	212.73		
	325.09	178.328	213.28		
$GrBr_4$ (5)			208.91		
			210.80		
			211.74		
			211.81		
$TiBr_4$ (6)		176.64		46.943	
		177.54		47.060	
		177.54		47.454	
		177.94		47.999	
$SnBr_4$ (7)	321.43	176.09	209.30	47.104	193.964
	323.57	177.73	212.21	47.628	197.778
	324.17	178.17	212.52	47.978	198.002
	324.53	178.30	212.70	48.889	198.283

Table 3. ^{79}Br NQR spectra of the impurity molecules of the group IV element tetrabromides with SnI_4 type structure (77 K, frequencies in MHz).

Lattice	Impurity				
	CBr_4 (I)	$SiBr_4$ (II)	$GeBr_4$ (III)	$TiBr_4$ (IV)	$SnBr_4$ (V)
$SiBr_4$ (1)	323.23 t	176.585 s	210.73 t	46.13 s	195.51 s
	323.85 s	176.663 t	211.13 s	47.55 t	196.00 t
$GeBr_4$ (2)	323.038 t	176.540 t	210.192 t	46.100 s	195.89 t
	324.840 s	176.795 s	210.629 s	46.284 t	196.62 s
$TiBr_4$ (3)		177.32 s		46.309 s	
		177.42 t		47.127 t	

t: triple intensity line; s: single intensity line.

Experimental

All ^{79}Br NQR spectra at 77 K and ^{79,81}Br NQR spectra in the temperature range 77–270 K for the solid solutions of $TiBr_4$ in $SiBr_4$ and $SiBr_4$ in $TiBr_4$ were studied with an ISSh-2-13 pulsed NQR spectrometer (production of SKB IRE AN SSSR [8]). In the latter case the accuracy is better than 0.1 K for T and amounts to 3 kHz for ν. The accuracy in measuring ν at 77 K is determined by the line width and lies in the range of 3–10 kHz.

Preparation of Samples

The melt of both components was quenched by plunging the ampule in liquid nitrogen, which virtually produced the required composition of the crystal [4]. The entering of the impurity molecules into the matrix lattice was recognized by the appearance of the "impurity" satellites in the NQR spectra of the matrix crystals (see Figure 1).

^{79}Br NQR Spectra of Tetrabromides of IV Group Elements in Matrix Lattices of the $SnBr_4$ Type

As is seen from Table 2, the ^{79}Br NQR spectra of the impurity molecules are always quadruples with varying mutual positions of the spectral lines. Thus, in tetrachloride matrices the spectrum of CBr_4 impurity is shifted towards higher frequencies compared to its spectrum in its own lattice (Table 1). Additionally, there is a characteristic high frequency shift of the high frequency triplet and a low frequency shift of the single low frequency line in the series of the CBr_4 solid solutions in $SiCl_4$, $GeCl_4$, $TiCl_4$ and $SnCl_4$ matrices. The dependence of the average frequency of the high frequency triplet $\bar{\nu}$ and that of the single low frequency line ν_1 on their difference Δ are seen in Figure 2. They

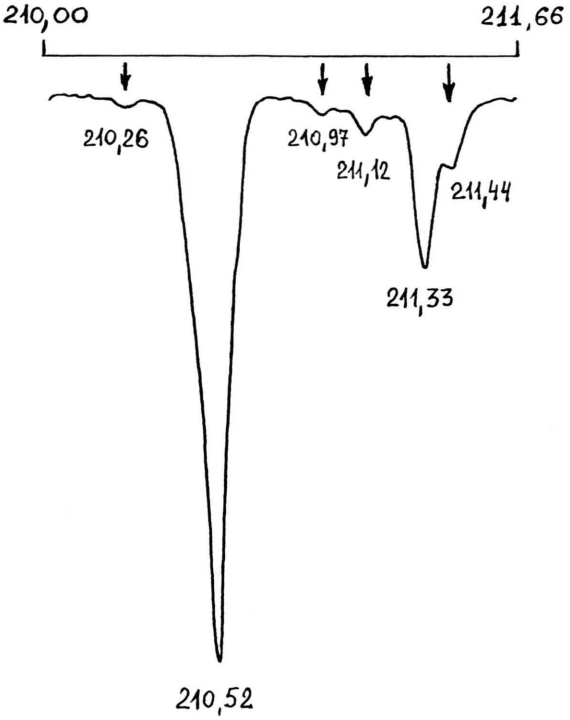

Fig. 1. ^{79}Br NQR spectrum of a $GeBr_4$ matrix (ST SnI_4) with 5 mol% $SnBr_4$ impurity. The "impurity" satellite lines are indicated by arrows.

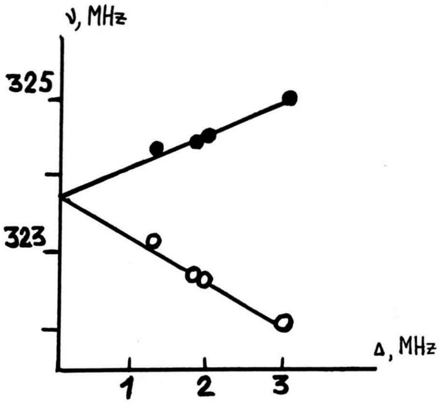

Fig. 2. Dependence of the ^{79}Br NQR frequencies of CBr_4 solved in solid tetrachlorides on the difference $\Delta = \bar{\nu} - \nu_1$. Open circles: ν_1, close circles: $\bar{\nu}$.

are well described by the linear equation

$$\nu = [\nu_0 + (b \pm 0.5)\,\Delta] \pm \delta\,. \qquad (1)$$

The parameters of (1) are listed in Table 4.

Table 4. Parameters of (1) for EBr_4 in EX_4 (E = C, Si, Ge, Ti, Sn).

	Impurity	ν_0	b	δ	n
In the ECl_4 lattice	CBr_4	323.72	−0.08	0.05	4
	$SiBr_4$	174.455	1.275	0.11	4
	$GeBr_4$	209.56	0.44	0.08	4
	$TiBr_4$	46.43	−0.97		2
In the EBr_4 lattice	$SiBr_4$	177.242	−0.083	–	2
	$GeBr_4$	207.36	1.11	–	2
	$TiBr_4$	46.40	−1.39	–	2

The behavior of the ^{79}Br frequencies for solid solutions of $SiBr_4$ and $GeBr_4$ in tetrachlorides is also well described by an equation of type (1). The $TiBr_4$ spectra in $SiCl_4$ and $GeCl_4$ lattices are inverted: The single line is at a higher frequency than the triplet. The latter shift agrees with well known regularities of NQR frequency shifts for coordinated atoms [12, 13]. Namely, NQR spectral lines, shifted to the lower frequencies, correspond to halogen atoms participating in the coordination with nontransitional elements, while participation of a halogen atom in coordination with a transitional element results in a shift to higher frequencies.

Unfortunately, only in the $SiCl_4$ matrix lattice we could succeed in obtaining the ^{79}Br NQR spectrum of $SnBr_4$. Our studies of tetrabromide impurities in tetrabromide lattices were also fragmentary. Therefore for the latter we could only roughly estimate the parameters of (1), as well as those of $TiBr_4$ (see Table 4).

^{79}Br NQR Spectra of Tetrabromides of IV Group Elements in Matrix Lattices of the SnI_4 Type

In the $SiBr_4$, $GeBr_4$ and $TiBr_4$[3] matrix lattices, characteristic doublet spectra of ^{79}Br with the line intensity ratio 1:3 were observed (see Table 3). The weak and strong lines sometimes changed their places.

The temperature dependence of the bromine NQR frequencies in the cubic phase (III) of $TiBr_4$ is of par-

---

[3] According to [9] there are three polymorphous modifications of $TiBr_4$. Two of them, studied by X-ray method, belong to the ST II [10] and III [11]. The structure of the third, birefringent, modification, has not been established. As is seen from Tables 2 and 3, the ^{79}Br NQR spectra of $SiBr_4$ in the $TiBr_4$ matrix lattice correspond to the crystal matrices of type II and III. The phase transition in $TiBr_4$ occurs much more easily than that in $GeBr_4$.

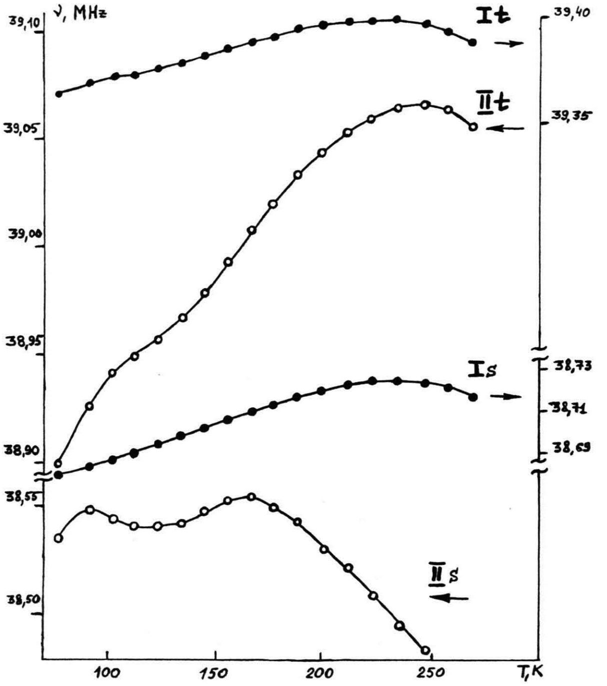

Fig. 3. Temperature dependence of ^{81}Br NQR frequencies in: I) pure $TiBr_4$ (close circles); II) solid solution of $TiBr_4$ in $SiBr_4$ matrix (open circles). The letters "t" and "s" refer to triple and single lines, respectively.

ticular interest. Its abnormal character in the temperature range 4.2–317 K can be explained by an effect of the volume or by a decreasing $d_\pi - p_\pi$ overlap in the Ti–Br bond due to its bending vibrations, resulting in an increase of the frequency.

The temperature dependence of the ^{81}Br NQR frequencies of $TiBr_4$ in its own lattice [13] and as small impurity in a $SiBr_4$ lattice in the range 77–270 K are represented in Figure 3. In the latter case the abnormal temperature dependence of bromine NQR frequencies is retained which serves as unambiguous evidence for the determining role of the intramolecular factor.

An additional evidence is the normal temperature dependence of the Br NQR frequencies of $SiBr_4$ in the $TiBr_4$ matrix (the temperature dependence of the ^{79}Br NQR frequency of $SiBr_4$ in its own lattice is also normal).

Results and Discussion

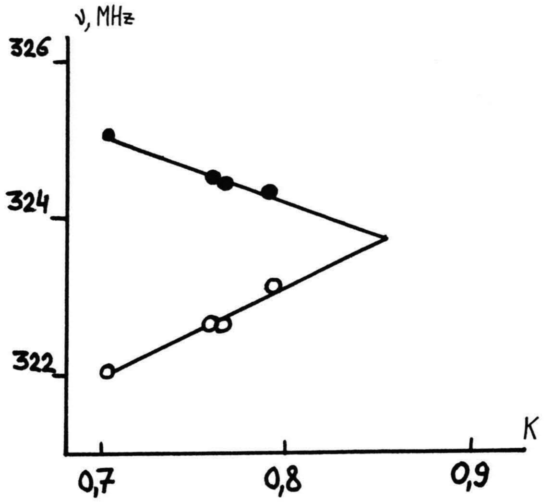

Fig. 4. Dependence of the average frequency of the high frequency triplet and of the low frequency line of ^{79}Br of CBr_4 on the formal close packing coefficient in tetrachloride matrix lattices. Open circles: ν_1, close circles: $\bar{\nu}$.

The ^{79}Br NQR spectra of the impurities in monoclinic lattices are mostly similar to that of the matrix crystals. Sometimes, however, a pair of lines in the distant triplet coalesces, which indicates a local symmetry increase in the nearest environment of the impurity molecule introduced into the tetrachloride lattice.

Changes in the close packing coefficient in lattices of the same type must evidently follow the law of the inverse cube distance from atoms of the nearest environment. Therefore, comparison of NQR frequency changes for the impurity molecule, used as "probes" in various similar matrices, with the formal close packing coefficients characteristic of each matrix lattice can serve as a measure of spectral shift changes caused by the crystal field. Here, by the formal close packing coefficient we mean $K = V_{mol}/V_{uc}^{m}$, where V_{mol} is the volume of the impurity molecule, and V_{uc}^{m} is the volume allotted for one molecule in the matrix crystal unit cell (see Table 5). The matrix lattice and the impurity molecule are assumed to be rigid. The dependence of the average frequency of the high frequency triplet and that of the low frequency line of K for CBr_4 impurity in the tetrachloride lattices are seen in Figure 4. We define (see Table 6)

$$\nu = \nu_0 + A \cdot K \,. \tag{2}$$

It is clearly seen that the average frequency of the triplet is inversely proportional to K, which entirely corresponds to what was earlier observed for molecular crystals [4]. It should be assumed that extrapola-

Table 5. Values of the formal close packing coefficients.

Structure type	Lattice	Impurity				
		CBr_4	$SiBr_4$	$GeBr_4$	$TiBr_4$	$SnBr_4$
$SnBr_4$	$SiCl_4$	0.792	0.834	0.889	0.912	0.968
	$GeCl_4$	0.769	0.806	0.859	0.882	0.935
	$TiCl_4$	0.762	0.803	0.856	0.878	0.932
	$SnCl_4$	0.703	0.740	0.790	0.810	0.859
	$GrBr_4$	0.636	0.670	0.715	0.733	0.778
	$TiBr_4$	0.621	0.654	0.697	0.715	0.759
	$SnBr_4$	0.585	0.616	0.657	0.674	0.715
SnI_4	$SiBr_4$	0.707	0.741	0.790	0.819	0.860
	$GeBr_4$	0.660	0.695	0.741	0.771	0.806
	$TiBr_4$	0.636	0.670	0.715	0.741	0.778

Table 6. Parameters of (2) for EBr_4 in EX_4 (E = C, Si, Ge, Ti, Sn).

	Impurity	Assignment	ν_0	A	δ	n
In the ECl_4 lattice	CBr_4	$\bar{\nu}$	331.03	−8.56	0.03	4
		ν_1	314.04	11.30	0.04	4
	$SiBr_4$	$\bar{\nu}$	189.869	−15.626	0.070	4
		ν_1	180.929	−6.437	0.130	4
	$GeBr_4$	$\bar{\nu}$	226.51	−17.31	0.09	4
		ν_1	208.72	0.83	0.08	4
	$TiBr_4$	$\bar{\nu}$	49.44	−2.80	–	2
		ν_1	55.89	−8.80	–	2
In the EBr_4 lattice	$SiBr_4$	$\bar{\nu}$	184.523	−10.479	–	2
		ν_1	167.078	14.628	–	2
	$GeBr_4$	$\bar{\nu}$	224.15	−6.75	–	2
		ν_1	213.73	−17.77	–	2
	$TiBr_4$	$\bar{\nu}$	54.46	−10.22	–	2
		ν_1	63.96	−21.76	–	2

Table 7. Difference $\nu_1 - \bar{\nu}$ for EBr_4 in EX_4 (X = Cl, Br).

	Impurity	$\nu_{01} - \bar{\nu}_0$	$A_1 - \bar{A}$	$(A_1 - \bar{A})/\bar{A}$
In the ECl_4 lattice	CBr_4	−16.99	19.86	−2.32
	$SiBr_4$	− 8.940	9.189	−0.588
	$GeBr_4$	−17.79	18.13	−1.05
	$TiBr_4$	6.45	−6.00	2.14
In the EBr_4 lattice	$SiBr_4$	−17.445	25.107	−2.396
	$GeBr_4$	−10.420	−11.02	1.63
	$TiBr_4$	9.099	−11.540	1.13

tion of the above dependence to $K = 0$ would allow to estimate the value of that frequency in vacuum [4, 6].

The low frequency line is directly proportional to K. This indicates an additional interaction of the atom corresponding to this line and agrees well with a weak intermolecular coordination E ... Br. The K-dependence of the low frequency line is determined by two contributions: coordination and volume (van der Vaals) factors. For Br atoms in CBr_4 the coordination factor is predominant, for $SiBr_4$ it is the volume factor. For $GeBr_4$ the contribution of both factors are approximately equal (see Table 7).

Conclusions

1. For the solid solutions of tetrabromides EBr_4 (E = C, Si, Ge, Ti, Sn), if the latter enter as small impurities the matrix crystal lattices EX_4 (E = Si, Ge, Ti, Sn; X = Cl, Br) the ^{79}Br NQR spectrum of the impurity is always similar to that of the matrix. In the monoclinic phase this similarity can be violated if the local symmetry of the environment of the impurity molecules is changed and becomes higher than the matrix lattice symmetry. Thus, for the cases I_4, II_6, II_2, II_4, IV_1, IV_2, III_2 (see Table 2), the ^{79}Br spectra of the impurity correspond to the symmetry 2 or *m*.

2. The totality of experimental fact points to the existence of a weak intermolecular coordination interaction of the central atom of the matrix molecule with one of the bromine atoms of the impurity molecule in the monoclinic phase.

3. As observed previously [4, 5], there is a linear dependence between the frequency shifts of the impurity molecules introduced into crystal matrices ECl_4 and EBr_4 (2 separate dependences) and the formal close packing coefficients defined for a rigid crystal lattice and impuritiy molecule.

4. The abnormal temperature dependence of the ^{79,81}Br NQR frequencies of $TiBr_4$ in the $SiBr_4$ lattice (as well as that in its own lattice) is shown to be determined by intramolecular factors.

[1] G. K. Semin and I. M. Alymov, Phys. Stat. Sol. (a) **33,** K 63 (1976).

[2] G. K. Semin and I. M. Alymov, Phys. Stat. Sol. (a) **33,** K 111 (1976).

[3] I. M. Alymov, G. K. Semin, T. L. Khotsyanova, and T. A. Babushkina, Izv. AN SSSR, Ser. Fiz. **39,** 2457 (1975) (in Russ.). Engl. transl.: Bull. Acad. Sci. USSR, Phys. Ser. **39,** 7 (1975) by Allerton Press, Inc.

[4] G. K. Semin, I. M. Alymov, and T. L. Khotsyanova, Izv. AN SSSR, Ser. Fiz. **42,** 2055 (1978) (in Russ.). Engl. transl.: Bull. Acad. Sci. USSR, Phys. Ser. **42,** 36 (1978) by Allerton Press, Inc.

[5] G. K. Semin, I. M. Alymov, T. A. Babushkina, and V. P. Kazakov, Zh. Fiz. Khim. **54,** 776 (1980) (in Russ.).

[6] G. K. Semin, A. M. Raevsky, E. V. Bryukhova, and T. L. Khotsyanova, Izv. AN SSSR, Ser. Fiz. **45,** 450 (1981) (in Russ.).

[7] S. I. Kuznetsov, I. M. Alymov, E. V. Bryukhova, and G. K. Semin, Izv. AN SSSR, Ser. Fiz. **39,** 2524 (1975) (in Russ.).

[8] B. N. Pavlov, in: Pribory i oborudovanije dlya nauchnych issledovanij, Moscow 1983 (in Russ.).

[9] H.Sackmann, D. Demus, and D. Pankow, Z. Anorg. Allg. Chem. **318,** 257 (1962).

[10] P. Brand and J. Schmidt, Z. Anorg. Allg. Chem. **348,** 257 (1966).

[11] S. I. Troyanov, V. B. Rybakov, and V. M. Ionov, Zh. Neorg. Khim. **35,** 883 (1990) (in Russ.).

[12] G. K. Semin, S. I. Kuznetsov, I. M. Alymov, T. L. Khotsyanova, E. V. Bryukhova, L. A. Nisselson, and K. V. Tretyakova, Inorg. Chim. Acta **13,** 181 (1975).

[13] S. I. Kuznetsov, E. V. Bryukhova, and G. K. Semin, Izv. AN SSSR, Ser. Fiz. **45,** 476 (1981) (in Russ.).