ATRANES

XXXI.* COMPLEXES OF CHROMATRANE-3,7,10-TRIONE

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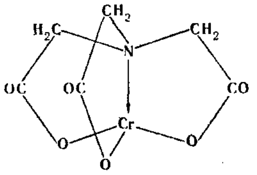
The tri- and monohydrates of chromatrane-3,7,10-trione $\overrightarrow{N(CH_2COO)_3Cr}$ and its complexes with mono- and diamines, dimethylformamide, H_2O_2, etc. were obtained. The structures of these compounds were studied by thermography and IR and UV spectroscopy.

The general methods for the preparation of metalloatrane-3,7,10-triones $\overrightarrow{N(CH_2COO)_3M}$ and some of their properties were examined in previous communications [2,3]. The present paper is devoted to the synthesis and study of derivatives of chromatrane-3,7,10-trione (I), which is a hypothetical compound.



I

A complex of aminotriacetic acid with chromium with the composition $[N(CH_2COO)_3Cr] \cdot 2H_2O$ had already been isolated in 1947 [4-6]. Complexes of trivalent chromium with aminotriacetic acid were subsequently obtained and investigated in the form of their ammonium derivatives [7]. The polarographic and spectrophotometric determination of a chromium derivative of aminotriacetic acid has been described, and its titration curves have been studied [8, 9].

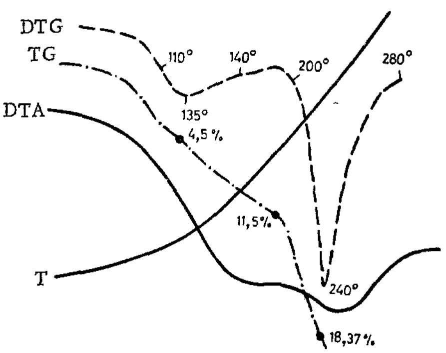


Fig. 1. Derivatogram of chromatrane-3,7,10-trione trihydrate $\overrightarrow{N(CH_2COO)_3Cr} \cdot 3H_2O$ (heating rate 12 deg/min): T) heating curve; TG) thermogravimetric curve; DTA) differential heating curve; DTG) weight-loss rate curve.

It seemed of interest to us to investigate the possibility of the existence of free chromatrane-3,7,10-trione (I) and to obtain its various derivatives. We have previously obtained [2] chromatrane-3,7,10-trione trihydrate ($I \cdot 3H_2O$) from free aminotriacetic acid (II) and the chromium salts of volatile acids:

$$\underset{II}{N(CH_2COOH)_3} + CrX_3 + 3H_2O \rightarrow \underset{III}{\overrightarrow{N(CH_2COO)_3Cr}} \cdot 3H_2O + 3HX$$

$X = Cl, CH_3COO$, etc.

A study of the thermograms of $I \cdot 3H_2O$ (Fig. 1) demonstrates that it does not undergo any change when it is heated to 110°C. An endothermic minimum, corresponding to the loss of the first molecule of water, is observed at 110-135-140°. A second molecule of water is lost on further heating to 200°. A second endothermic

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*See [1] for communication XXX.

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TABLE 1. Complexes of Chromatrane-3,7,10-trione

Comp.	Formula*	Crystal color	Aqueous-solution color	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	N	Cr	C	H	N	Cr	
III	$[XCr(OH_2)_2]H_2O$	Violet	Violet	$C_6H_{12}NCrO_9$	24,3	4,7	4,4	17,3	24,5	4,8	4,8	17,7	98
IV	$XCrOH_2$	Dark-violet	Dark-violet	$C_6H_8NCrO_7$	28,2	3,7	5,4	19,7	27,9	3,1	5,4	20,1	94
V	$NH_4[XCrOHOH_2] \cdot H_2O$	Violet	Violet	$C_6H_{14}N_2CrO_8$	23,5	4,9	9,6	17,5	23,2	4,5	9,0	16,8	84
VI	$(NH_4)_3[XCrOH \cdot OH_2]$	Blue	Blue-violet	$C_6H_{23}N_4CrO_{10}$	20,1	7,6	14,8	15,7	19,8	6,4	15,4	14,3	83
VII	$[C_2H_5NH_3][XCrOHOH_2] \cdot H_2O$	Blue	Dark-blue	$C_8H_{19}N_2CrO_9$	28,0	5,8	7,8	15,8	28,3	5,7	8,3	15,3	72
VIII	$[(C_2H_5)_2NH_2][XCrOHOH_2] \cdot 2H_2O$	Green	Greenish-blue	$C_{10}H_{25}N_2CrO_{10}$	31,8	6,6	7,5	13,9	31,2	6,5	7,3	13,5	72
IX	$[CH_2(CH_2)_4NH_2][XCrOHOH_2]$	Grayish-blue	Blue	$C_{11}H_{21}N_2CrO_8$	36,8	5,9	7,5	14,6	36,6	5,9	7,5	14,4	80
X	$[C_5H_5NH]^+[XCrOHOH_2]$	Red-violet	Cherry-red	$C_{11}H_{15}N_2CrO_8$	37,4	4,0	7,8	14,2	37,2	4,3	7,9	14,6	83
XI	$[XCr \cdot HCON(CH_3)_2 \cdot H_2O]HCON(CH_3)_2$	Dark-violet	Dark-violet	$C_{12}H_{24}N_3CrO_{10}$	33,9	5,9	9,6	12,7	34,1	5,7	9,9	12,3	87
XII	$[XCr \cdot NH_2CH_2CH_2NH_2] \cdot H_2O$	Rose	Rose	$C_8H_{16}N_3CrO_7$	29,5	5,7	13,8	16,8	30,2	5,1	13,2	16,3	84
XIII	$[XCr \cdot 1,2\text{-}(H_2N)_2C_6H_4] \cdot H_2O$	Brown	Brown-red	$C_{12}H_{16}N_3CrO_7$	38,5	4,7	11,0	14,0	38,9	4,3	11,2	13,9	74
XIV	$[XCr \cdot NC_5H_4{-}C_5H_4N] \cdot 6H_2O$ †	Brown	Lilac	$C_{16}H_{26}N_3CrO_{12}$	36,2	5,1	8,2	10,4	37,8	5,6	8,3	10,0	80
XV	$[XCr \cdot C_{12}H_8N_2] \cdot 8H_2O$	Gray-violet	Violet	$C_{18}H_{30}N_3CrO_{14}$	38,6	4,8	7,3	9,4	38,3	5,4	7,4	9,2	78
XVI	$[XCr \cdot C_9H_8NOH] \cdot 3H_2O$	Rose	Light-rose	$C_{15}H_{19}N_2CrO_{10}$	40,7	4,7	6,8	11,5	41,0	4,4	6,4	11,8	74
XVII	$K[XCrOH] \cdot H_2O$	Dark-lilac	Green	$C_6H_{11}NCrO_9K$‡	22,7	3,1	4,0	16,0	21,7	3,3	4,2	15,6	78
XVIII	$[XCr \cdot H_2O_2 \cdot H_2O] \cdot H_2O$	Red-violet	Red	$C_6H_{14}NCrO_{11}$	22,0	4,5	4,6	16,0	22,0	4,3	4,3	15,8	97

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* $H_3X = N(CH_2COOH)_3$.

† $NC_5H_4{-}C_5H_4N$ is α,α-dipyridyl.

‡ Found: K 12.0%. Calculated: K 11.8%.

TABLE 2. Absorption Maxima (cm^{-1}) in the IR Spectra of Complexes of Chromatrane-3,7,10-trione*

III	V	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
		355 s		400 m							400 m		
	410 m	430 w		420 w	490 m	430w		430 m			435 vs		430 w
											490 m		
	520 vs		525 s	520 s	555 s	540s	540 w	535 m	535 m	540 m	530 s	545 m	520 m
550 s	570 w	540 s									535 m		
											565 s		
											580 m		
											590 w		600 w
620 s	630 s	630 s	620 s	625 w	625 s	620s		620 s	615 m	620 m	620 s		620 w
					655 m	665 w					680 w	660 m	
	690 m				705 s					725 s	720 m		
750 s	750 vs	760 s	755 s	740 m	755 s	750s	750 m	750 s	760 s	750 m	750 s	755 m	750 s
				765 w	775 s						785 s		
	830 m			830 w		805 m				850 m	820 vs		
											880 m		
	910 vs	920 vs	915 s	905 s	920 vs	915s		910 s	910 s	915 s	925 vs	915 s	905 vs
940 s	940 w			935 m	945 w	940w							
				950 m							990 s		970 m
985 m	975 m			965 m	960 w								
					980 w					1005 w			1005 m
1020 m	1010 s	1020 m		1015 m	1015 m	1010m		1015 m	1010 m			1010 m	
	1050 s			1045 w	1080 m		1055 s		1035 m		1080 w	1090 w	1040 m
1110 m	1110 m	1115 m			1110 w	1110m		1105 m		1100 w	1115 vs		1100 m

			1155 w	1175 w	1165 w			1165 m	1170 w		1145 m		
											1195 vs		
					1215 m					1215 w	1220 s		1215 w
1310 w				1320 m	1305 m	1305 w		1300 s	1310 m	1315 m	1305 vs		1270 m
					1345 s								
1380 vs			1375 vs	1380 vs	1385 vs	1375 vs	1380 vs	1380 vs	1375 vs	1380 vs	1375 vs	1380 vs	1385 vs
		1400 vs									1400 s		
	1460 vs	1460 vs	1450 vs	1460 vs	1455 vs	1455 vs	1460 vs	1460 vs	1465 vs	1460 vs	1455 vs	1460 vs	1460 vs
1590 vs				1574 m		1580 s		1500 m					
	1620 vs		1620 vs								1610 vs		1610 vs
		1630 vs			1632 vs		1635 m	1630 vs		1635 vs		1630 vs	
				1650 vs		1640 s			1655 vs		1745 s		
	2090 m				2356 w			2350 w		2365 w	2350 m		
	2380 m												
								2600 w			2605 m		
2775 m					2755 s				2745 w		2730 m		2725 m
			2845 s	2851 s		2850 s	2845 s	2860 vs	2765 w				
2862 w		2885 s	2875 s		2880 w		2875 s		2850 s	2855 vs	2850 vs	2845 vs	2850 vs
				2900 vs									
2920 s		2940 s				2930 vs		2920 vs	2940 s	2920 vs	2915 vs	2925 vs	2920 vs
			2965 vs				2970 vs						
3015 s				3110 m	3090 s					3070 w			
	3190 s						3275 m						3200 m
	3350 m	3440 m	3415 m	3415 s	3435 m			3370 m	3380 s		3350 s		
	3524 m									3410 m			3490 m
	3570 m												

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*Abbreviations: s is strong, m is medium, w is weak, vs is very strong.

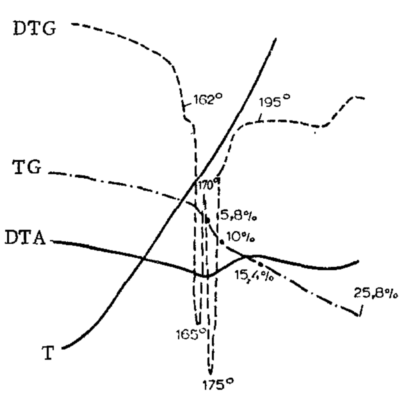


Fig. 2. Derivatogram of chromatrane-3,7,10-trione monohydrate $\overline{N(CH_2COO)_3Cr} \cdot \cdot H_2O$.

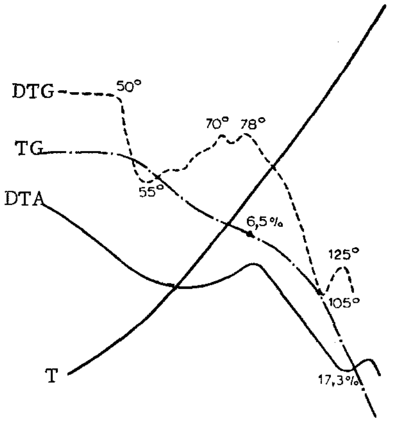
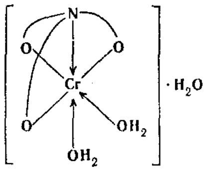


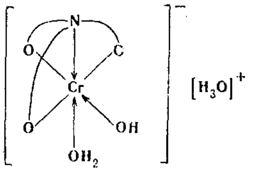
Fig. 3. Derivatogram of $NH_4[\overline{N(CH_2COO)_3Cr} \cdot \cdot (OH)OH_2]$.

minimum (200-240-280°), corresponding to the loss of the third molecule of water, then appears. The second and third molecules of water from I · $3H_2O$, which are lost at high temperatures (200-280°) with ultimate destruction of the structure of the atrane skeleton, apparently enter into the inner sphere of chromatrane-3,7,10-trione. For this reason we were unable to obtain anhydrous chromatrane-3,7,10-trione and isolated only its monohydrate, the further dehydration of which leads to the formation of decomposition products.

Thus I · $3H_2O$ apparently has the III* or, most likely, the IIIa structure (this compound behaves like an acid), in which the chromium atom has a coordination number of six and is coordinately bonded to two water molecules (the third H_2O molecule is water of crystallization).



III



IIIa

The monohydrate of I [I · H_2O (IV)], obtained by heating I in vacuo, is isolated as dark-violet crystals. Two endothermic minima are observed on the derivatographic curve (Fig. 2) of I · H_2O: the first at 160-165-170° corresponds to the loss of 0.5 mole of water, the second at 170-175-195° corresponds to the loss of another 0.5 mole of water. The substance decomposes above 200°. Thus the dehydration of I · H_2O is intermolecular in character (anhydrocondensation) and leads to crosslinking of two chromium atoms by an oxygen bridge. Compound IV most likely does not contain a pentacoordinated chromium atom and has a polymeric structure.

Compound I · $3H_2O$ forms complexes with ammonia, amines, and diamines in aqueous solutions (Table 1).

Heating of I · $3H_2O$ with excess 20% ammonium hydroxide gives, after removal of the solvent by vacuum distillation, violet crystals with the composition $C_6H_{14}CrN_2O_8$ (V), which are readily soluble in water. The thermogram of this compound is represented by two endothermic minima (Fig. 3). The first (50-55-70°) corresponds to the loss of one molecule of water of crystallization. The second endothermic minimum (80-105-125°) corresponds to the loss of a second molecule of water and a molecule of ammonia. This character of the thermal decomposition makes it possible to assign the V structure to the complex obtained.

Blue crystals that are readily soluble in water and have the $C_6H_{23}CrN_4O_{10}$ (VI) composition were obtained from the reaction of III with excess 20% ammonium hydroxide in the cold after removal of the solvent in vacuo. This compound is more thermally stable than V, described above, and does not change on heating to 170°. Compound VI loses one molecule of water at 170-192°. The great endothermic minimum at 192-225-273° corresponds to the loss of the remaining three molecules of water and three molecules of ammonia. This makes it possible to assign structure VI, in which II is a tridentate ligand, to this compound. (See scheme on following page.)

Ammonium salts VII-X, which are similar to V (VII contains one molecule of crystallization water, while VIII contains two molecules of crystallization water), are formed in the reaction of III with ethylamine, diethylamine, piperidine, and pyridine.

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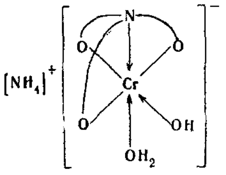
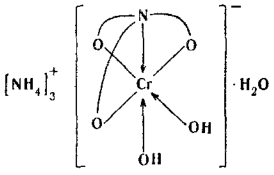
*In the structural formulas, N ⌒ O corresponds to the $N-CH_2CO-O$ fragment.

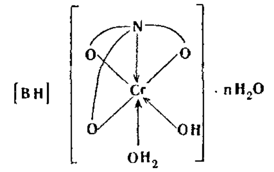


V



VI

Endotherms that indicate the loss of three and four molecules of water, respectively, are present on the thermograms of these compounds.

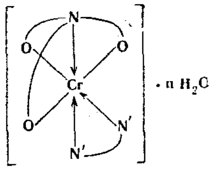


VII-X

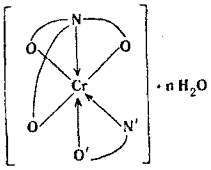
VII $B = C_2H_5NH_2$, $n = 1$; VIII $B = C_2H_5NH$, $n = 2$;
IX $B = CH_2(CH_2)_4NH$, $n = 0$; X $B = C_5H_5N$, $n = 0$

Dimethylformamide displaces two molecules of water from III and forms complex XI with the composition $[N(CH_2COO)_3Cr \cdot B \cdot H_2O]B$, where B is $(CH_3)_2NCHO$.

Compound III reacts with 1,2-diamines (ethylenediamine, o-phenylenediamine, α,α-dipyridyl, and o-phenanthroline) to give derivatives XII-XV with a 1 :1 composition, to which one can most likely assign the XIX structure (where N'–N' is the 1,2-diamine molecule).



XIX



XX

One cannot, however, exclude the possibility that these complexes have the $[CrO_4N_2]$ structure, in which one nitrogen atom is protonated, rather than the $[CrO_3N_3]$ structure (XIX).

8-Hydroxyquinoline reacts with III to form complex XVI, which corresponds to formula XX (O'–N' is the 8-hydroxyquinoline molecule).

Potassium salt XVII – a blue crystalline substance with the formula $K[N(CH_2COO_3CrOH) \cdot H_2O]$ – is formed in the reaction of III with KOH in aqueous solution. This serves as an additional confirmation of the acid character of III, i.e., structure IIIa.

The reaction of III with H_2O_2 leads to the formation of a red-violet crystalline substance (XVIII) of the formula $[N(CH_2COO)_3Cr \cdot H_2O_2 \cdot H_2O] \cdot 2H_2O$.

The IR spectra of III and all of its studied derivatives (Table 2) contain two strong bands at 1610-1650 and 1450-1480 cm^{-1}, which correspond, respectively, to the antisymmetrical and symmetrical stretching vibrations of the COO^- group. The absence of an absorption band at 1710-1730 cm^{-1} indicates that there is no free carboxyl group in these compounds. These data are evidence that all of the bonds of the chromium atom with the carboxyl groups are equivalent.

The IR spectra of the compounds contain an absorption band at 620-630 cm^{-1}, which corresponds to the vibrations of the Cr–O bonds [10].

A strong band at 520-540 cm^{-1}, which apparently corresponds to the vibrations of the $Cr \leftarrow N$ coordinate bond, is observed in the spectra of all of the investigated complexes. There is a band at 750-760 cm^{-1}, which we assigned to the vibrations of H–O–H in the coordinately bonded water molecule. The absorption at 3350-3490 cm^{-1} corresponds to the symmetrical and antisymmetrical vibrations of the OH group of the water of crystallization.

TABLE 3. Absorption Maxima in the UV Spectra (λ_{max}, nm)

Compound	1	2
X	250	253
XIII	225	275
XIV	225	300
XV	225	268

An absorption band at 3190-3570 cm^{-1}, which corresponds to the NH_3 stretching vibrations, is observed in the spectrum of V.

The spectra of VII-IX (amine derivatives) contain an absorption band at 1650 cm^{-1}, which is due to the deformation vibrations of the NH_2 group. However, since the $\nu_{as}(COO^-)$ vibrations also appear in this region, the presence of vibrations of the NH_2 group can be judged from the two absorption bands at 3440 and 3415 cm^{-1}.

In addition to the bands indicated above, the spectrum of X contains strong absorption bands at 755 cm^{-1}, which corresponds to the deformation vibrations of the C–H bonds, and at 1385 cm^{-1}, which corresponds to the vibrations of the C=C and C=N bonds in the pyridine ring.

The spectrum of XIV contains absorption bands at 1195 and 1220 cm^{-1}, which correspond to the ring vibrations and the deformation vibrations of the C–H bonds of the hydroxyquinoline ring [11].

The UV spectra of III and its derivatives (V-IX) do not have absorption maxima. There are two absorption maxima in the UV spectra of X and XIII-XV (Table 3). The first of them (1) corresponds to the absorption of the heteroaromatic or aromatic ring, while the second (2) is due to the coordination of the latter with the central chromium atom.

EXPERIMENTAL

Aminotriacetic acid (II) was obtained via the method in [12] and was purified by recrystallization from hot water. The chromium acetate was a chemically pure preparation . All of the starting amines and dimethylformamide were chemically pure preparations, which were additionally purified by distillation or recrystallization prior to introduction into the reaction.

The carbon and hydrogen were determined by combustion in a stream of oxygen, while nitrogen was determined by the Dumas micromethod. Chromium was determined as Cr_2O_3 after calcining the substances at 1000° in a stream of oxygen.

The derivatograms were obtained with the derivatograph of the system in [13].

The IR spectra of KBr pellets of the solid compounds were recorded with UR-10 and IKS-14 spectrographs. The UV spectra were recorded with a UV-2 automatic recording spectrophotometer, which was constructed in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR. The investigated substances were recorded in $2 \cdot 10^{-4}$ M aqueous solutions (for complexes with o-phenanthroline and α,α-dipyridyl, 10^{-4} M solutions were investigated). The cuvette thickness was 1 cm.

$[N(CH_2COO)_3Cr(OH)_2]\cdot H_2O$ (III). A solution of 22.9 g (0.1 mole) of chromium acetate in 300 ml of distilled water was added to a hot aqueous solution of 19.1 g (0.1 mole) of II, and the mixture was refluxed for 30 min. The hot solution, which changed from dark green to dark violet, was filtered, and the water was completely removed from it in a rotary vacuum film evaporator. The residual shiny violet crystals were reprecipitated twice from aqueous solution by the addition of alcohol and ether and dried in vacuo to give 29.0 g (98%) of III. During the evaporation of the solution obtained above to about 20 ml, III can be precipitated from it by the addition of alcohol. Similar purification of the latter gave 25.0 g (85.5%) of III. Compound III was obtained as shiny violet crystals that were readily soluble in water (the solution is violet) and insoluble in the usual organic solvents. It dissolved readily in dimethyl sulfoxide, and mono-, di-, and triethanolamines on heating. It gave an orange coloration (reaction for Cr^{3+}) with alkaline H_2O_2 solutions.

$[N(CH_2COO)_3Cr(OH_2)]$ (IV). Finely ground powdered III was dehydrated by heating to constant weight in vacuo at 2 mm and 200°.

$NH_4[N(CH_2COO)_3CrOH\cdot OH_2]\cdot H_2O$ (V). A 1.17-g (4 mmole) sample of III was dissolved in 20 ml of cold 20% ammonium hydroxide, and the water was removed from the dark blue solution by vacuum distillation. The residual dark blue crystals were washed with absolute alcohol and ether and dried in vacuo.

$(NH_4)_3[N(CH_2COO)_3CrOHOH_2]$ (VI). A 1.17-g (4 mmole) sample of III was dissolved by heating in 20 ml of 20% ammonium hydroxide, the solution was refluxed for 10 min, and the solvent was removed by vacuum distillation. The residual violet crystals were washed with absolute alcohol and ether and dried in vacuo.

Complexes of $[\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{C}}}\mathrm{r(OH_2)_2]H_2O}$ with Ethylamine (VII), Diethylamine (VIII), Piperidine (IX), Pyridine (X), and Ethylenediamine (XII). A 5-ml sample of the appropriate amine was added to a solution of 1.17 g (4 mmole) of III in 5 ml of water. The solutions changed color during the addition. The solvent was removed by vacuum distillation, and the residue was suspended in absolute ethanol. The suspension was filtered, and the solid was washed with absolute alcohol and ether and dried in vacuo.

$\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{C}}}\mathrm{r \cdot HCON(CH_3)_2 \cdot OH_2] \cdot HCON(CH_3)_2}$ (XI). A hot solution of 1.91 g (0.01 mole) of II in 40 ml of dimethylformamide was added to a solution of 2.32 g (0.01 mole) of $Cr(OCOCH_3)_3$ in 30 ml of dry dimethylformamide, during which the color of the solution gradually changed from green to dark violet. The reaction mixture was refluxed for 4 h, and the solvent was removed in vacuo. The residue was washed with absolute ether and dried in vacuo.

Complexes of $[\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{C}}}\mathrm{r(OH_2)_2]H_2O}$ with 1,2-Phenylenediamine (XIII), *α,α*-Dipyridyl (XIV), o-Phenanthroline (XV), and Hydroxyquinoline (XVI). A solution of 4 mmole of the appropriate diamine or hydroxyquinoline in 10 ml of water was added to a solution of 1.17 g (4 mmole) of III in 20 ml of water, and the mixture was heated on a water bath for 30 min, during which the color of the solution changed. The solvent was removed in a rotary vacuum evaporator, and the residue was suspended in absolute ethanol. The precipitated crystals were treated with acetone and dried in vacuo.

$\mathrm{K}[\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{C}}}\mathrm{rOH] \cdot H_2O}$ (XVII). A total of 5 ml of 50% KOH solution was added to a solution of 1.17 g (4 mmole) of III in 5 ml of water. The solvent was removed in vacuo, and the residual blue crystals were washed with absolute alcohol and ether and dried in vacuo.

$[\overline{\mathrm{N(CH_2COO)_3}\overset{\downarrow}{\mathrm{C}}}\mathrm{r \cdot H_2O_2 \cdot H_2O] \cdot 2H_2O}$ (XVIII). A solution of 1.17 g (4 mmole) of III in 20 ml of 30% hydrogen peroxide was heated cautiously with stirring on a water bath. A vigorous reaction ensued, as a result of which the dark violet color of the solution changed to red violet. Violet crystals were precipitated from the cooled solution by the addition of absolute alcohol.

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