ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 11, pp. 2339–2346. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © M.G. Voronkov, A.I. Albanov, T.N. Aksamentova, S.N. Adamovich, N.N. Chipanina, R.G. Mirskov, T.A. Kochina, D.V. Vrazhnov, M.Yu. Litvinov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 11, pp. 1817–1824.

Tris(2-hydroxyethyl)ammonium Salts: 2,8,9-Trihydroprotatranes

**M. G. Voronkov[a,b], A. I. Albanov[b], T. N. Aksamentova[b], S. N. Adamovich[b],
N. N. Chipanina[b], R. G. Mirskov[b], T. A. Kochina[a], D. V. Vrazhnov[a], and M. Yu. Litvinov[a]**

[a] *Grebenshchikov Institute of Chemistry of Silicates of the Russian Academy of Sciences,
nab. Makarova 2, St. Petersburg, 199034 Russia
e-mail: voronkov@isc.nw.ru*

[b] *Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: mir@irioch.irk.ru*

Received March 31, 2009

Abstract—New method of synthesis of tris(2-hydroxyethyl)ammonium salts, 2,8,9-trihydroprotatranes $X^-[HN(CH_2CH_2OH)_3]^+$, based on the reaction of tris(2-hydroxyethyl)amine (triethanolamine) with ammonium salts NH_4X (X = F, Cl, Br, I, NO_3, ClO_4) was developed. ^1H, ^{13}C, ^{15}N NMR and IR spectra of these protatranes were investigated, as well as those of their analogs with X = RCH_2COO (R = H; 2-MeC_6H_4O; 2-Me-4ClC_6H_3O; 2-MeC_6H_4S; 4-ClC_6H_4S; 4-$ClC_6H_4SO_2$; 3-IndS; 3-($PhCH_2$-IndS) prepared from the corresponding acids RCH_2COOH and triethanolamine. The parameters of IR and NMR spectra of the studied protatranes were governed by the nature of substituent X, which also determined the character of the intra and intermolecular hydrogen bonds NH···O and OH···O in the protatrane framework.

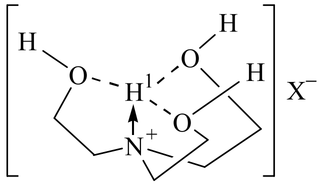
DOI: 10.1134/S1070363209110097

We developed a novel original method of synthesis of tris(2-hydroxyethyl)ammonium salts of general formula $X^-[NH(CH_2CH_2OH)_3]^+$, where X = F (**I**) Cl (**II**), Br (**III**), I (**IV**), NO_3 (**V**), ClO_4 (**VI**) based on the reaction of triethanolamine (TEA) with the corresponding ammonium salts NH_4X both in aqueous or nonaqueous medium as well as in the absence of a solvent:

$$NH_4X + N(CH_2CH_2OH)_3$$
$$\rightarrow NH_3 + X^-[NH(CH_2CH_2OH)_3]^+.$$

Reaction of TEA with NH_4F [1] proceeded in an unusual way: the product was a very viscous liquid corresponding to the composition TEA·3HF. This is not surprising since similar hydrofluorides are formed in the reaction of tertiary amines (Me_3N, Et_3N, pyridine) with HF. They have low (below 0°C) melting point and correspond to the composition $R_3N \cdot nHF$ (n = 3–6). The molecules of HF in these hydrofluorides are linked by hydrogen bonds [2].

From the XRD analysis [3–14], the triethanolammonium salts have tricyclic atrane structure **A** closed by three intramolecular trifurcate hydrogen bonds. Following Verkade [15], we called them protatranes (PA), more correctly, 2,8,9-trihydroprotatranes, of the formula:



A

The earlier known method of synthesis of PA (for example, compound **VI**) [10] was the reaction of TEA with the corresponding acid. Using this method, we have earlier first synthesized PA, which are triethanolammonium salts of carboxylic acids of general formula $RCH_2COO^-[NH(CH_2CH_2OH)_3]^+$, where R = H (**VII**); 2-MeC_6H_4O (**VIII**); 2-Me-4ClC_6H_3O (**IX**); 2-MeC_6H_4S (**X**); 4-ClC_6H_4S (**XI**); 4-$ClC_6H_4SO_2$ (**XII**); 3-IndS (**XIII**); 3-($PhCH_2$-IndS) (**XIV**) [16–20].

Compounds of this type are not only of theoretical but also of practical interest since they have unique biological activity substantially exceeding or different from the action of the starting biologically active acids.

Such compounds include, first of all, triethanolammonium salts of 2-methylphenoxyacetic acid **VIII** , “trecrezan” preparation, which have already found wide application in medicine [3, 16–33], and also 2-methyl-4-chlorophenoxyacetic acid (**IX**), “chlorocrezacin” [17, 31], etc. Under the name “crezacin,” trecrezan is successfully used in agriculture (in plant-growing, cattle-breeding, breeding of useful insects) [34–38]. It was also shown to be a stimulator of microbiological synthesis [37].

Crystal structure of PA was first established by the XRD method during our studies of their biological activity [3, 4]. Later on, the crystal structure of PA with X = SH [5], Cl [5], Br [6–8], NO_3 [9], ClO_4 [10], $HSeO_3$ [11], BPh_4 [12], 2-(2,3-$Me_2C_6H_3$)NHC_6H_4COO [13], 2-$HCOC_6H_4COO$ [14] was examined. Their crystals are formed by layers of cations and anions linked by hydrogen bonds. Inside each layer, the cation and anion are linked by hydrogen bridges $O–H\cdots X^-$. In PA containing the anion of functionally substituted carboxylic acid, the bonding with the anion can be accomplished by means of the functional group.

The protatrane cation $[HN(CH_2CH_2OH)_3]^+$ has tricyclic structure with the N→H directed inward the protatrane framework. The length of this bond depends on the nature of the anion and varies from 0.88 Å (X = Cl) [5] to 1.01 Å (X = 4-$ClC_6H_4SCH_2COO$) [4]. For comparison, the N–H bond length in organic ammonium salts R_3NHX lies within 0.87–0.89Å [2]. Three oxygen atoms in the cations of PA form the surrounding of the hydrogen atom of NH group resulting in trifurcate hydrogen bond.

The effect of the anion’s nature on the protatrane cation is first studied by us using the methods of NMR and IR spectroscopy.

The resonance signals of the NCH_2 and OCH_2 groups in the ^1H NMR spectra of solutions of all PA in DMSO-d_6 are broadened, and their fine structure cannot be observed. Only at a low concentration of the solutions (when the intensity of the signals are comparable with those of the residual protons of DMSO-d_6) the signals appear as multiplets: triplet of NCH_2 ($^3J_{HH}$ 4.7 Hz), doublet of triplets of OCH_2 (^3J 5.0, 4.7 Hz), triplet of OH. In all ^1H NMR spectra separate signals are observed which belong to the traces of water in DMSO-d_6 at 3.48–3.63 ppm, OH groups at 4.4–5.3 ppm, and NH groups at 8.5–8.7 ppm. The data of Table 1 suggest that the chemical shifts of protons of the NCH_2 and OCH_2 groups are shifted downfield relative to the initial TEA by 0.76 and 0.34 ppm, respectively. ^{13}C NMR chemical shifts of the protatrane cation in the spectra of the studied PA are displaced upfield relative to TEA by 2 ppm for the NCH_2 and by 4 ppm for the OCH_2 group. The ^{13}C NMR chemical shifts of these groups in the spectra of PA **II–VI** are very close.

Protonation of nitrogen atom in tertiary amines is known to be followed by a downfield shift of the ^{15}N resonance (4–16 ppm) [39]. The chemical shifts in the ^{15}N NMR spectra of PA **II–VI** are shifted downfield relative to TEA by 20 ppm, which is indicative of the positive charge on the nitrogen atom.

In the ^1H, ^{13}C, ^{15}N NMR spectra of PA **VII–XIV** , which are the derivatives of carboxylic acids (Table 2), chemical shifts of the NCH_2 and OCH_2 groups show no regular dependence on the nature of substituent RCH_2. The internal chemical shift (the difference between the chemical shifts of these groups) is 0.5–0.6 ppm. The signals of the carbon atoms of the protatrane cation are shifted upfield by 2.2–2.4 ppm on going from acetate **VII** to PA (**IX**). The ^{15}N NMR chemical shift in the spectra of PA **VII–XIV** is displaced downfield relative to free TEA, on the average, by 14 ppm (–354.5 ppm). Moreover, variation of this chemical shift in the spectra of PA **VII–XIV**

Table 1. Parameters of ^1H, ^{13}C, ^{15}N NMR spectra of PA $[HN(CH_2CH_2OH)_3]^+X^-$ (**II–VI**) and triethanolamine (TEA) in DMSO-d_6

Comp. no.	X^-	pK_a of HX [21]	δ_H, ppm				δ_C, ppm		δ_N, ppm
			NCH_2	OCH_2	OH	NH	NCH_2	OCH_2	
II	Cl	–	3.29	3.75	5.35	9.31	55.46	55.49	–330.07
III	Br	–9	3.27	3.70	5.13	7.27	55.30	55.38	–330.71
IV	I	–11	3.28	3.72	5.18	8.7	55.24	55.24	–331.57
V	NO_3	–1.64	3.29	3.74	5.30	8.7	55.38	55.43	–331.54
VI	ClO_4	–8	3.27	3.73	5.24	8.5	55.51	55.47	–332.17
TEA	–	–	2.52	3.39	4.44	–	57.42	59.54	–354.50

Table 2. ^{1}H, ^{13}C, ^{15}N NMR spectra of PA **VII–XIV** (20% solutions in D_2O, 25°C)

Comp. no.	δ_H, ppm					δ_C, ppm[a]					δ_N, ppm
	CH_2N	CH_2O	CH_2CO	Ar; CH_2Ph	Me	Me	CH_2N	CH_2O	CH_2CO	CO	
VII[b]	3.25	3.85	–	–	1.94	23.21	57.01	57.46	–	179	–341.4
VIII	3.42	3.92	4.48	6.80(H^6) 6.95(H^4) 7.21(H^5) 7.25(H^3)	2.26	15.51	54.89	55.14	66.94	177.00	–339.0
IX	3.44	3.93	4.45	6.70(H^6) 7.11(H^5) 7.18(H^3)	2.21	15.33	54.77	55.03	66.98	176.51	–338.6
X	3.41	3.9	3.63	7.16(H^4) 7.24($H^{3,5,6}$)	2.34	19.23	54.91	55.16	37.13	176.88	–340.5
XI	3.46	3.94	3.64	7.30($H^{2,6}$) 7.35($H^{3,5}$)	–	–	54.93	55.19	38.15	176.71	–338.9
XII	3.48	3.95	4.19	7.66($H^{2,6}$) 7.89($H^{3,5}$)	–	–	54.94	55.21	62.90	167.63	–338.9
XIII	3.36	3.88	3.38	7.22–7.30 ($H^{6,7}$) 7.52(H^5) 7.51(H^2) 7.79(H^8)	–	–	54.86	55.11	41.43	178.16	–339.1
XIV	3.19	3.78	3.41	4.66(CH_2) 6.66($H^{6,7}$) 6,74($H^{5,o}$) 6.78(H^m) 6.89(H^p) 7.20(H^2) 7.64(H^8)	–	–	55.08	55.08	41.96	177.20	–340.1

[a] Chemical sifts of aromatic carbons: **VIII**: 111.39(C^6); 130.90(C^3); 121.05(C^4); 156.02(C^1); 126.78(C^2); 127(C^5). **IX**: 112.31 (C^6); 124.64 (C^5); 126.09(C^2); 128.66(C^4); 130.08(C^3); 154.61(C^1). **X**: 125.72(C^4); 126.31(C^5); 126.76(C^6); 130.05(C^3); 135.26(C^2); 136.63(C^1). **XI**: 128.97($C^{3,5}$); 129.33($C^{2,6}$); 131.25(C^1); 134.68(C^4). **XII**: 129.54($C^{3,5}$); 129.59($C^{2,6}$); 136.15(C^1); 140.58(C^4). **XIII**: 102.88(C^3); 112.21 (C^8); 118.59(C^6); 120.17(C^5); 122.40(C^7); 128.30(C^4); 130.67(C^2); 136.15(C^9). **XIV**: 103.46(C^3); 110.36(C^8); 119.18(C^6); 120.17(C^5); 122.17(C^7); 126.61(C^o); 127.28(C^4); 128.40(C^m); 129.41(C^p); 133.44(C^2); 136.13(C^9); 137.09(C^i). [b] In CD_3OD.

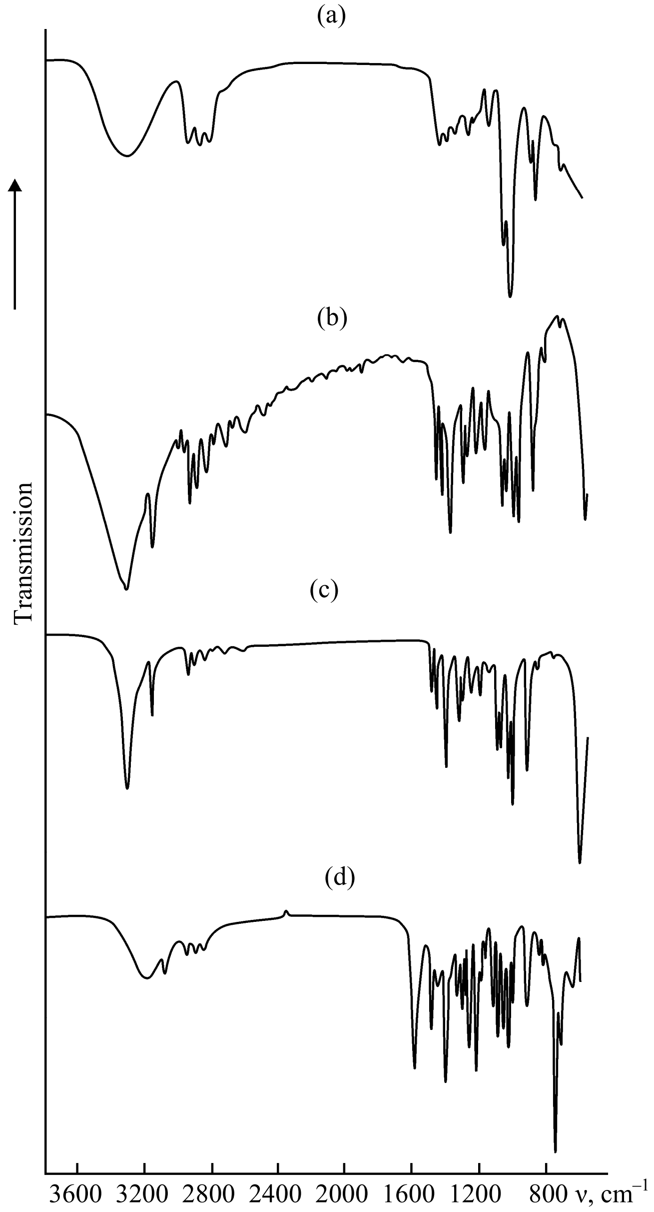
allows to rank them in the following sequence, which corresponds to the strength of acids RCH_2COOH (Table 2): **VII** < **X** < **XIV** < **XIII** < **VIII** < **XI** = **XII** < **IX**.

The ^{15}N NMR chemical shift of PA **II–VI** , which are derivatives of inorganic acids, is more displaced downfield than that of their organic analogs **VII–XIV**. This is due to stronger protonating ability of inorganic acids HX, precursors of PA **II–VI** . Unlike the observed for PA **VII–XIV** dependence of δ_N on the strength of the carboxylic acid, the ^{15}N NMR chemical shift of PA derived from inorganic acids (330–332 ppm) is practically independent on the strength of acid HX [40] (Table 1).

Apparently, for strong acids this dependence is leveled out due to the presence of H-bonds between their anions and the protatrane cation.

In the IR spectroscopic study of crystalline PA **II–VI** in comparison with TEA we have investigated their spectra of absorption and FTIR (see the figure) in order to exclude the effect of pressing of compounds in KBr pellets. In the absorption IR spectra (KBr pellets) of these PA a wide ammonium band $\nu(N^+H)$ is observed with a number of separate maxima in the range of 2500–3000 cm^{-1}. In the FTIR spectra of PA **II–VI** the intensity of this band is substantially lower relative to the absorption spectra. In the spectrum of liquid TEA the strong band at 3311 cm^{-1} of half-width

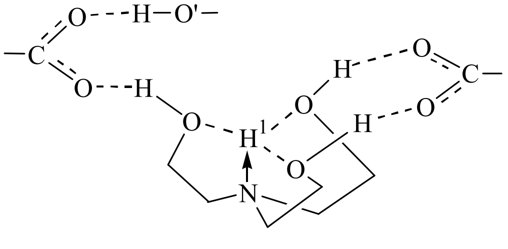
$\Delta\nu_{1/2}$ ~400 cm^{-1} corresponds to the stretching vibrations of the OH groups involved in intramolecular hydrogen bonds. In the spectra of chloro- (**II**), bromo- (**III**) and iodoprotatranes (**IV**) the strong ν(OH) band is much narrower than in TEA itself ($\Delta\nu_{1/2}$ ~25 cm^{-1}). This band is due to vibrations of the three hydroxy groups of the cation whose oxygen atoms form intramolecular hydrogen bonds with the endocyclic hydrogen atom of the N^+H group whereas their hydrogen atoms form hydrogen bonds with anions **X**. The form of this band is defined by high symmetry of the molecules of these salts. The decrease in the frequency in its maximum in the spectra of protatranes from 3380 (**IV**) to 3346 (**III**) and further to 3306 cm^{-1} (**I**) is due to an increase in the strength of the formed O–H···X bonds with the electronegativity of the halogen atom (I < Br < Cl). In the spectrum of PA **V** (X = NO_3), three ν(OH) bands are present (3440, 3400, and 3255 cm^{-1}) corresponding to its structure with different in strength hydrogen bonds between the OH groups and the oxygen atoms of the NO_3 anion. Three bands at 3480, 3350 and 3276 cm^{-1} in the spectrum of PA **VI** are also due to vibrations of the OH groups involved in the formation of hydrogen bonds with ClO_4^- anion.



FTIR spectra: (a) TEA, (b) $TEAH^+Cl^-$ (**II**) (absorption spectrum in KBr), (c) $TEAH^+Cl^-$ (**II**), and (d) $TEAH^+O\cdot(O)CCH_2OC_6H_4CH_3$ (**VII**).

The bands of TEA observed in the range of 1500–700 cm^{-1} of the IR spectrum are due to the stretching vibrations of the C–C, C–O, and C–N bonds and the bending vibrations of the C–H and O–H bonds [41]. IR spectra of isostructural PA **II–IV** in this range are similar and differ only in the range 1100–900 cm^{-1} by the ratio of intensities of separate bands having the same frequencies in their maxima. They differ from the spectrum of TEA mainly by the presence of an intense band at 1402 cm^{-1} caused by mixed bending vibrations of the CH, OH and N^+H groups in the molecules. In the spectra of these salts the bands of bending vibrations of the methylene groups are shifted to high-frequencies up to 1490–1400 cm^{-1} relative to TEA (1450–1360 cm^{-1}). The band of stretching vibrations of the C–N bonds which in the spectrum of TEA appears at 1152 cm^{-1} is shifted in the spectra of PA **II–IV** to 1090 cm^{-1}, and the band of C–C stretching vibrations at 1067 cm^{-1} is split in two components. The most intensive band ν(C–O) in the spectrum of TEA at 1030 cm^{-1} is also split in two components with maxima at ~1030 and ~1000 cm^{-1}. The spectra of PA **V** and **VI** contain strong bands at 1390 and 1060 cm^{-1}, respectively, corresponding to vibrations of anions NO_3^- and ClO_4^- [41]. Changes of the bands in these spectra as compared with TEA are identical to those observed in the spectra of PA **II–IV** . This is indicative of similarity of their structure in spite of different strength of hydrogen bonds.

In the FTIR spectra of protatranes **VII–XIV** containing organic anions, as well as in those of PA **II–VI** , the vibration band $\nu(N^+H)$ is weaker than in the absorption spectra (see the figure). The interaction between the cations and anions in these molecules affects the frequencies of the symmetrical and asymmetrical vibrations $\nu(COO)^-$, as well as ν(OH) vibrations (Table 3). This was demonstrated earlier on the example of PA **VIII** and *O*-hydrometalloatranes [42], for which the difference between the corresponding frequencies of the negatively charged carboxylic group Δν = ν(C=O) – ν(C–O) was used to study structural features of the molecules and their complexes [43]. Thus, in the spectrum of 2-methylphenoxyacetic acid the doublet band of the C=O group stretching vibrations with maxima at 1737, 1702 cm^{-1} and a wide band ν(OH) in the range 3000–2500 cm^{-1} are due to participation of the corresponding groups in the hydrogen bonds OH···O=C forming its chain and cyclic self-associates. The distances between the carbon and oxygen atoms of the acetate group COO^- of this acid in the molecule of PA **VIII** are very similar (1.265 and 1.238 Å). This suggests uniform charge distribution between the oxygen atoms [3]. In the IR spectrum the bands of stretching vibrations of the carboxylate ion of molecule **VII** appear at 1590 and 1404 cm^{-1}, and the value of Δν 186 cm^{-1} corresponds to structure **B**, where each cation, judged from the XRD data [3], is connected with two oppositely charged carboxylate groups by hydrogen bond OH···O.



B

Table 3. Stretching vibration frequencies of the carboxylic and hydroxy groups in the FTIR spectra of PA **VII–XIV** $[\text{HN(CH}_2\text{CH}_2\text{OH)}_3]^+\text{X}^-$ and values of Δν = ν(C=O) – ν(C–O)

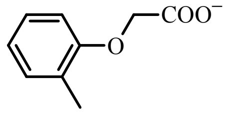
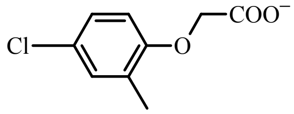
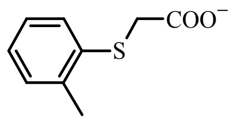
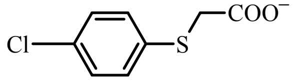
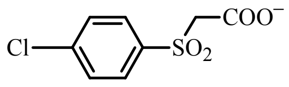
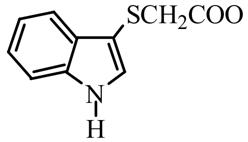
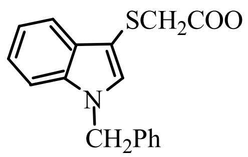
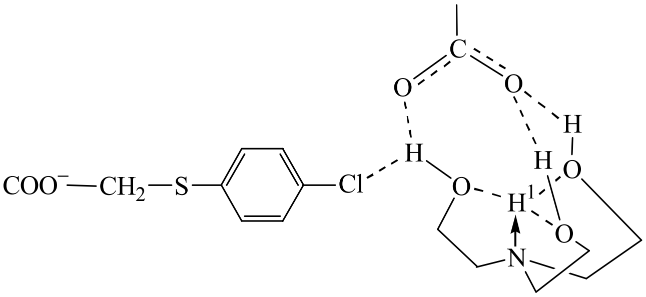
Comp. no.	X^-	ν(COO^-), cm^{-1}		Δν, cm^{-1}	ν(OH), cm^{-1}
VII	MeCOO	1574	1400	174	3133
VIII		1590	1404	186	3182
IX		1606	1397	209	3156
X		1589	1368	221	3177
XI		1588	1362	226	3150
XII		1620	1380	240	3190
XIII		1588	1367	221	3181
XIV		1589	1364	225	3173

Table 4. Elemental analysis of PA **I–VI** $[HN(CH_2CH_2OH)_3]^+X^-$

Comp. no.	X^-	Elemental analysis, %		mp, °C
		found	calculated	
I	F	C 32.55; H 7.61; F 26.58; N 7.01	(for adduct TEA·3HF) C 34.45; H 8.60; F 27.22; N 6.76	–
II	Cl	C 35.92; H 8.01; Cl 19.20; N 7.46	C 38.82; H 8.69; Cl 19.10; N 7.54	160
III	Br	C 31.38; H 6.73; Br 36.20; N 6.42	C 31.32; H 7.01; Br 34.73; N 6.09	180
IV	I	C 25.94; H 5.83; I 47.42; N 5.02	C 26.01; H 5.82; I 45.80; N 5.05	125
V	NO_3	C 31.65; H 7.27; N 12.13	C 33.96; H 7.60; N 13.20	75
VI	ClO_4	C 26.33; H 6.21; Cl 15.11; N 5.46	C 28.87; H, 6.46; Cl 14.20; N 5.61	250 (decomp)

Similar structure, apparently, has PA **VII** with X = CH_3COO, for which the value of Δν(COO) in the IR spectrum is 174 cm^{-1} .

In the spectra of PA **IX–XIV** the values of Δν (COO) (209–240 cm^{-1}) are higher than in PA **VII**, **VIII**, being characteristic of the same structure **C**, established for PA **XI** by the XRD method [4]. The oxygen atoms of the carboxylic group in these PA form nonequivalent H-bonds: one with two OH groups of the cation, and another, with that OH group, whose hydrogen atom is also involved in the OH···Cl bonding with the second molecule of the anion.



C

A wide vibration band ν(OH) in the IR spectra of PA **VII–XIV** is located at lower frequencies (3130–3190 cm^{-1}) than that of PA **II–VI** containing an inorganic anion X^-. This is indicative of a larger strength of hydrogen bonds of the hydroxy groups with the carboxylate anion. The largest strength of this bond in PA **VII** corresponds to the lowest frequency of 3133 cm^{-1} .

The shifts of vibration bands of TEA in the range 1500–700 cm^{-1} in the spectra of PA **VII–XIV** are similar to those observed in the spectra of PA **II–VI** containing inorganic anions X^-. This fact points to the similarity of structure of the cation in all PA **II–XIV** regardless of the character of hydrogen bonds formed by its OH groups.

EXPERIMENTAL

^1H, ^{13}C, ^{15}N NMR spectra of solutions of PA **II–XIV** in DMSO-d_6 were registered on a Bruker DPX 400 spectrometer (400.13, 100.61 and 40.56 MHz, respectively). IR absorption spectra (KBr pellets) and FTIR spectra were taken on a Varian 3100 FT–IR spectrophotometer.

PA **II** was prepared by the reaction of TEA with saturated boiling aqueous solution of NH_4Cl (molar ratio of the reagents 1:1) until the evolution of ammonia ceased. After evaporation of water, the crystals of PA **II** were kept for one more day over P_2O_5 in a vacuum. The yield of PA **II** was quantitative. Note that with butanol as a solvent as well as under solvent-free conditions (finely dispersed powder of NH_4Cl was heated with TEA on a water bath) the yield of PA **II** also exceeded 95%.

PA **I** [1], **III–V** were synthesized similarly by the reaction of TEA with the corresponding ammonium salt. The elemental composition and the properties of PA **I–VI** are given in Table 4.

Compounds **VII–XIV** were synthesized by the reaction of TEA with acetic acid, 2-methylphenoxy-, 2-methyl-4-chlorophenoxy-, 2-methylphenylsulfanyl-, 4-chlorophenylsulfanyl-, 4-chlorophenylsulfanyl-, indol-3-ylsulfanyl-, and 1-benzylindol-3-ylsulfanylacetic acids [16–20].

ACKNOWLEDGMENTS

The work was performed with a financial support from the Council on Grants of the President of RF (grant no. NSh-255.2008.3) and the Program of Basic Research of Presidium RAS “Elaboration of methods of preparation of chemical substances and new materials,” 2009.

REFERENCES

1. Voronkov, M.G., Kochina, T.A., Vrazhnov, D.V., and Litvinov, M.Yu., *Russ. J. Gen. Chem.,* 2008, vol. 78, no. 11, p. 2160.
2. Wiechert, D., Mootz, D., Franz, R., and Siegmund, G., *Chem. Eur. J.*, 1998, vol. 4, no. 6, p. 1043.
3. Starova, G.L., Frank-Kamenetskaya, O.V., Fundamenskii, V.S., Semenova, N.V., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR,* 1981, vol. 260, no. 4, p. 888.
4. Sklover, V.E., Gridunova, G.V., Struchkov, Yu.T., Voronkov, M.G., Kryukova, Yu.I., and Mirskova, A.N., *Dokl. Akad. Nauk SSSR*, 1983, vol. 269, no. 2, p. 387.
5. Mootz, D., Brodalla, D., and Wiebke, M., *Acta Cryst., Sect. C*, 1990, vol. 46, p. 797.
6. Párkányi, L., Hencsei, P., Nyulászi, L., and Baryshok, V.P., *Kemiai Közlemenyek*, 1991, vol. 73, p. 279.
7. Párkányi, L., Hencsei, P., and Nyulászi, L., *J. Mol. Struct*., 1996, vol. 377, no. 1, p. 27.
8. Yilmaz, V.T., Icbudak, H., Olmez, H., and Howie, R.A., *Turk, J. Chem*., 1996, vol. 20, p. 69.
9. Bracuti, A.J., *Crystallogr. Spectrosc. Res*., 1993, vol. 23, p. 669.
10. Naiini, A.A., Pinkas, J., Plass, W., Young, V.G., Jr., and Verkade, J.G., *Inorg. Chem*., 1994, vol. 33, no. 10, p. 2137.
11. Lukevics, E., Arsenyan, P., Shestakova, I., Domracheva, I., Kanepe I, Belyakov, S., Popelis, J., and Pudova, O., *Appl. Organometal. Chem*., 2002, vol. 16, no. 4, p. 228.
12. Steiner, T., Schreurs, A.M.M., Lutz, M., and Kroon, J., *New J. Chem*., 2001, vol. 25, no. 1, p. 174.
13. Fang, L., Numajiri, S., Kobayashi, D., Ueda, H., Nakayama, K., Miyamae, H., and Morimoto, Y., *J. Pharm. Sci*., 2004, vol. 93, p. 144.
14. Odabasoglu, M. and Buyukgungor, O., *Acta Crystallogr., Sect. E: Struct. Rep. Online*., 2007, vol. 63, p. 186.
15. Verkade, J., *Coord. Chem. Rev*., 1994, vol. 137, p. 233.
16. Voronkov, M.G., D’yakov, V.M., Stetsenko, N.A, Prokhoda, E.F., Aurtir’s Certificate no. 1954859, 1973; *Byull. Iizobret.,* 1976, no., 20.
17. Sof’ina, Z.P., Voronkov, M.G., D’yakov, V.M., Semenova, N.V., Platonova, A.T., Peretolchina, N.M., Lesnaya, N.A, and Smetankina, O.Z., *Pharm. Chem. J.*, 1978, vol. 12, no. 4, p. 489.
18. Levkovskaya, G.G., Guseva, S.A., Kazimirovskaya, V.B., Kholdeeva, L.N., Voronkov, M.G., and Mirskova, A.N., *Pharm. Chem. J*., 1986, vol., 20, no. 3, p. 180.
19. Mirskova, A.N., Levkovskaya, G.G., and Tizenberg, G.M., RF Patent no. 2034540, 1992; *Byull. Izobret*., 1992, no. 3.
20. Levkovskaya, G.G., Rudyakova, E.V., and Mirskova, A.N., *Russ. J. Org. Chem*., 2002, vol. 38, no. 11, p. 1641.
21. Nefedova, T.V., Kazimirovskaya, V.B., Levkovskaya, G.G., Bryuzgin, A.A., Guseva, S.A., Mirskova, A.N., and Voronkov, M.G., *Pharm. Chem. J*., 1986, vol. 20, no. 3, p. 176.
22. Nefedova, T.V., Kubatiev, A.A., Martynov, A.V., Guseva, S.A., Kazimirovskaya, V.B., Mirskova, A.N., Novikova, N.V., Lobanova, E.G., Nepsha, V.D., Moskvitina, L.T., and Voronkov, M.G., *Pharm. Chem. J*., 1987, vol. 21, no. 9, p. 648.
23. Nefedova, T.V., Kubatiev, A.A., Kazimirovskaya, V.B., Chernyakhovskaya, B.I., Mirskova, A.N., Guseva, S.A., Levkovskaya, G.G., and Voronkov, M.G., *Pharm. Chem. J*., 1988, vol. 22, no. 10, p. 759.
24. Kazimirovskaya, V.B., Nefedova, T.V., Annenkova, V.M., Annenkova, V.Z., and Voronkov, M.G., *Pharm. Chem. J*., 1989, vol. 23, no. 7, p. 581.
25. Nefedova, T.V., Boiko, M.I., Kazimirovskaya, V.B., Ivanov, A.A., Levkovskaya, G.G., Guseva, S.A., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1990, vol. 310, no. 5, p. 1256.
26. Nefedova, T.V., Korytov, L.I., Oshchepkova, O.M., Malyshev, V.V., Vvedenskii, V.Yu., Kolbaseeva, O.V., Noskova, L.K., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1994, vol. 334, no. 1, p. 115.
27. Nefedova, T.V., Oshchepkova, O.M., Malyshev, V.V., Mirskova, A.N., Levkovskaya, G.G., Vvedenskii, V.Yu., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1995, vol. 344, no. 5, p. 700.
28. Voronkov, M.G., Gubanova, L.I., D’yakov, V.M., Kazimirovskaya, V.B., and Platonova, A.T., Author’s Certificate no. 944286, 1979; *Byull. Izobret*., 1982, no. 15.
29. Voronkov, M.G. and Rasulov, M.M., *Pharm. Chem. J*., 2007, vol. 41, no. 1, p. 1.
30. Voronkov, M.G., Kolesnikova, O.P., Rasulov, M.M., and Mirskova, A.N., *Pharm. Chem. J*., 2007, vol. 41, no. 5, p. 244.
31. Voronkov, M.G., Mirskova, A.N., and Levkovskaya, G.G., *Dokl. Biol. Sci.,* 2002, vol. 386, p. 404.
32. Shabanov, P.D., Ganapol’skii, V.P., Zarubin, I.V., Zhumasheva, A.B., and Elistratov, A.A., *Neuroscience*, 2006, no. 3(5), p. 43.
33. Kolesnikova, O.P., Mirskova, A.N., Adamovich, S.N., Mirskov, R.G., Kudaeva, O.T., and Voronkov, M.G., *Dokl. Biol. Sci*., 2009, vol. 425, p. 107.
34. Khankhodzhaeva, D.A. and Voronkov, M.G., *Dokl. Akad. Nauk SSSR*, 1993, vol. 333, no. 1, p. 124.
35. Voronkov, M.G., Dolmaa, G., Tserenpil, S., Ugtakhbayar, O., and Chimidtsogzol, A., *Dokl. Biol. Sci*., 2005, vol. 404, p. 367.
36. Voronkov, M.G., Dyban, A.P., D’yakov, V.M., and Simbirtsev, N.L., *Dokl. Biol. Sci*., 1999, vol. 364, p. 23.

37. Voronkov, M.G., Gorbalinskii, V.A., and D'yakov, V.M., *Dokl. Biochemistry*, 1999, vol. 369, p., 195.
38. Makarova, L.E., Borovskii, G.B., Bulatova, A.M., Sokolova, M.G., Voronkov, M.G., and Mirskova, A.N., *Agrokhimiya*, 2006, no. 10, p. 1.
39. Witanowski, M., Stefaniak, L., and Webb, G.A., *Nitrogen NMR Spectroscopy. In: Annual reports on NMR spectroscopy*, Webb, G.A., Ed., London: Academic Press, 1981, vol. 11B, p. 33.
40. Albert, A. and Sergeant, E.P., *Ionization Constants of Acids and Bases*, New York: Wiley, 1962
41. Brannon, D.G., Morrison, R.H., Hall, J.L., Humphrey, G.L., and Zimmerman, D.N., *J. Inorg. Nucl. Chem*., 1971, vol. 33, no. 4, p. 981.
42. Adamovich, S.N., Kuznetsova, G.A., Kashik, T.V., Zykova, E.V., Chipanina, N.N., Aksamentova, T.N., Mirskov, R.G., Mirskova, A.N., and Voronkov, M.G., *Russ. J. Gen. Chem.,* 2008, vol. 78, no. 9, p. 1754.
43. Deakon, G.B. and Phillips, R.J., *Coord. Chem. Rev*., 1980, vol. 33, p. 227.