^{121,123}Sb NQR study of antimony(III) fluoride complexes

L. A. Zemnukhova and R. L. Davidovich*

Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,
159 prosp. 100-letiya Vladivostoka, 690022 Vladivostok, Russian Federation.
Fax: +7 (423 2) 31 1889. E-mail: chemi@online.ru

Antimony(III) complexes with nitrogen-containing ligands: $2SbF_3 \cdot Gly$, $SbF_3 \cdot Gly$, $SbF_3 \cdot 2NA$, $SbFO \cdot Gly$, MSb_2F_7 (M = Et_2NH_2, Bu_4N, HNA^+), $MSbF_4$ (M = Et_2NH_2, Pr_2NH_2, Bu_4N, HNA^+, $HGly^+$), M_2SbF_5 (M = Et_2NH_2 and Pr_2NH_2), where Gly is glycine ($^+NH_3CH_2COO^-$) and NA is nicotinamide (β-$C_5H_4NCONH_2$), were studied by ^{121,123}Sb NQR spectroscopy at 77 K.

Key words: ^{121,123}Sb NQR spectra; antimony(III), fluoride complexes, nitrogen-containing ligands, glycine, nicotinamide, diethyl ammonium, dipropyl ammonium, tetrabutyl ammonium.

Nuclear quadrupole resonance (NQR) is successfully used for studying the electron density distribution in molecules of crystalline substances containing elements whose nuclei have electric quadrupole moments. The latter are specific local probes highly sensitive to changes in the electric field gradient (EFG) at their sites.[1—3]

The nuclei of both stable natural antimony isotopes (^{121}Sb and ^{123}Sb) have nonzero electric quadrupole moments and their spins are 5/2 and 7/2, respectively. This suggests that at least five lines (two from the nuclei of ^{121}Sb isotope and three from those of ^{123}Sb isotope) corresponding to crystallographically (structurally) equivalent Sb atoms must be observed in the antimony NQR spectrum. The procedures for calculation of main spectral parameters obtained from the experimental NQR frequencies, the quadrupole coupling constant (QCC) e^2Qq_{zz} (e is the charge of electron, eQ is the electric quadrupole moment of the nucleus, and eq_{zz} is the maximum diagonal component of the EFG tensor at the site of the quadrupole nucleus), and the asymmetry parameter of the EFG tensor (η) have been reported previously.[1] The QCC value serves as a measure of the electron distribution and changes as the state of chemical bonds changes, while the parameter (η) characterizes the degree of deviation of the EFG symmetry from axial symmetry. Various antimony(III) complexes including those with nitrogen-containing ligands have been studied by the NQR method. Compounds based on $SbCl_3$ and $SbBr_3$ [1—4] have been studied in most detail.

In a continuation of our studies of compounds based on SbF_3, in this work we investigated the ^{121,123}Sb NQR spectra of complexes whose molecules contain the amine nitrogen atoms.

Experimental

The syntheses of SbF_3 adducts with aliphatic amines (diethylamine (Et_2NH), dipropylamine (Pr_2NH), and tetrabutylammonium hydroxide (Bu_4NOH)),[5] with nicotinamide (NA),[6] and with glycine (Gly)[7] have been described. The ^{121,123}Sb NQR spectra of polycrystalline specimens were recorded on an ISSh-1-13 NQR spectrometer at 77 K (see Ref. 8). For both Sb isotopes, the positions of the maxima of spectral lines were determined with an accuracy of 5 kHz.

Results and Discussion

The experimental ^{121,123}Sb NQR frequencies at 77 K and the corresponding calculated parameters e^2Qq_{zz} and η of antimony(III) adducts with nitrogen-containing ligands are listed in Table 1.

Previously,[8,9] the ^{121,123}Sb NQR spectrum of antimony trifluoride has been studied. Each Sb atom in the crystal structure of SbF_3 is bonded to three F atoms (the Sb—F distances are 1.90, 1.9, and 1.94 Å, respectively).[10] The SbF_3 molecules are linked by three bridging bonds (the Sb—F distances are 2.61 Å) with the formation of a three-dimensional network.

Aliphatic amines and nicotinamide are N-donor ligands, whereas glycine has a zwitterionic structure ($^+NH_3CH_2COO^-$) and is usually coordinated to the oxygen atom.

The crystal structures of fluoroantimonates(III) with aliphatic amines as ligands (**1—7**) are unknown. The bond nature in these compounds has been studied by IR spectroscopy.[5]

The structure of compound **10** belonging to adducts of antimony trifluoride with nicotinamide (**8—10**) has been studied.[11] It is formed by molecular complexes of composition $SbF_3[β\text{-}C_5H_4NC(O)NH_2]_2$, linked by hydrogen bonds to form infinite chains. The NA molecules were found to be coordinated to the Sb atom through the N atom of the heterocycle. The coordination polyhedra of antimony atoms $[SbF_3N_2E]^{2-}$ have the square bipyramidal configuration with the vacant axial vertex occupied by the lone electron pair (E).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2232—2236, November, 1998.

Table 1. ^{121,123}Sb NQR spectral parameters of antimony(III) fluoride complexes at 77 K

Compound	Formula	Transition frequencies, ν/MHz					e^2Qq_{zz}/MHz		η (%)
		^{121}Sb		^{123}Sb			^{121}Sb	^{123}Sb	
		±(1/2 ⇌ 3/2)	±(3/2 ⇌ 5/2)	±(1/2 ⇌ 3/2)	±(3/2 ⇌ 5/2)	±(5/2 ⇌ 7/2)			
	Antimony(III) adducts with derivatives of aliphatic amines								
1	$(Et_2NH_2)Sb_2F_7$	78.04,	155.07,	48.18,	94.27,	141.70,	517.4,	661.8,	7.3,
		84.98	168.53	52.40	101.98	153.43	562.5	716.5	8.1
2	$(Et_2NH_2)SbF_4$	77.53,	149.70,	50.66,	91.09,	138.26,	501.8,	647.0,	16.7,
		77.84	153.73	48.66	93.92	141.50	513.4	660.9	9.9
3	$(Et_2NH_2)_2SbF_5$	75.87	150.70	47.14	92.23	138.68	502.9	647.5	7.3
4[a]	$(Pr_2NH_2)SbF_4$	79.82	157.48	49.64	95.11	143.34	526.1	669.6	10.3
5	$(Pr_2NH_2)_2SbF_5$	76.56	153.12	46.40	92.81	139.21	510.4	649.6	0
6[b]	$(Bu_4N)Sb_2F_7$								
7	$(Bu_4N)SbF_4$	70.79	137.09	45.34	82.15	124.57	459.3	582.9	16.0
	Antimony(III) adducts with nicotinamide								
8[a,c]	$(C_6H_7N_2O)Sb_2F_7$			51.43,	102.90,	154.35,	565.0,	720.2,	0
				47.67	95.34	143.01	523.5	667.4	0
9	$(C_6H_7N_2O)SbF_4$	76.23	151.50	47.08	92.27	138.71	505.5	647.7	7.0
10	$SbF_3 \cdot 2C_6H_6N_2O$	76.97	153.81	46.92	93.59	140.42	512.8	655.4	2.5
	Antimony(III) adducts with glycine								
11[a]	$2SbF_3 \cdot (NH_3CH_2COO)$	76.63,	151.07,	47.94,	91.64,	138.15,	504.7,	645.4,	10.6,
		81.96	162.94	50.29	98.69	148.35	543.6	692.6	6.8
12	$SbF_3 \cdot (NH_3CH_2COO)$	75.73	145.80	49.54	88.35	134.22	488.9	628.3	17.4
13[b]	$SbFO \cdot (NH_3CH_2COO)$								
14	$(NH_3CH_2COOH)SbF_4$	79.43	151.99	51.97	91.14	138.71	510.2	649.5	18.8
	Reference compounds								
15[d]	SbF_3	80.67	160.9	49.17	97.64	146.59	536.7	684.2	4.3
16[d]	$NH_4Sb_2F_7$	79.93,	159.1,	48.97,	96.53,	145.02,	530.8,	677.0,	5.9,
		80.94	161.3	49.62	97.65	146.67	538.0	684.9	6.3
17[d]	NH_4SbF_4	75.28,	148.92,	46.61,	90.17,	135.65,	497.3,	633.9,	9.0,
		80.01	158.9	48.98	96.42	144.92	530.3	676.4	6.2
18[d]	$(NH_4)_2SbF_5$	73.08	144.85	45.12	87.96	131.97	483.5	616.2	8.4

[a] Piezoelectric noises are detected.

[b] No signals were found.

[c] No ^{121}Sb signals were observed in the starting reagent SbF_3; the e^2Qq_{zz} values for ^{121}Sb were calculated using the ratio of the quadrupole moments of the antimony isotopes: $Q(^{123}Sb)/Q(^{121}Sb)$ = 1.27475 (see Ref. 1).

[d] Data taken from Ref. 8.

Four complexes of antimony trifluoride with glycine (**11**—**14**) were obtained and for two of them (**12** and **14**) the crystal structures have been determined.[7] The crystals of adduct **12** are formed by $SbF_3(^+NH_3CH_2COO^-)$ molecular complexes linked by hydrogen bonds into a three-dimensional framework. The Sb atoms in the structure are surrounded by three F atoms and one O atom of the glycine molecule. The coordination polyhedron of antimony atoms $[SbF_3OE]^-$ has the trigonal bipyramidal configuration with the vacant vertex occupied by the lone electron pair of Sb atom and lying in the equatorial plane. The crystal structure of compound **14** is formed by the $(NH_3CH_2COOH)^+$ cations and SbF_4^- anions linked by electrostatic forces and hydrogen bonds into a three-dimensional framework.[7] As in structure **12**, the coordination polyhedron of the antimony atom has the trigonal bipyramidal configuration with the vacant equatorial vertex. The shortest distance between the antimony atom of the SbF_4^- group and the fluorine atom of the neighboring SbF_4^- group in the structure **14** is 3.121 Å.

Fluoroantimonates(III) with nitrogen-containing ligands (see Table 1) can be divided into two groups. One of them comprises the adducts SbF_3L_n **10**, **11**, **12**, and **13** belonging to three types of composition (1 : 2, 2 : 1, and 1 : 1), while the other group consists of three types of ionic complexes, *viz.*, MSb_2F_7 (**1**, **6**, **8**), $MSbF_4$ (**2**, **4**, **7**, **9**, **14**), and M_2SbF_5 (**3**, **5**). The ^{121,123}Sb e^2Qq_{zz} values calculated for these compounds were compared with the results of NQR studies of similar antimony(III) complexes synthesized previously.[8]

To explain the characteristic changes in the QCC values, we used the approximate Townes—Dailey theory,[1—3] according to which the EFG at antimony nuclei is due to the filling of the states of p-orbitals of the outer valence shell of Sb atoms

$$e^2Qq_{zz} = U_pe^2Qq_0; \quad U_p = (N_x + N_y)/2 - N_z, \qquad (1)$$

where e^2Qq_0 is the QCC value for the free Sb atom; N_x, N_y, and N_z are the populations of p_x-, p_y-, and p_z-orbitals, respectively; and U_p is the number of unbalanced p-electrons.

One s- and three p-orbitals of the outer electron shell of Sb atoms are filled with five electrons. To a first approximation it is assumed that s-electrons make the zero contribution to the EFG at the nuclei of Sb atoms because of the spherical symmetry of their orbitals and that the major contribution is due to p-electrons.[1–3] The excess electron density on one of the p-orbitals induces the EFG at the nuclei of Sb atoms; the magnitude of this gradient is proportional to e^2Qq_{zz}. If the antimony atoms form three equivalent bonds, then the EFG is axially symmetrical, directed along the orbital of the lone electron pair, and $\eta = 0$. If the bonds are nonequivalent, the EFG symmetry is violated, which is characterized by a non-zero η value. According to Eq. (1), a decrease in e^2Qq_{zz} corresponds to an increase in the populations of p_x- and p_y-orbitals, whereas an increase in e^2Qq_{zz} corresponds to increased population of the p_z-orbital. However, it should be noted that the interpretation of QCC shifts in terms of populations is ambiguous; because of this, additional contributions to the NQR parameters (*e.g.*, due to changes in the bond hybridization[3]) should be taken into account when analyzing the experimental results.

Using the e^2Qq_0 value for the ^{121}Sb isotope (734 MHz),[2] we calculated the U_p values for the compounds listed in Table 1 and compared them with the values of the Δe^2Qq_{zz} shifts for ^{121}Sb with respect to the QCC of the antimony atom in the SbF_3 molecule. The results obtained are shown in Fig. 1.

Adducts $SbF_3 \cdot L_n$ (L_n = 2NA, 10) and $SbFO \cdot Gly$ (11, 12). The NQR spectrum of adduct **11** corresponds to two crystallographically nonequivalent positions of Sb atoms in the structure, which is characteristic of antimony(III) complexes of composition 2 : 1.[2–4,12] The QCC shifts of Sb atoms in adduct **11** are −1.3 and +6.0% with respect to the QCC of antimony atoms in SbF_3. According to Eq. (1), the opposite signs of QCC shifts reflect changes in the populations of p-orbitals of Sb atoms upon the formation of adduct that occur in opposite directions. For one Sb atom the population increases and an increase in the e^2Qq_{zz} with respect to the QCC of the antimony atom in the SbF_3 molecule is observed (see Fig. 1, point *11'*). The population of the p_z-orbital of the other Sb atom decreases (see Fig. 1, point *11*), which manifests itself as a decrease in the QCC value (see Table 1) and indicates the acceptor properties of this atom. As can be judged by the η values, the distortion of the SbF_3 fragments in the molecule of compound **11** is different. Additionally, the larger values of the EFG asymmetry parameters at the nuclei of both Sb atoms in adduct **11** compared to those of SbF_3 are evidence of a greater distortion of the local electric field distribution in the complex. Similar changes in the ^{121,123}Sb NQR spectrum were observed for the previously studied antimony(III) adduct with DMSO (an O-donor ligand) of composition 2 : 1:[12] the QCC values for the Sb atoms in the molecule of this compound are larger than that for SbF_3, while their shifts are 3.2 and 3.7%.

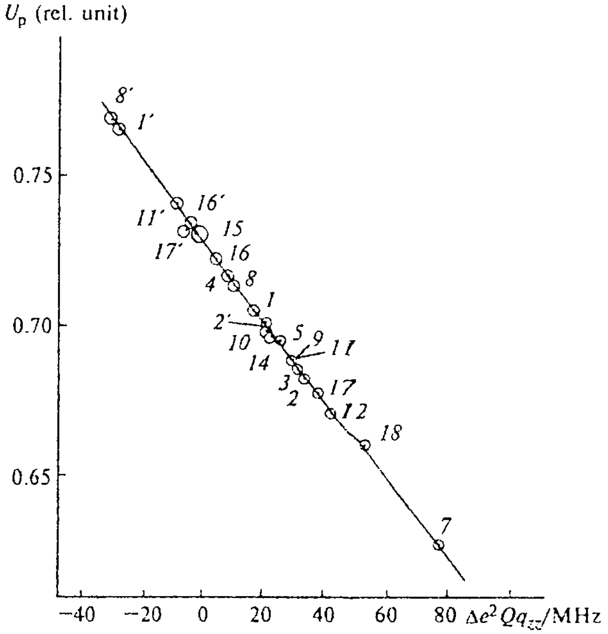

Fig. 1. Dependence of the number of unbalanced p-electrons (U_p) on the value of the QCC shift (Δe^2Qq_{zz}) ^{121}Sb in antimony(III) fluoride complexes with nitrogen-containing ligands. The numbering of points corresponds to that of compounds in Table 1. For compounds **1**, **2**, **8**, **11**, **16**, and **17** the points corresponding to all structurally nonequivalent Sb atoms are shown.

The unit cells of crystals of adducts **10** and **12** contain only crystallographically equivalent Sb atoms, which is confirmed by their ^{121,123}Sb NQR spectra (see Table 1) correlated with their crystal structures.[7,11] The antimony(III) complexes of composition 1 : 1 always have similar ^{121,123}Sb NQR spectra.[4]

The quadrupole coupling constants of Sb atoms in adduct **12** of composition 1 : 1 are 8.1% smaller than those in the SbF_3 molecule (see Fig. 1, point *12*). These parameters in the complex with DMSO [12] of the same type are 3.5% smaller than those in the SbF_3 molecule. Comparison of the e^2Qq_{zz} values shows that glycine is a stronger donor of electrons. The electron density distribution in the adduct with DMF of composition 1 : 1 is different:[13] for this compound the QCC of antimony atoms are 1.7% larger than those for SbF_3.

The strong distortion of the SbF_3 fragment (η = 17.4%, see Table 1) in the molecule of compound **12** is likely due to changes in the geometry of the SbF_3 molecule upon complex formation.[7,10]

The QCC of Sb atoms in adduct **10** of composition 1 : 2 are 4.5% smaller than those in SbF$_3$, which is indicative of the acceptor properties of Sb atoms and is in agreement with the structure of this compound.[11] The small value of the parameter η (2.5%) indicates the highly symmetric electron density distribution around the nuclei of Sb atoms in complex **10**. No NQR spectrum of compound with DMSO of the same type was observed.[12]

We failed to detect NQR signals in adduct **13**. It is possible that the p-orbitals of Sb atoms in this compound are equally populated and, hence, there is the spherically symmetric electron density distribution in the atoms..

Compounds **11** and **12** are piezoelectrics.

Heptafluoroantimonates(III) MSb$_2$F$_7$. The ^{121,123}Sb NQR spectra of compounds MSb$_2$F$_7$ (**1**, **8**) listed in Table 1 are characteristic of antimony(III) complexes of such a composition.[8] The QCC shifts for Sb atoms in molecules **1** and **8** with respect to QCC of antimony atoms in SbF$_3$ are 2.5 to 5.3% and their signs are opposite (see Fig. 1, points *1*, *8* and *1'*, *8'*, respectively). The cation effect on the electron density distribution in molecule is well illustrated by comparing these data with the value of the QCC shift of Sb atoms for compound **16** of the same type (0.1 to 0.2%). It should be noted that the same regularity for the QCC shifts with respect to SbF$_3$ is observed at 77 K for all heptafluoroantimonates(III) MSb$_2$F$_7$ with two crystallographically nonequivalent Sb atoms in the unit cell:[8,13] the QCC of one Sb atom increases, which corresponds to the increase in the populations of the p$_z$-orbital, whereas the QCC of the other antimony atom decreases due to the increased populations of p$_x$- and p$_y$-orbitals. The values of the EFG asymmetry parameter for compounds of composition MSb$_2$F$_7$ lie in the range 4.9—9.8% (see Table 1).[8,13] The only exception is compound **8** for which $\eta = 0$ (see Table 1). This is the first example of axial symmetry of the electron density distribution around the nuclei of Sb atoms among the compounds MSb$_2$F$_7$.

Tetrafluoroantimonates(III) MSbF$_4$. The ^{121,123}Sb NQR spectra of tetrafluoroantimonates(III) MSbF$_4$ (**4**, **7**, **9**, **14**) are typical of most studied compounds of such composition[8,13] and correspond to crystallographically equivalent antimony atoms. Ten signals are observed in the ^{121,123}Sb NQR spectrum of compound **2**, which corresponds to two crystallographically nonequivalent Sb atoms in the unit cell. The ^{121,123}Sb NQR spectra of tetrafluoroantimonates(III) with ammonium[8] and aminoguanidinium[13] cations are analogous.

The quadrupole coupling constants of Sb atoms in all the studied MSbF$_4$ compounds are smaller than the QCC of antimony atoms in SbF$_3$ (see Fig. 1), and their shifts are 2—14%. This is in agreement with conventional decrease in the QCC of the central electron acceptor atom on going from the initial compound (in this case, SbF$_3$) to the complex.[3] The changes in the observed QCC values of Sb atoms are due to the changes in the geometry of the SbF$_3$ molecule upon complex formation, which is confirmed by structural data for compounds **14** and **15**.[7,10] The values of the asymmetry parameters η for tetrafluoroantimonates(III) change within the limits 4.4—26.8% (see Table 1).[8,13]

Pentafluoroantimonates(III) M$_2$SbF$_5$. The ^{121,123}Sb NQR spectra of pentafluoroantimonates(III) M$_2$SbF$_5$ (**3**, **5**) are similar to those of most antimony(III) compounds of the same composition.[8] The QCC values of Sb atoms in the molecules **3** and **5** are smaller than those in SbF$_3$ (see Fig. 1, points *3* and *5*) and their shifts are 6.3 and 4.9%, respectively. The ammonium cations in compound **18** of the same type shift the QCC of Sb atoms by 9.9%. The largest QCC shift of antimony atoms (19.7%) was observed for one of the two crystallographically nonequivalent Sb atoms in aminoguanidinium pentafluoroantimonate(III).[13] For compound 5, the EFG asymmetry parameter is equal to zero (see Table 1), which corresponds to axial symmetry of the electron density distribution around the nuclei of Sb atoms and is the only example in the group of M$_2$SbF$_5$ compounds.

Thus, the results of studying the ^{121,123}Sb NQR spectra of antimony(III) complexes obtained on the basis of SbF$_3$ and amines show that the values of the shifts of the antimony quadrupole coupling constant, which is a measure of the electron density distribution in Sb atoms, vary within the limits from 0.1 to 19.7% with respect to the QCC of Sb atoms in SbF$_3$ depending on their composition and structure and can have opposite signs. The magnitude of the asymmetry parameter that characterizes the degree of deviation of the EFG symmetry from axial symmetry varies from 0 to 26.8%.

References

1. G. K. Semin, T. A. Babushkina, and G. G. Yakobson, *Nuclear Quadrupole Resonance in Chemistry*, Keter Publishing House, Ltd., Jerusalem; J. Wiley and Sons, New York, 1975, 517 pp.
2. V. S. Grechishkin, *Yadernye kvadrupol'nye vzaimodeistviya v tverdykh telakh* [*Nuclear Quadrupole Interactions in Solids*], Nauka, Moscow, 1973, 263 pp. (in Russian).
3. L. Guibe and G. Jugie, in *Molecular Interactions*, Eds. H. Ratajczak and W. J. Orwille-Thomas, Wiley, Chichester—New York—Brisbane—Toronto, 1981, 2, 597 pp.
4. Landolt—Börnstein, *Numerical Data and Functional Relationships in Science and Technology. New Series. Group III: Crystal and Solid State Physics*, Vol. 20, *Nuclear Quadrupole Resonance Spectroscopy Data*, Subvolumes a—c, Eds. K.-H. Hellwege and A. M. Hellwege, Springer-Verlag, Berlin—Heidelberg, 1988—1990.
5. R. L. Davidovich, L. A. Zemnukhova, G. A. Fedorishcheva, V. B. Logvinova, and L. V. Teplukhina, *Ftorantimonaty organicheskikh osnovanii* [*Fluoroantimonates of Organic Bases*], Deposited in VINITI, 1989, Moscow, No. 1013-B89 (17.10.89), 16 pp. (in Russian).

6. R. L. Davidovich, V. B. Logvinova, L. A. Zemnukhova, and L. V. Teplukhina, *Koord. Khim.*, 1991, **17**, 29 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
7. R. L. Davidovich, V. B. Logvinova, L. A. Zemnukhova, A. A. Udovenko, and I. P. Kondratyuk, *Koord. Khim.*, 1991, **17**, 1342 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
8. E. A. Kravchenko, R. L. Davidovich, L. A. Zemnukhova, and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, 1974, **214**, 611 [*Dokl. Chem.*, 1974 (Engl. Transl.)].
9. L. A. Zemnukhova, R. L. Davidovich, S. I. Kuznetsov, and V. N. Rykovanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1956 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1812 (Engl. Transl.)].
10. A. Edwards, *J. Chem. Soc. A*, 1970, 2751.
11. R. L. Davidovich, V. V. Tkachev, and L. O. Atovmyan, *Koord. Khim.*, 1995, **21**, 20 [*Russ. J. Coord. Chem.*, 1995, **21** (Engl. Transl.)].
12. L. A. Zemnukhova, R. L. Davidovich, and T. L. Semenova, *Koord. Khim.*, 1983, **9**, 1369 [*Sov. J. Coord. Chem.*, 1983, **9** (Engl. Transl.)].
13. L. A. Zemnukhova, R. L. Davidovich, and G. A. Fedorishcheva, *Koord. Khim.*, 1988, **14**, 1641 [*Sov. J. Coord. Chem.*, 1988, **14** (Engl. Transl.)].

Received January 8, 1998;
in revised form March 17, 1998