COMPLEX SALTS OF SOME HYDROXY AND HALO DERIVATIVES OF PIPERIDINE AND PYRROLIDINE WITH 7,7,8,8-TETRACYANOQUINODIMETHANE

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It is known that 7,7,8,8-tetracyanoquinodimethane (TCNQ) is capable of entering into the composition of complex anions, which form highly conductive salts with many organic cations [1-8]. In [4-7] the theory is expressed that a correlation exists between the polarizability of the cation and the conductivity of the solid salt. It is also assumed that the conductivity depends on the packing of the molecules in the crystal. In view of this it seemed interesting to synthesize a group of salts containing complex anions, in the cations of which conjugation would be absent, but functional groups would be present, which would assure the possibility of intermolecular reactions.

In this paper is reported the synthesis of such complex compounds, containing hydroxy and halo derivatives of the piperidinium and pyrrolidinium ions as the cations. The simple salts of TCNQ (Table 1) were obtained by the exchange reaction of the lithium salt of TCNQ with the quaternary salts of the corresponding bases [3].

Two methods were used to synthesize the complex salts (Table 2): recrystallization of the appropriate simple salts in the presence of equimolecular amounts of TCNQ (method A), and reaction of tertiary bases with TCNQ (method B).

It is known that the ratios of the optical densities of the bands at 395, 420, and 842 nm (D_{420}/D_{842} for the simple salts, and D_{395}/D_{842} for the complex salts) can serve as a useful criterion for estimating the composition of TCNQ salts [5]. The UV and IR spectra were taken for the obtained compounds. In most cases the calculated ratios of the optical densities at λ_{max} 420 and 395 nm to λ_{max} 842 nm (see Tables 1 and 2) are in good agreement with the postulated composition of the complexes. The absence of color for solutions of complexes (VII) and (XI) in acetonitrile and the absorption bands in the UV spectrum at λ_{max} 842 nm both apparently testify to the fact that the given complexes do not dissociate in solution.

The characteristic for the IR spectra of the complex salts of TCNQ is a broadening of the absorption band of the C ≡ N group, and a splitting and shift of this band toward longer wavelengths when compared with the neutral TCNQ molecule, which is in agreement with the literature data [3, 7].

The data on the magnetic and electrical properties of the synthesized compounds will be reported separately.

EXPERIMENTAL

β,β'-Di-(1-methyl-3-hydroxypiperidinium)diethyl Ether Dibromide (I). A mixture of 5.35 of β,β'-dibromodiethyl ether [9] and 5.3 g of 1-methyl-3-hydroxypiperidine [10] in 20 ml of isopropyl alcohol was heated at 30°C for several days. We obtained 3.36 g (31.60%) of (I) (from isopropyl alcohol); mp 207-209°C. Found: C 41.54; H 7.70; N 5.93%. $C_{16}H_{34}Br_2N_2O_3$. Calculated: C 41.57; H 7.36; N 6.05%.

1-Methyl-1-bromomethylpiperidinium Bromide (II). A mixture of 8.46 g of dibromomethane and 8.9 g of 1-methylpiperidine in 20 ml of isopropyl alcohol was heated at 40-50°C for 3 days. The obtained crystals

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TABLE 1. Simple Salts of TCNQ from Hydroxy and Bromo Derivatives of Piperidines and Pyrrolidines

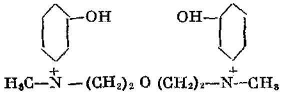
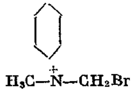
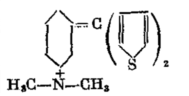
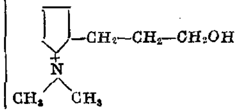
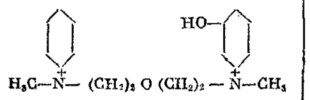
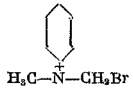
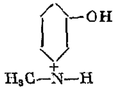
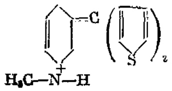
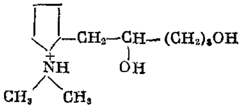
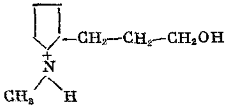
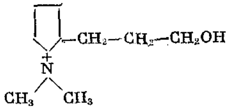
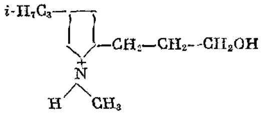
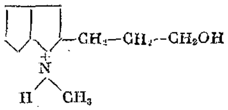
Compound	Cation	Solvent	mp, °C (decompn.)	Yield, %	Found, %			Empirical formula	Calc., %			D_{420}/D_{842}
					C	H	N		C	H	N	
VI		Ethanol	175—200	53	67,25	5,56	19,22	$C_{40}H_{42}N_{10}O_3$	67,58	5,95	19,72	0,59
VII		Methanol	183—185	50,4	57,50	5,08	17,68	$C_{19}H_{19}BrN_5$	57,37	4,81	17,71	—
VIII		The same	174—177	36	67,81	4,75	13,80	$C_{28}H_{24}N_5S_2$	67,98	4,89	14,15	0,56
IX		Ethanol	195—197	72	69,98	7,08	19,30	$C_{21}H_{24}N_5O$	69,58	6,67	19,39	—

TABLE 2. Complex Salts of TCNQ

Compound	Cation	Method and solvent	mp, °C (decompn.)	Yield, %	Found, %			Empirical formula	Calc., %			D_{395}/D_{842}
					C	H	N		C	H	N	
X		A Acetonitrile	350—370	62	68,33	4,82	21,73	$C_{52}H_{46}N_{14}O_3$	68,25	5,06	21,43	1,3
XI		The same	204—220	30	61,99	3,98	21,02	$C_{31}H_{23}BrN_9$	61,89	3,86	20,96	—
XII		B Chloroform-acetonitrile	200—213	73	68,45	4,59	23,93	$C_{30}H_{22}N_9O$	68,64	4,17	24,08	2
XIII		B Acetonitrile	179—183	36	68,30	3,81	18,55	$C_{39}H_{26}N_9S_2$	68,40	3,83	18,41	2,2
XIV		The same	166—172	27	69,30	5,16	20,07	$C_{36}H_{34}N_9O_2$	69,23	5,44	20,19	2,4
XV		B THF	165—169	28	69,22	4,82	22,20	$C_{32}H_{26}N_9O$	69,54	4,72	22,82	1,6
XVI		A THF	203—205	65	70,25	5,10	22,17	$C_{33}H_{28}N_9O$	69,96	4,99	22,27	—
XVII		B THF	162—165	34	70,60	5,10	21,04	$C_{35}H_{32}N_9O$	70,69	5,42	21,16	1,9
XVIII		B Acetonitrile	177—178	32	70,81	5,46	21,29	$C_{35}H_{30}N_9O$	70,89	5,11	21,28	1,9

were filtered and dried over P_2O_5 to give 6.5 g (38%) of (II); mp 70-71°C (acetone). Found: C 31.00; H 5.77; N 5.51%. $C_7H_{15}Br_2N$. Calculated: C 30.77; H 5.53; N 5.149%.

(1,1-Dimethylpiperididen–3-ium)–di-(α-thienyl)methane Iodide (III). To 1.7 g of 1-methyl–3-piperidyl–di-(α-thienyl)methane [11] in 10 ml of absolute ether was added 1.6 g of methyl iodide in 5 ml of absolute ether. The obtained pale yellow precipitate of (III) was filtered and dried over P_2O_5. We obtained 2 g (80%) of (III) with mp 213-214°C (ethanol). Found: C 46.30; H 4.40; N 3.53%. $C_{16}H_{20}INS_2$. Calculated: C 46.03; H 4.83; N 3.73%.

1,1-Dimethyl–2-γ-hydroxypropylpyrrolidinium Iodide (IV). To a solution of 1.065 g of 1-(1-methyl–2-pyrrolidyl)–3-propanol [12] in 3.2 ml of absolute benzene was added a solution of 3.2 g of methyl iodide in 10 ml of absolute benzene. The obtained crystals of (IV) were filtered and washed with absolute benzene. We obtained 1.84 g (87%) of (IV) with mp 106°C (THF–isobutyl alcohol). Found: C 37.64; H 7.08; N 4.90%. $C_9H_{20}INO$. Calculated: C 37.89; H 7.07; N 4.90%.

1-(1-Dimethylamino–2-cyclopentyl)–2,5-pentanediol (V). To a solution of 7.72 g of 1-(1-amino–2-cyclopentyl)–2,5-pentanediol were added, with cooling, 15 ml of 80% formic acid and 10 ml of 35% formaldehyde solution. The mixture was heated on the water bath for 10 h in the presence of 1.2 ml of HCl solution. The solvent was distilled off, and the residue was treated with 50% KOH solution. The amine layer was separated, while the aqueous layer was extracted with ether. The ether extracts were combined with the amine and dried over granulated KOH. The ether was distilled off. Distillation of the residue in vacuo gave 4.5 g (52%) of (V); bp 161-163°C (1 mm); n_D^{20} 1.4874. Found: C 66.70; H 12.00; N 6.92%. $C_{12}H_{25}NO_2$. Calculated: C 66.96; H 11.62; N 6.53%.

Synthesis of Simple Salts of TCNQ Anion-Radical. Diethyl Ether of β,β'-Di-(1-methyl–3-hydroxypiperidinium) $(TCNQ^{\bar{\cdot}})_2$ (VI). To a filtered solution of 0.2 g of Li TCNQ in 50 ml of boiling absolute ethyl alcohol was added a boiling solution of 0.23 g of (I). The mixture was let stand at room temperature for 3 h. The obtained bluish-black needle crystals were filtered and dried in a vacuum-desiccator over P_2O_5. We obtained 0.18 g (53%) of (VI); mp 175-200°C.

In a similar manner were obtained: (VII) from (II), (VIII) from (III), and (IX) from (IV).

Preparation of Complex Salts of TCNQ. Diethyl Ether of β,β'-Di-(1-methyl–3-hydroxypiperidinium) $(TCNQ^{\bar{\cdot}})_2$ (TCNQ) (X). To a hot solution of 0.2 g of the simple salt (VI) in 20 ml of acetonitrile was added 0.05 g of TCNQ. The solution was filtered hot. The needle crystals that were obtained after several hours were suction-filtered, washed with acetonitrile, and dried in a vacuum-desiccator over P_2O_5. We obtained 0.17 g (62%) of (X); mp 350-370°C (decompn.).

(XI) was obtained from (VII) in a similar manner.

1-Methyl–3-hydroxypiperidinium $(TCNQ^{\bar{\cdot}})_2$. To a boiling solution of 0.2 g of TCNQ in a mixture of 40 ml of chloroform and 10 ml of acetonitrile was added a boiling solution of 0.23 g of 1-methyl–3-hydroxypiperidine in 10 ml of chloroform. After several hours the bluish-green needle crystals were suction-filtered, washed with chloroform, and dried over P_2O_5. We obtained 0.23 g (72.7%) of (XII); mp 200-213°C (decompn.).

In a similar manner were obtained (XIII) from (III), (XIV) from (V), (XV) from 1-(1-methyl–2-pyrrolidyl)–3-propanol [12], (XVII) from 1-(1-methyl–4-isopropyl–2-pyrrolidyl)–3-propanol [12], and (XVIII) from 1-(1-methylcyclopentano(b)–2-pyrrolidyl)–3-propanol [12].

CONCLUSION

Salts were synthesized from the $TCNQ^{\bar{\cdot}}$ anion-radical and the $(TCNQ^{\bar{\cdot}})_2$ complex anion and the cations of unconjugated, substituted ammonium bases containing functional groups, which assured the possibility of intermolecular reactions in the crystal.

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