Table I. Mössbauer Data and Proportions of Eu^{II} and Eu^{III} in Eu_xMoO_4

		Percentage Eu^{II}			Percentage Eu^{III}	
Material	$\delta(Eu^{II})$,[a] mm s^{-1}	Exptl	Theor	$\delta(Eu^{III})$,[a] mm s^{-1}	Exptl	Theor
$Eu_{0.9}MoO_4$	−11.7	73 ± 2	77.8	+0.6	27 ± 1	22.2
$Eu_{0.7}MoO_4$	−12.1	15 ± 2	14.3	+0.6	85 ± 2	85.7
$Eu_{0.67}MoO_4$		0 ± 0.1	0	+0.7	100 ± 0.1	100
"$Gd_{0.5}Eu_{0.5}MoO_4$"	−12.0	55 ± 0.8	See text	+0.9	45 ± 00.7	See text

[a] Chemical isomer shifts δ are quoted relative to EuF_3 as zero.

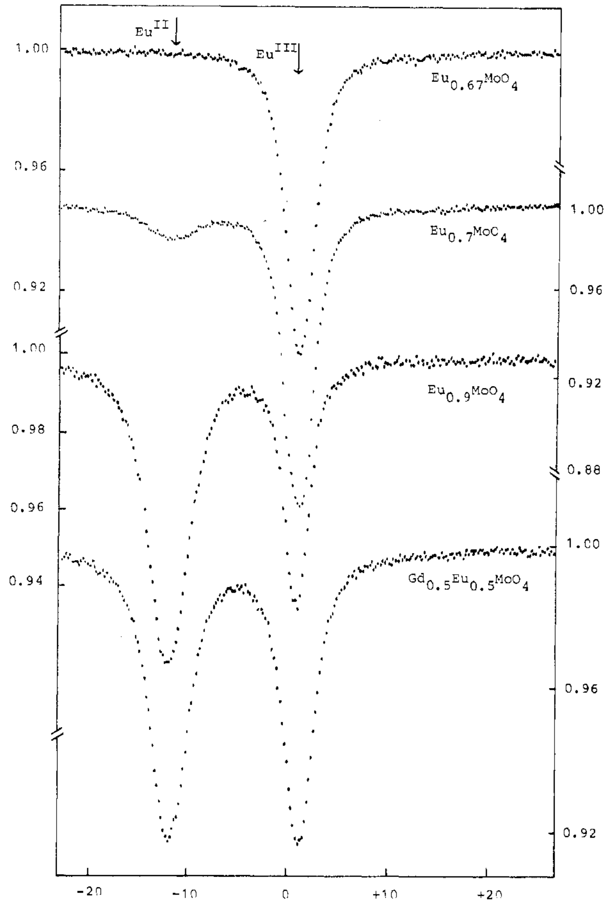

Figure 1.

nances on the assumption that both species have the same Mössbauer recoil-free fraction. The theoretical values were calculated according to the cation vacancy defect model with no contribution from Mo^V. Since saturation effects will tend to decrease the intensity of stronger peaks,[6] the concentration of Eu^{II} in $Eu_{0.9}MoO_4$ will be slightly greater than the uncorrected experimental value of 73% and the concentration of Eu^{III} in $Eu_{0.7}MoO_4$ will be slightly greater than 85%. The close agreement of these values with those calculated on the basis of the cation vacancy model rules out the possibility of any significant reduction of molybdenum to Mo^V and the presence of $[Mo^VO_4]^{3-}$ ions in these phases since this would substantially reduce the concentration of Eu^{II} required for charge balance.

In the case of "$Gd_{0.5}Eu_{0.5}MoO_4$", the two-phase mixture of limiting solid solutions was studied because no samples of the single-phase materials remained from previous work. Table I shows that 45% of all the europium is Eu^{III}. The phase $Gd_{0.85}Eu_{0.15}MoO_4$ contained predominantly $[Mo^VO_4]^{3-}$ ions, implying that both gadolinium and europium are in the 3+ state; this accounts for one-third of the Eu^{III} resonance area. The second phase ($Gd_{0.15}Cu_{0.85}MoO_4$) contains the other two-thirds of the Eu^{III} (i.e., $Eu^{III}_{0.30}$); charge balance then requires that part of the molybdenum in this phase is also present as Mo^V, the detailed formulation being $Gd^{III}_{0.15}Eu^{II}_{0.55}Eu^{III}_{0.30}Mo^V_{0.45}Mo^{VI}_{0.55}O_4$.

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Registry No. Eu_xMoO_4, 52322-41-5; $Gd_{0.5}Eu_{0.5}MoO_4$, 59753-15-0.

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Evidence for a Dissociative Mechanism in the Reaction of Glycine with $Cr(NH_3)_5H_2O^{3+}$. Ionic Strength Contributions (as a 1:1 Electrolyte) and Ion-Pairing(K_{IP}) Ability of the Glycine Zwitterion

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There is at present no general agreement as to the mechanism of substitution of H_2O in aquopentaamminechromium(III), $Cr(NH_3)_5H_2O^{3+}$,[1-4] and the reaction with glycine is of interest in further evaluating the substitution behavior of this complex. Features of the recently studied reaction of oxalate with $Cr(NH_3)_5H_2O^{3+}$ are the initial replacement of H_2O[5] at a rate comparable to that of water exchange,[2] followed by the chelation of the oxalate with displacement of ammonia.[6]

Experimental Section

Materials. The complex $[Cr(NH_3)_5H_2O](ClO_4)_3$ was prepared as previously described.[6,7] Glycine (BDH Analar) was used without further purification. Triply distilled and CO_2-free water was used in making up solutions. Lithium perchlorate was prepared from $HClO_4$ (Analar 72%) and Li_2CO_3 (reagent grade) and recrystallized.

Kinetics. Preliminary experiments on the reaction of $Cr(NH_3)_5H_2O^{3+}$ (5.8×10^{-3} M) with glycine (5.8×10^{-2} M), $[H^+] = (3.2–16) \times 10^{-4}$ M, $I = 1.00$ M, 50 °C, indicated nonretention of isosbestic points and therefore the formation of more than one product. Ion-exchange separation of reactant solutions (for details see ref 6), over periods in which there was up to 50% consumption of $Cr(NH_3)_5H_2O^{3+}$, indicated two products, $Cr(NH_3)_5(O_2CCH_2NH_3)^{3+}$ and $Cr(NH_3)_4(H_2O)(O_2CCH_2NH_3)^{3+}$, which have previously been characterized.[6] The kinetics were monitored at the 506-nm isosbestic point for the two products (ϵ 39.8 M^{-1} cm^{-1}). Concentration ranges

Table I. Rate Constants, k_{obsd}, for the Anation Reaction of Glycine with $Cr(NH_3)_5H_2O^{3+}$ at λ 506 nm, $I = 1.00$ M ($LiClO_4$)

Temp, °C	$10^3[H^+]$, M	10^3[Cr-(III)], M	$[Gly]_T$, M	10^4k_{obsd}, s^{-1}
40.0	0.50	4.0	0.15	0.30
		3.5	0.30	0.55
		4.0	0.45	0.76
		3.0	0.60	0.99
		14.0	0.60	0.99
	1.26	4.0	0.15	0.23
		4.0	0.30	0.45
		3.5	0.45	0.67
		3.5	0.60	0.86
		16.0	0.60	0.88
	3.16	4.0	0.15	0.17
		3.5	0.30	0.32
		3.0	0.45	0.48
		3.5	0.60	0.63
		16.0	0.60	0.62
47.5	0.50	4.0	0.15	0.75
		3.5	0.30	1.34
		4.0	0.45	1.85
		3.0	0.60	2.35
	1.26	4.5	0.15	0.58
		4.0	0.30	1.15
		3.0	0.45	1.70
		3.0	0.60	2.06
	3.16	4.0	0.15	0.45
		4.0	0.30	0.87
		3.5	0.45	1.32
		12.0	0.60	1.60
55.0	0.50	4.0	0.15	1.89
		3.5	0.30	3.75
		4.0	0.45	5.08
		4.0	0.60	6.15
	1.26	4.0	0.15	1.61
		4.0	0.30	2.78
		3.5	0.45	4.62
		3.0	0.60	5.27
	3.16	4.0	0.15	1.17
		3.0	0.30	2.20
		3.5	0.45	3.12
		3.0	0.60	3.93

covered were total glycine, $[Gly]_T = 0.15–0.60$ M, and free $[H^+] = (0.5–3.2) \times 10^{-3}$ M. The total perchloric acid concentration $[H^+]_T$ required in making up solutions was calculated from (1), where K_a

$$[H^+]_T = [H^+] + \frac{[Gly]_T\,[H^+]}{K_a + [H^+]} \qquad (1)$$

is the acid dissociation constant for glycine, (2). The free $[H^+]$ was

$$^+NH_3CH_2CO_2H \overset{K_a}{\rightleftharpoons} {}^+NH_3CH_2CO_2^- + H^+ \qquad (2)$$

measured on a Radiometer pH meter 4 calibrated with 10^{-3} M $HClO_4$ at $I = 1.00$ M ($LiClO_4$). Plots of log $(A_\infty - A_t)$ against time, where A_∞ was calculated from known spectra, were linear to 40–50% completion, and from the slopes (×2.303) pseudo-first-order rate constants k_{obsd} were obtained which were independent of complex concentration. The ionic strength was adjusted to 1.00 M using $LiClO_4$. When $NaClO_4$ was used, rate constants differed by 20–30%.

It was not clear at first whether the presence of the zwitterion, $^+NH_3CH_2CO_2^-$, should be taken into account or not in ionic strength calculations. From an extensive series of runs in which it was assumed that $^+NH_3CH_2CO_2^-$ (0.07–0.52 M) did not contribute to I, the kinetic interpretation gave a value of $K_a = 2.8 \times 10^{-4}$ M at 30 °C, $I = 1.00$ M ($LiClO_4$). Potentiometric measurements indicated a higher value consistent with the literature determination of 3.55×10^{-3} M at 25 °C, $I = 1.00$ M ($NaClO_4$).[8] Since the lower K_a was unacceptable, a different approach was tried in which it was assumed that the zwitterion behaves as a 1:1 electrolyte.

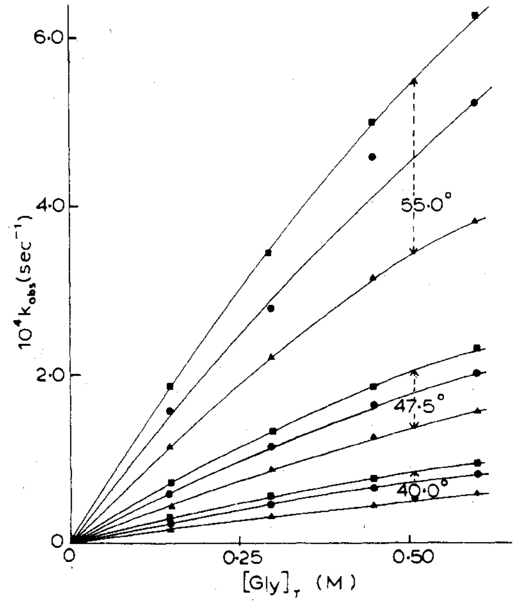

Figure 1. Dependence of pseudo-first-order rate constants, k_{obsd}, on $[Gly]_T$ for the reaction of $Cr(NH_3)_5H_2O^{3+}$ with glycine at temperatures as indicated and $[H^+] = 3.16 \times 10^{-3}$ M (▲), 1.26×10^{-3} M (●), and 0.50×10^{-3} M (■); $I = 1.00$ M ($LiClO_4$).

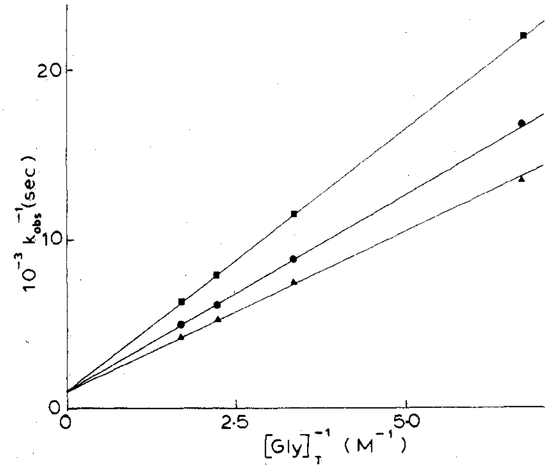

Figure 2. Linear dependence of k_{obsd}^{-1} on $[Gly]_T^{-1}$ for the reaction of $Cr(NH_3)_5H_2O^{3+}$ with glycine at 47.5 °C, $I = 1.00$ M ($LiClO_4$), and $[H^+] = 3.16 \times 10^{-3}$ M (▲), 1.26×10^{-3} M (●), and 0.50×10^{-3} M (■).

Table II. Data Obtained from Kinetics of the Reaction of Glycine with $Cr(NH_3)_5H_2O^{3+}$, $I = 1.00$ M ($LiClO_4$)

Temp, °C	$10^4k_{an}K_{IP}$ M^{-1} s^{-1}	K_{IP}, M^{-1}	10^3K_a, M
40.0	2.31 ± 0.06	0.38 ± 0.06	3.12 ± 0.13
47.5	5.73 ± 0.23	0.54 ± 0.11	3.91 ± 0.31
50.0	16.2 ± 0.9	0.66 ± 0.15	3.04 ± 0.28

Results and Discussion

$$Cr(NH_3)_5H_2O^{3+} + {}^+NH_3CH_2CO_2^- \xrightarrow{k_{obsd}} Cr(NH_3)_5(O_2CCH_2NH_3)^{3+} + H_2O \qquad (3)$$

$$Cr(NH_3)_5(O_2CCH_2NH_3)^{3+} \xrightarrow{H^+} Cr(NH_3)_4(H_2O)(O_2CCH_2NH_3)^{3+} + NH_4^+ \qquad (4)$$

Preliminary studies were consistent with a reaction sequence, (3) and (4), where subsequent reactions of $Cr(NH_3)_4(H_2O)(O_2CCH_2NH_3)^{3+}$ occur at >50% conversion of $Cr(NH_3)_5H_2O^{3+}$. At the 506-nm isosbestic point reaction 3 only is monitored. The dependence of k_{obsd} on $[H^+]$ and $[Gly]_T$, Table I and Figure 1, is consistent with an ion-pairing mechanism, (5) and (6). It was assumed that, because of the unfavorable charge factor, there is no significant ion pairing of $^+NH_3CH_2CO_2H$ with $Cr(NH_3)_5H_2O^{3+}$ and that this

Table III. Details of Ion-Pairing Constants (K_{IP}) and Rate Constants (k_{an}) for Replacement of H_2O in $Cr(NH_3)_5H_2O^{3+}$ (after Ion-Pair Formation) at 50 °C, $I = 1.00$ M ($LiClO_4$)

Reactant	$10^4k_{an}K_{IP}$, M^{-1} s^{-1}	K_{IP}, M^{-1}	10^4k_{an}, s^{-1}	Ref
$^+NH_3CH_2CO_2^-$	7.82	0.55[a]	14.2[a]	This work
$HC_2O_4^-$	6.45	1.16	5.86	5
$C_2O_4^{2-}$	29.1	4.5	6.46	5
H_2O			13.7[b]	2

[a] From data at 40, 47.5, and 55 °C. [b] Extrapolated from data at other temperatures.

$$Cr(NH_3)_5H_2O^{3+} + {}^+NH_3CH_2CO_2^- \overset{K_{IP}}{\rightleftharpoons} Cr(NH_3)_5H_2O^{3+},{}^-O_2CCH_2NH_3^+ \tag{5}$$

$$Cr(NH_3)_5H_2O^{3+},{}^-O_2CCH_2NH_3^+ \xrightarrow{k_{an}} Cr(NH_3)_5(O_2CCH_2NH_3)^{3+} + H_2O \tag{6}$$

species is nonreactive. Accordingly (7) can be derived and

$$k_{obsd} = \frac{k_{an}K_{IP}K_a[Gly]_T}{[H^+] + K_a + K_{IP}K_a[Gly]_T} \tag{7}$$

can be rearranged to give (8). Plots of k_{obsd}^{-1} against $[Gly]_T^{-1}$

$$\frac{1}{k_{obsd}} = \frac{[H^+] + K_a}{k_{an}K_aK_{IP}}\frac{1}{[Gly]_T} + \frac{1}{k_{an}} \tag{8}$$

at constant $[H^+]$ should therefore be linear with a common intercept for all $[H^+]$. This is the case as illustrated in Figure 2. The slopes give a first-order dependence on $[H^+]$ as required by (8). From a least-squares fit[9] of rate constants k_{obsd} to (7) at 40, 47.5, and 55 °C, respectively, $k_{an}K_{IP}$ and K_{IP} were obtained, Table II. The K_a term was allowed to float yielding the values shown in Table II, which are in good agreement with those determined potentiometrically, e.g., 3.42×10^{-3} M at 47.5 °C. Activation parameters for the composite term $k_{an}K_{IP}$ for formation of the glycinato complex are $\Delta H^\ddagger = 25.3 \pm 0.9$ kcal mol^{-1} and $\Delta S^\ddagger = 5.6 \pm 2.9$ cal K^{-1} mol^{-1}. Thermodynamic parameters for K_{IP} are less precise, $\Delta H = 5.1 \pm 4.7$ kcal mol^{-1} and $\Delta S = 14.5 \pm 14.6$ cal K^{-1} mol^{-1}.

Reactions of $Cr(NH_3)_5H_2O^{3+}$ in which K_{IP} has been obtained, thus allowing k_{an} for anation within the ion pair to be evaluated, are listed in Table III. Values of k_{an} are seen to lie within a narrow range (5–14) × 10^{-4} s^{-1} at 50 °C and are comparable to the rate constant for H_2O exchange on $Cr(NH_3)_5H_2O^{3+}$.[2] This observation that rate constants k_{an} for 1–, 2–, and zero charged reactants as well as the glycine zwitterion are comparable is indicative of $Cr–OH_2$ bond breaking being the dominant factor. It has previously been demonstrated that substitution reactions of $Co(NH_3)_5H_2O^{3+}$ occur by a dissociative mechanism.[10] For $Cr(H_2O)_6^{3+}$ however there is a strong case for an associative process.[3,11] The effect of different ligand environments on the mechanism of substitution and other results are discussed elsewhere.[12]

There are two additional points which emerge from this study with regard to the behavior of the glycine zwitterion, $^+NH_3CH_2CO_2^-$. First of all, the zwitterion behaves as a 1:1 electrolyte as far as ionic strength calculations are concerned. Second, values of the ion-pairing constant K_{IP} are as expected for a 3+,1– interaction.[13]

There is no evidence for chelation of glycine in the present study. For reaction times corresponding to >50% completion, product analyses indicate that there is entry of a second glycine and formation of diamine and triamine complexes. It is known that the reaction of glycine with some Cr(III) complexes at pH ~7 yields the chelated tris(glycinato) complex $Cr(Gly)_3$ along with the now well-characterized binuclear complex $Cr_2(Gly)_4(\mu OH)_2$.[14-17] By reacting excess glycine with $Cr(NH_3)_5H_2O^{3+}$ at pH ~5.0 (20 °C) we find that $Cr(Gly)_3$ is obtained.

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Registry No. $[Cr(NH_3)_5H_2O](ClO_4)_3$, 32700-25-7; glycine, 56-40-6; $Cr(NH_3)_5(O_2CCH_2NH_3)^{3+}$, 59765-77-4.

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Fluoro-Containing Complexes of Chromium(III). 7. Isolation and Some Reactions of the *cis*-Fluoroaquobis(ethylenediamine)chromium(III) Cation[1]

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The *cis*-fluoroaquobis(ethylenediamine)chromium(III) cation was first detected in solution by Fehrmann and Garner[3] during an investigation of the perchloric acid hydrolysis of the *cis*-difluorobis(ethylenediamine)chromium(III) ion. In 1968 Vaughn, Stvan, and Magnuson[4] prepared the ion in solution by utilizing the Ag^+-induced aquation of *cis*-chlorofluorobis(ethylenediamine)chromium(III). More recently the ion was again detected and characterized in solution by Wirth and Linck.[5]

Since this particular cation would appear to be a good starting material for the rapid preparation of a number of cis FX complexes, this investigation was undertaken to develop a reliable method for the synthesis of solid salts of this cation in quantity. In addition some reactions of the *cis*-fluoroaquo complex were to be studied.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive and care should be exercised when handling these materials.

Preparation of Starting Material. *cis*-Difluorobis(ethylenediamine)chromium(III) tetrafluoro(ethylenediamine)chromate(III)-1-water was prepared by the reaction of 42.0 g (0.24 mol) of