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The Structure and Lability of Some New Titanium(IV) Complexes

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A variable-temperature proton magnetic resonance study of the complexes bis(dimethylamino)bis(dimethylmalonato)-titanium(IV), bis(dimethylamino)bis(N,N,N′,N′-tetramethylmalonamidato)titanium(IV), dimethoxybis(dimethylmalonato)titanium(IV), and dimethoxybis(N,N,N′,N′-tetramethylmalonamidato)titanium(IV) indicates that they exist in solution as *cis* isomers which fairly rapidly rearrange stereochemically. The Arrhenius energies of activation and the entropies of activation were determined by pmr kinetic studies over the temperature range −10 to 80°. The mechanism of the stereochemical rearrangement probably proceeds by rupture of one bond to give a symmetrical five-coordinate intermediate.

β-Diketones react with titanium alkoxides and halides to form the complexes, Ti(β-diketone)$_2$X$_2$, whose structure and lability have recently been of considerable interest.[1–5] All evidence now points to a *cis* structure for these complexes. Our recent interest in the reactions of tetrakis(dialkylamino)titanium compounds[6] prompted us to investigate the similar complexes Ti(β-diketone)$_2$(N(CH$_3$)$_2$)$_2$. Unfortunately, the reactions of β-diketone compounds with tetrakis(dimethylamino)titanium give complexes which spontaneously decompose with amination of the β-diketones.[7] However, the reaction of Ti(N(CH$_3$)$_2$)$_4$ with dimethylmalonate, Hdmm, and N,N,N′,N′-tetramethylmalonamide, Htmm, does give stable complexes, *viz.*, bis(dimethylamino)bis(dimethylmalonato)titanium, ((CH$_3$)$_2$N)$_2$Ti(dmm)$_2$, and bis(dimethylamino)bis(N,N,-N′,N′-tetramethylmalonamidato)titanium, ((CH$_3$)$_2$N)$_2$-Ti(tmm)$_2$.[7b] Also synthesized were the methoxy complexes of titanium with the above bidentate ligands, dimethoxybis(dimethylmalonato)titanium, (CH$_3$O)$_2$Ti-(dmm)$_2$, and dimethoxybis(N,N,N′,N′-tetramethylmalonamidato)titanium, (CH$_3$O)$_2$Ti(tmm)$_2$. Although donor complexes of diesters and diamides of malonic acid have been reported,[8,9] there appear to be no studies of anionic chelate complexes.

The pmr spectra of the complexes at 35° all contained one broad resonance suggesting that stereochemical rearrangements were taking place. To investigate this, a pmr study was made over the temperature range −10 to 80°. Activation parameters were obtained from these data. Experiments with the complexes in the presence of the free ligand acids and anions were performed to investigate the mechanism of the rearrangements.

Experimental Section

Synthesis.—All of the compounds were synthesized in an atmosphere of dry nitrogen. Analyses for C, H, N, and Ti were performed in the Physical Sciences Center, Central Research Department, Monsanto Co. Bis(dimethylamino)bis(dimethylmalonato)titanium(IV) and bis(dimethylamino)bis(N,N,N′,N′-tetramethylmalonamidato)titanium(IV) were prepared by the method of Weingarten and Miles.[7b]

Dimethoxybis(dimethylmalonato)titanium(IV).—A solution of bis(dimethylamino)bis(dimethylmalonato)titanium (1.99 g, 0.005 mole) in benzene (20 ml) was treated with methanol (0.32 g, 0.01 mole) in benzene (10 ml). The deep red solution of the complex became paler as the methanol solution was added, and after the addition was complete, the solution was heated under reflux until no further change in color was observed (approximately 1 hr). The solvent was removed and the remaining oil was distilled using a molecular still at 0.0012 mm with a bath temperature of 100°. The product was obtained in 80% yield as a pale yellow viscous liquid which slowly crystallized on standing at room temperature. *Anal.* Calcd for C$_{12}$H$_{20}$O$_{10}$Ti: C, 38.7; H, 5.4; Ti, 12.9; mol wt, 372. Found: C, 38.3; H, 5.2; Ti, 13.0; mol wt, 360 ± 15 (cryoscopy in benzene).

Dimethoxybis(N,N,N′,N′-tetramethylmalonamidato)titanium-(IV).—A solution of bis(dimethylamino)bis(N,N,N′,N′-tetramethylmalonamidato)titanium (2.25 g, 0.005 mole) in ether (30 ml) was treated with a solution of methanol (0.32 g, 0.01 mole) in ether (10 ml). The solution slowly lightened to a yellow color, and yellow crystals started to separate. The solution was left standing overnight in the refrigerator and the crystals were then collected and recrystallized from benzene; yield 1.7 g (80%); mp 148–150°. *Anal.* Calcd for C$_{16}$H$_{32}$N$_4$O$_6$Ti: C, 45.3; H, 7.6; N, 13.2; Ti, 11.3; mol wt, 424. Found: C, 44.9; H, 7.8; N, 13.3; Ti, 11.6; mol wt, 415 ± 12 (cryoscopy in benzene).

Ligand Exchange.—Reactions were run on the nmr scale using 2:1 molecular weight ratios of free ligand (acid or anion) to complex. The ligand anions were prepared as the hexamethylguanidinium salts by the reaction of tetrakis(dimethylamino)-methane with the ligand acids.[10]

Infrared Spectra.—A Beckman IR-4 with sodium chloride optics was used and the spectra were obtained from Nujol mulls. The bands observed in the carbonyl region of the spectra are given in Table I. The assignments are based on the recent work of Behnke and Nakamoto.[11]

Proton Magnetic Resonance Spectra.—A Varian A-56/60 with a variable-temperature probe was used. The spectra were run in trideuterioacetonitrile[12] with TMS as internal standard.

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[3] M. Cox, R. J. H. Clark, and H. J. Milledge, *Nature*, **212**, 1357 (1966).

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[6] H. Weingarten and W. A. White, *J. Am. Chem. Soc.*, **88**, 850 (1966); *J. Org. Chem.*, **31**, 4041 (1966); **32**, 213 (1967).

[7] (a) H. Weingarten, *et al.*, *J. Am. Chem. Soc.*, **89**, 5974 (1967); (b) H. Weingarten and M. G. Miles, *J. Org. Chem.*, **33**, 1506 (1968).

[8] M. G. Romova, O. A. Osipov, and L. K. Isaeva, *Russ. J. Inorg. Chem.*, **11**, 291 (1966).

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[10] H. Weingarten and N. K. Edelmann, *J. Org. Chem.*, **32**, 3293 (1967).

[11] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

[12] The dimethylamino complexes are soluble in acetonitrile, ether, benzene, and saturated hydrocarbons but they slowly react with halocarbon solvents. The dimethoxy complexes are soluble in halocarbons, acetonitrile, and ether but only sparingly soluble in benzene and saturated hydrocarbons.

Table I

Infrared Spectra of the Complexes in the Carbonyl Region

Complex	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$, cm^{-1}	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, cm^{-1}
$((CH_3)_2N)_2Ti(dmm)_2$	1643	1614
$((CH_3)_2N)_2Ti(tmm)_2$	1574	1539
$(CH_3O)_2Ti(dmm)_2$	1631	1602
$(CH_3O)_2Ti(tmm)_2$	1562 sh	1546

Chemical shifts were determined by the side-band technique. The results obtained at 35° are given in Table II.

Table II

Proton Magnetic Resonance of the Complexes in CD_3CN at 35°

Complex	τ(OCH_3 or $N(CH_3)_2$ on Ti), ppm	Integral	τ(chelate ring H ppm),	Integral	τ(OCH_3 or $N(CH_3)_2$ on ligand), ppm	Integral
$((CH_3)_2N)_2Ti(dmm)_2$	6.68	6	5.59	1	6.39 vb, d[a]	6
$((CH_3)_2N)_2Ti(tmm)_2$	6.83	6	5.78	1	7.12 vb	12
$(CH_3O)_2Ti(dmm)_2$	5.82	3	5.55	1	6.32 vb	6
$(CH_3O)_2Ti(tmm)_2$	5.98	3	5.79	1	7.13 vb	12
Hdmm			6.67	2	6.37	6
Htmm			6.56	2	7.11 vb	12

[a] vb, very broad; d, doublet.

Calculation and Results of Kinetic Data.—The first-order rate constants, k, were obtained from the mean residence times, 2τ, for an OCH_3 or an $N(CH_3)_2$ group of the ligand in a particular site since mean residence times are independent of the concentration of the complex. Values of 2τ over the temperature range −10 to +80° were obtained using equations given in the literature.[13,14] Values of T_2 were obtained from the line widths of the TMS signals which varied with sample and instrumental conditions but were always in the range 0.35–0.65 cps. This was certainly a reasonable approximation for the dmm complexes since for very slow and fast exchange the line widths for the resonance of the CH_3O groups on the dmm were the same as those for the TMS resonance. However, for the tmm complexes the reliability of the approximation was uncertain since broadening due to loss of free rotation of the $N(CH_3)_2$ groups prevented line-width measurements at the slow-exchange limit. When more than one equation was applied over a kinetic range, the average value was used. Sample temperatures were calculated from the chemical shifts of methanol and ethylene glycol. The average results of several measurements on different samples are given in Tables III–VI.

Plots of log k *vs.* $1/T$ were linear, and values of k extrapolated to 25°, the Arrhenius activation energy, E_a, and the frequency factor, A, were obtained by least-squares analyses of the data. Values for the entropy of activation at 25°, ΔS^*, were obtained using Eyring's rate equation with a transmission coefficient of 1. The results are given in Table VII, together with the coalescence temperature, T_c, and the peak separation, $\Delta\nu_{AB}$, at −48°.

Table III

Temperature Dependence of k for $((CH_3)_2N)_2Ti(dmm)_2$

Temp, °C	$\delta\nu^a$	$\Delta\nu_e{}^b$	r^c	W^d	k, sec^{-1}
−10.7	0.16	18.22			0.50
0	0.59	17.67			1.86
4	0.80	17.60			2.5
15	1.72	17.4			5.4
17.5	1.95	17.23			6.2
23.5	3.46	16.58	6.34	27.8	10
30		15.25	2.22	27.3	20
36		12.8	1.40	22.3	30
42	14.5			15.0	49
50	9.5			10.0	66
60.5	4.22			4.85	130
72.5	1.35			1.80	390

[a] $\delta\nu$ is the line broadening due to exchange in cps. [b] $\Delta\nu_e$ is the frequency separation between the two absorption maxima. [c] r is the ratio of the maximum amplitude to the amplitude at $(\nu_A + \nu_B)/2$ (below the coalescence temperature). [d] W is the line width at half-amplitude above the coalescence temperature and the width at half-amplitude at $(\nu_A + \nu_B)/2$ below the coalescence temperature (W^* in eq 12 and 13 in ref 14).

Table IV

Temperature Dependence of k for $((CH_3)_2N)_2Ti(tmm)_2{}^a$

Temp, °C	$\delta\nu$	$\Delta\nu_e$	r	W	k, sec^{-1}
0	0.63	11.96			2.0
4	0.84	11.98			2.6
7	1.00	11.80			3.2
11	1.5	11.65			4.7
15	2.15	11.47	5.89	18.11	7.6
17.5	2.72	11.00	3.71	17.90	9.6
20	3.0	10.8	2.73	17.50	10
23.5	4.23	10.2	1.87	17.16	16
28		8.5	1.27	15.2	20
30		7.12	1.16	14.75	23
36	8.85			9.25	39
42	5.07			5.45	57
49	3.5			4.0	79
50	3.83			4.3	74
60.5	1.91			2.36	138
72.5	0.55			0.93	468
80	0.8			1.40	323

[a] Symbols as defined in Table III.

Table V

Temperature Dependence of k for $(CH_3O)_2Ti(dmm)_2{}^a$

Temp, °C	$\delta\nu$	$\Delta\nu_e$	r	W	k, sec^{-1}
−6.7	0.35	12.83			1.0
0	0.48	12.80			1.5
4	0.79	12.80			2.5
15	1.73	12.33	9.38	22.10	6.2
23.5	4.7	10.25	2.75	19.35	13.5
30		9.25	1.34	17.92	20
36	11.76			12.1	33
42	5.84			6.24	55
50	3.05			3.60	96
60.5	1.63			2.04	174
72.5	0.55			0.9	513

[a] Symbols as defined in Table III.

Results and Discussion

The infrared spectra of the four complexes $((CH_3)_2N)_2Ti(dmm)_2$, $((CH_3)_2N)_2Ti(tmm)_2$, $(CH_3O)_2Ti(dmm)_2$, and $(CH_3O)_2Ti(tmm)_2$ all show carbonyl stretching bands at lower energy (~100 cm^{-1}) than that observed for the free ligand, and the absence of any significant bands in the free-carbonyl region indicates that the ligands are coordinated to the titanium through the carbonyl oxygens. The monomeric nature of the complexes demonstrates the absence of bridging ligands. Therefore, the compounds can be formulated as six-coordinated complexes, Ti(β-dicarbonyl)$_2X_2$.

The pmr spectra of the complexes at 35°, Table II, exhibit a sharp line in the region of τ 5.5–5.8 for the chelate ring proton. This resonance is at higher fields than is found for the α-hydrogen of acetylacetonato complexes[4] due presumably to the greater electron-

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(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 218–224.

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TABLE VI

TEMPERATURE DEPENDENCE OF k FOR $(CH_3O)_2Ti(tmm)_2$[a]

Temp, °C	$\delta\nu$	$\Delta\nu_e$	r	W	k, sec^{-1}
0	0.74	9.64			2.3
4	1.06	9.72			3.3
15	2.65	8.8	3.26	14.71	8.9
23.5		7.2	1.34	12.85	15
30	9.41			10.00	22
36	4.07			4.87	38
42	2.81			3.21	55
50	1.80			2.35	89
60.5	1.02			1.54	155
72.5	0.40			0.78	400

[a] Symbols as defined in Table III.

donating nature of the OCH_3 and $N(CH_3)_2$ groups over that of the CH_3 group. The spectra also exhibit a sharp line for the monodentate ligands and a very broad line for the OCH_3 or $(NCH_3)_2$ groups on the chelating ligands. At elevated temperatures (70–80°), the substituents on the bidentate ligand exhibit a sharp line which at lower temperature (30–40°) passes through a classical coalescence process[13] and eventually gives two sharp equivalent signals (0 to −10°). Throughout this temperature range, the resonances for the monodentate ligands and the ring protons remain sharp. The low-temperature spectra suggest that these complexes exist in solution as the *cis* geometrical isomer. The coalescence phenomena are then interpreted in terms of exchange of the OCH_3 or $N(CH_3)_2$ groups on the chelating ligands between the two nonequivalent environments of the *cis* isomers. The alternative explanation in terms of *cis–trans* isomerization is not favored since it is highly improbable that the *cis* and *trans* isomers for all four complexes would be present below coalescence in equal concentrations, particularly over a temperature range of at least 40°. It may therefore be concluded that these complexes are analogous to the acetylacetonato complexes of titanium[2,5] and exist in solution as the *cis* isomers.

For the complexes with tmm as the ligand a minimum line width for the two $N(CH_3)_2$ peaks was found to occur at −10° in trideuterioacetonitrile. To investigate further the broadening at lower temperatures, spectra of $(CH_3O)_2Ti(tmm)_2$ were run in methylene chloride down to −65°. At this temperature, the low-field resonance had split into two equal peaks and the high-field resonance had broadened considerably. This effect is characteristic of the loss of rotation in compounds containing $N(CH_3)_2$ groups.[15] The different coalescence temperatures for the two types of $N(CH_3)_2$ groups may be attributed to differences in the steric hindrance in the two sites. Examination of models shows that the $N(CH_3)_2$ groups on the amide functions *trans* to the monodentate ligands are, in fact, the more sterically hindered, and consequently the low-field resonance may be assigned to these groups.

The activation energies for the stereochemical rearrangements of these compounds are all approximately 2 kcal/mole higher than those obtained for the dihalobis(acetylacetonato)titanium(IV) complexes[5] and between 2 and 6 kcal/mole higher than the results reported by Bradley and Holloway[2] for dialkoxybis(acetylacetonato)titanium(IV) complexes. Since the values of E_a for the complexes under study are all within experimental error, little significance can be attributed to the differences. However, a relative order of lability of these various titanium complexes at 25° can be proposed, *viz.*, acac > tmm ~ dmm. Also, the monodentate ligands enhance this lability in the order halide > OCH_3 ~ $N(CH_3)_2$.

TABLE VII

VALUES OF k AT 25°, E_a, ΔS^* at 25°, T_c, AND $\Delta\nu_{AB}$ at −48° FOR THE COMPLEXES

Complex	$10^{-1}k$, sec^{-1}	E_a, kcal/mole	ΔS^*, eu	T_c, °C	$\Delta\nu_{AB}$, cps
$((CH_3)_2N)_2Ti(dmm)_2$	1.3	13.8 ± 0.7[a]	-7.2 ± 2.2[a]	40 ± 2	18.4 ± 0.3
$((CH_3)_2N)_2Ti(tmm)_2$	1.5	13.2 ± 0.8	-9.0 ± 2.4	33 ± 2	12.8 ± 0.3
$(CH_3O)_2Ti(dmm)_2$	1.5	13.6 ± 0.8	-5.5 ± 1.9	34 ± 2	13.4 ± 0.3
$(CH_3O)_2Ti(tmm)_2$	1.7	12.4 ± 0.5	-9.6 ± 1.4	29 ± 2	9.9 ± 0.3

[a] Errors are estimated at the 95% confidence level.

Three mechanisms have been postulated for stereochemical rearrangements of this type: dissociation,[16] the rhombic twist,[17] and bond rupture[18] to give a five-coordinate intermediate. If a dissociative mechanism

$$X_2TiL_2 \rightleftharpoons X_2TiL^+ + L^-$$

was taking place, there would have been a small concentration of free ligand anion in solution. Since ligand anions were observed to exchange relatively rapidly with ligand acid at ambient temperatures, addition of ligand acid to the complex should have caused exchange phenomena to appear in the pmr. Addition of free ligand acid to the complexes gave no evidence of exchange indicating that the rate constant for dissociation is $k < 1$ sec^{-1}. Furthermore, addition of Htmm to $(CH_3O)_2Ti(dmm)_2$ gave slow exchange of ligand over a period of days; also, addition of Hdmm to $(CH_3O)_2Ti(tmm)_2$ indicated very little exchange over a similar time period. This indicates that the dissociation mechanism plays little part in these processes. On the other hand, added ligand anion exchanges with the complexed ligand at a comparable rate to the isomerization. (No quantitative measurements were made to determine the reaction order with respect to L^-.) Although this does not rigorously exclude the rhombic twist mechanism, the most prob-

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[17] P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[18] A. Werner, *Ber.*, **45**, 3061 (1912).

able mechanistic model involves rupture of one ligand bond to give a symmetrical five-coordinate intermediate. A similar mechanism has been proposed for the stereochemical rearrangements of the dihalobis(β-diketonato)titanium complexes[5] and the coordination compounds of trivalent metals with unsymmetrical 1,3-diketones.[19]

(19) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

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Some Decomposition Reactions of Diperoxotriamminechromium(IV)[1a]

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Decomposition of $Cr(NH_3)_3(O_2)_2$ in 1 *F* $HClO_4$ at 20–25° gives $Cr(NH_3)_3(OH_2)_3^{3+}$ (*ca.* 40%, probably the pure 1,2,3 (*cis*) isomer), $Cr(NH_3)_2(OH_2)_4^{3+}$ (*ca.* 35%, probably largely or wholly the *cis* isomer), $Cr(NH_3)(OH_2)_5^{3+}$ (*ca.* 15%), and $Cr(OH_2)_6^{3+}$ (*ca.* 10%). In 1 *F* NaOH at 102° the diperoxo compound decomposes *ca.* 95% *via* a path forming CrO_4^{2-}, NH_3, O_2, and H_2O (or possibly some H_2O_2); the other *ca.* 5% of reaction produces CrO_4^{2-} and a nitrogen-containing species which is neither NH_3 nor NO_2^- and which slowly reacts with the CrO_4^{2-} or which catalyzes the oxidation of H_2O by CrO_4^{2-}. Explosion of the diperoxo compound by sudden heating occurs *ca.* 90% *via* formation of Cr_2O_3, NH_3, and O_2; the other *ca.* 10% of reaction yields Cr_2O_3, N_2O, N_2, and H_2O.

Introduction

In recent papers[2-6] we have reported our studies of the decomposition of diperoxochromium(IV) amines in acid solutions so as to prepare new chromium(III) amine complexes. Here we report the decomposition of diperoxotriamminechromium(IV), $Cr(NH_3)_3(O_2)_2$, in 1 *F* perchloric acid to give a series of aquoamminechromium(III) complexes. We also describe observations on the decomposition of this diperoxo compound in 1 *F* sodium hydroxide at *ca.* 102° and by explosion in a closed vessel.

Experimental Section

Diperoxotriamminechromium(IV).—The method of Kauffman and Acero[7] was used to prepare some lots of this compound. For other lots, the less efficient but more convenient method of Wesch[8] was employed, giving lustrous black needles; yield, 7%. *Anal.* Calcd for $Cr(NH_3)_3(O_2)_2$: N, 25.0; Cr, 31.1. Found: N, 25.3; Cr, 31.0.

The diperoxo compound must be handled with care because it may explode on sudden heating or shock. When heated from 20–25° at 2°/min, the compound charred at *ca.* 300° but did not explode. When the heating rate was increased to 4°/min, the crystals exploded mildly at 255°, and with a 20°/min heating rate a more violent explosion occurred at *ca.* 120°. At 20–25°, the compound can apparently be kept without change for at least 1 year.

Decomposition in 1 *F* Perchloric Acid.—*Ca.* 0.2 g of $Cr(NH_3)_3(O_2)_2$ was dissolved cautiously in 50 ml of 1 *F* $HClO_4$ at 20–25°; effervescence occurred. *Ca.* 5 ml of an aqueous slurry of H^+ Dowex AG50W-X4 cation-exchange resin (200–400 mesh) was added to the pink solution and shaken gently for 5 min, by which time all color was adsorbed. The resin was removed, washed with two 25-ml portions of 1 *F* $HClO_4$, and then transferred to the top of a 25-cm × 1-cm diameter column of fresh resin. Elution at 20–25° with a solution 0.15 *F* in $Ca(ClO_4)_2$ and 0.15 *F* in $HClO_4$ at 1 ml/min (a low rate is essential for the separation) yielded four bands as follows.

Ca. 500 ml of eluent separated the lowest band and brought it to the bottom of the column. A further 100–150 ml eluted this band to give a grayish blue solution. To remove Ca^{2+} from this effluent, it was readsorbed on a 3-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 20–25°, the Ca^{2+} was eluted with 200 ml of 1 *F* $HClO_4$, and then the complex was eluted with 50 ml of 3 *F* $HClO_4$. The resulting solution was 1.3 m*M* in $Cr(OH_2)_6^{3+}$, identified as such by its visible absorption spectrum.[9] The hexaaquo complex constituted *ca.* 10% of the total chromium.

Ca. 100 ml of eluent brought the next band to the bottom of the column, and 100–150 ml more eluted the band as a pink-red solution. Removal of Ca^{2+} was effected as above, giving a solution 1.7 m*M* in $Cr(NH_3)(OH_2)_5^{3+}$, characterized by its visible absorption spectrum.[10] *Ca.* 15% of the total chromium was as this pentaaquo species.

The third band was brought down with *ca.* 100 ml of eluent and eluted as a pink effluent with an additional 100–150 ml of eluent. The Ca^{2+} was removed, giving a solution 2.0 m*M* in complex, with an N:Cr atom ratio of 1.95, in acceptable agreement with the formula $Cr(NH_3)_2(OH_2)_4^{3+}$. This diammine species constituted *ca.* 35% of the total chromium.

The last band was brought down and eluted in the same way. After removal of Ca^{2+}, a pink solution 3.7 m*M* in complex was obtained. The N:Cr atom ratio found for this effluent was 2.81, in acceptable agreement with the formula $Cr(NH_3)_3(OH_2)_3^{3+}$. *Ca.* 40% of the total chromium was in this form.

The decomposition and chromatographic separations were repeated several times with essentially the same results.

Decomposition in Hot 1 *F* Sodium Hydroxide.—In each of

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