rinato skeleton appeared as single though somewhat elongated peaks of electron density. Sections of the electron density map approximately in the plane of the amide group are presented in Figure 7 along with an interpretation. A region of electron density at hydrogen-bonding distance from the amide group was interpreted as a water molecule. Upon refinement the values for R and R_w on F dropped to 0.161 and 0.209. A somewhat ill-resolved region of electron density surrounding an inversion center was interpreted as a disordered toluene molecule. It was included in the model as a rigid group (C–C = 1.392 Å, C–C–C = 120°, C–CH$_3$ = 1.521 Å) with individual isotropic thermal parameters; it behaved reasonably upon refinement. Group constraints on the pyrrole rings were released and the absorption correction applied (Gaussian integration on a 4 × 4 × 4 grid). Most of the hydrogen atoms (except for some on the linking chain and those of the water molecule) were then located in difference Fourier syntheses and were included as a fixed contribution to F_c at their idealized positions (C–H = 0.95 Å, C–C–H = 109.5°, $B_H = B_C + 1.0$ Å^2). The final four cycles of refinement used all data; all atoms except the toluene solvate molecule were assigned anisotropic thermal parameters; the number of variable parameters was 438. At convergence the values for R and R_w on F^2 were 0.103 and 0.152. The standard error in an observation of unit weight was 1.48 e^2. For the portion of data having $F_o^2 > 3\sigma(F_o^2)$ the values for R and R_w on F were 0.063 and 0.073.

The minimized function was independent of the magnitude of F_o, but it did exhibit a not unexpected but slight dependence on the magnitude of $\lambda^{-1} \sin \theta$, with low-angle data returning a higher value. One atom in the linking chain has a grossly over-accentuated thermal ellipsoid. Removal of its contribution to F_c followed by a difference Fourier synthesis failed to reveal reasons for its anomalous shape. The highest peaks in the final difference Fourier map, which was mostly flat and featureless, had heights 0.84 and 0.62 e Å^{-3} and were associated with the toluene solvate molecule.

Final nonhydrogen parameters are listed in Tables XII and XIII. Hydrogen atom parameters are given in Table XIV.[24] Table XV lists the values of $10|F_o|$ vs. $10|F_c|$.[24] A negative value indicates that $F_o^2 \le 0$.

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Supplementary Material Available: Table IV, Selected Non-Bonded Intramolecular Contacts between Porphyrinato Planes; Table V, Non-Bonded Intermolecular Contacts (<3.75 Å); Table VI, Non-bonded Intermolecular Contacts (<2.80 Å and Involving Hydrogen Atoms); Table XIV, Hydrogen Atom Parameters; Table XV, Calculated and Observed Structure Amplitudes (21 pages). Ordering information is given on any current masthead page.

The Synthesis and X-ray Crystal Structure of a Novel Vilsmeier–Haack Adduct: [Tris(2-aminoethyl)amine][3-(dimethylamino)-2-aminoacrylyl chloride]cobalt(III) Chloride–Zinc Tetrachloride–Water[1]

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Contribution from the Department of Chemistry, Faculty of Military Studies, University of New South Wales, Royal Military College, Duntroon A.C.T., 2600, and the Research School of Chemistry, The Australian National Univeristy, CANBERRA A.C.T., 2600, Australia.

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Abstract: A dimethyliminium species, formed from dimethylformamide and phosphorus oxychloride, adds at the methylene carbon of the bidentate glycinato complex (p)-[Co(tren)(gly)](ClO$_4$)$_2$ to form the (p)-[Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]$^{3+}$ ion. The crystal structure of the tetrachlorozincate chloride salt has been established by X-ray diffraction. Crystals of (p)-[Co^{III}(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]ZnCl$_4$·Cl·H$_2$O are monoclinic, space group $P2_1/n$, with a = 14.608 (3) Å, b = 15.517 (4) Å, c = 10.562 (2) Å, β = 100.75 (2)°, V = 2352.1 Å^3, and Z = 4. Full-matrix least-squares refinement gave a final value of the conventional R factor of 0.035 (4631 reflections with $I > 3\sigma(I)$). The cation contains an approximately planar *cis*-3-(dimethylamino)-2-aminoacrylyl chloride ligand, the amine function of which is trans to the tertiary nitrogen of the tren ligand. Bond lengths in the framework of this bidentate ligand are (Cl)C–O = 1.267 (4), (Cl)C–C(NH$_2$) = 1.387 (5), (NH$_2$)C–C(H) = 1.387 (5), and C–N = 1.306 (4) Å, respectively, and provide evidence of considerable π-electron delocalization. The Co–O bond length is 1.936 (2) Å and the Co–N bond lengths range from 1.938 to 1.963 Å. The conformations adopted by the tren ligand are discussed. The Vilsmeier–Haack reaction has been carried out also on the complexes (t)-[Co(tren)(gly)](ClO$_4$)$_2$ and β_2-[Co(trien)(gly)](ClO$_4$)$_2$ and a proposed mechanism for the reaction is discussed.

Introduction

The use of POCl$_3$ and disubstituted formamides to transfer a formyl group from the amide nitrogen to a substrate carbon atom has proved useful in organic syntheses since its discovery by Vilsmeier and Haack in 1927.[4] A great range of substrates undergo this addition, including aromatic and heterocyclic compounds, olefins, enamines, ketones, carboxylic acids, acetals, nitriles, and a variety of activated methylene compounds.[5]

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(2) The following abbreviations are used throughout this paper: trien, triethylenetetraamine (definition of α, β_1, and β_2 as in ref 3); en, ethylenediamine; tren, tris(2-aminoethyl)amine; gly, bidentate glycinate ion; p and t refer to two geometrical isomers which arise in tren complexes due to the oxygen of the glycinate coordinating trans to the tertiary nitrogen (t) or the primary (p) nitrogen of the tren ligand.

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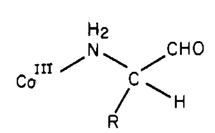
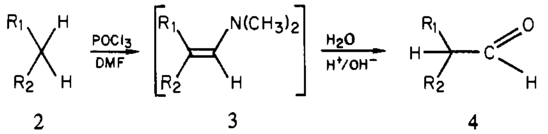
For some time in this laboratory we have been endeavoring to prepare Co(III)-protected polyfunctional aldehyde complexes (1)



1

by a variety of methods with mixed success.[6] One method involves the formylation of active methylene groups (2) by the Vilsmeier–Haack procedure,[4] and since it is known that the methylene protons in chelated glycine are activated by coordination,[7] some complexes of this type were examined. The most suitable of these was (p)-$[Co(tren)(gly)](ClO_4)_2$; (t)-$[Co(tren)(gly)](ClO_4)_2$ and β_2-$[Co(trien)(gly)](ClO_4)_2$ were also investigated briefly.

In the regular organic reaction shown below, the Vilsmeier–Haack intermediate 3 usually hydrolyzes rapidly in dilute acidic or basic aqueous solution to yield a formylated product[8] 4 (eq 1),



2 3 4 (1)

and similar chemistry could be anticipated for the chelated glycine moiety. Such *C*-formylglycine chelates would then have substantial synthetic potential for building organic molecules about the metal ion while controlling the reactivity of the coordinated amine groups and perhaps modifying other aspects of the organic chemistry.

Experimental Section

^1H NMR spectra were recorded by using a JEOL Minimar 100 MHz spectrometer (external lock) with the internal reference sodium 3-(trimethylsilyl)propane sulfonate. Fourier transform ^{13}C NMR spectra were measured by using a JEOL JNM-FX60 spectrometer (internal lock, D_2O) using dioxane as the internal reference. Values of δ are reported as positive downfield from the reference. Electronic absorption spectra were recorded with a Cary 118C Spectrophotometer as molar absorptivities ($M^{-1}\ cm^{-1}$). For ion-exchange chromatography, Dowex 50W-X2, (H^+ form, 200–400 mesh) resin was used. The dimethylformamide (DMF) was Mallinckrodt AR grade and phosphorus oxychloride was Ajax Technical Grade. All evaporations were conducted at reduced pressure by using Büchi rotary evaporators.

(p)-$[Co(tren)(gly)](ClO_4)_2$. μ-$[Co(tren)(NO_2)]_2O_2(ClO_4)_2$[9,10] was used to obtain $[Co(tren)(CO_3)]ClO_4$, via $[Co(tren)Br_2]Br{\cdot}HBr$ and $[Co(tren)(Me_2SO)Br](ClO_4)_2$. Upon treatment with $HClO_4$ (4 M, 3 equiv), being heated at 80 °C (10 min) to remove CO_2, and then the addition of NaOH (4 M, 2 equiv) to pH 7, purple needles of $[Co(tren)(OH_2)(OH)](ClO_4)_2$ separated. The mixture was cooled (4 °C, 1 h), and the hydroxoaqua complex was collected, washed with ethanol followed by ether, and air-dried. To this material (12.5 g) in H_2O (20 mL) was added glycine (2.5 g, 1.2 equiv), and the solution was heated at 80 °C for 45 min, during which time the color changed from violet to orange-red. Excess $NaClO_4$ was added and the solution cooled (4 °C, 24 h) to yield golden orange needles of (p)-$[Co(tren)(gly)](ClO_4)_2$ (12.0 g, 88%):[11] $\epsilon_{max}{}^{471} = 105$, $\epsilon_{max}{}^{343} = 100\ M^{-1}\ cm^{-1}$ (H_2O); ^{13}C NMR spectrum (D_2O) δ +117.8 (COO), −4.9 (2 C), −7.5, −21.2, −21.8 (2 C) (tren CH_2), −20.3 (glycine CH_2). Anal. Calcd for $[CoC_8N_5H_{22}O_{10}Cl_2]$: C, 20.08; H, 4.64; N, 14.64; Co, 12.33; Cl, 14.83. Found: C, 20.3; H, 4.7; N, 14.5; Co, 12.1; Cl, 14.8.

(p)- and (t)-$[Co(tren)(gly)](ClO_4)_2$. Glycine ethyl ester (5 g) was freshly prepared from the hydrochloride salt (10 g) suspended in ether (50 mL) by bubbling $NH_3(g)$ through the solution (20 min). Rapid evaporation of the ether at <25 °C gave the free crude ester which was added in one portion to a stirred aqueous solution (50 mL) of $[Co(tren)(OH_2)(OH)](ClO_4)_2$ (20 g). The mixture was allowed to stand (25 °C, 24 h), during which time the color changed from violet to a deep red-orange. The solution was then diluted with H_2O (500 mL), sorbed on a column (300 × 400 mm) of cation-exchange resin, and washed with H_2O (1 L). Elution with 1 M Na^+ (pH 7, phosphate buffer) yielded three well-separated bands. After the mixture was washed with HCl (0.5 M, 4 L) to remove Na^+, these bands were eluted separately from the column with HCl (2–3 M). The first (violet, $[Co(tren)(OH_2)Cl]^{2+}$, ~10)% was discarded. The next, orange, (p)-$[Co(tren)(gly)]^{2+}$, was crystallized as described above. The final eluate containing red (t)-$[Co(tren)(gly)]^{2+}$ was reduced to near dryness, and $HClO_4$ (6 M, 50 mL) and ethanol (50 mL) were added. The solution was cooled (4 °C, 24 h) to yield red needles of (t)-$[Co(tren)(gly)](ClO_4)_2$ (10 g, 45%):[11] $\epsilon_{max}{}^{498} = 114$, $\epsilon_{max}{}^{345} = 98$ (H_2O); ^{13}C NMR spectrum (D_2O) δ +118.8 (COO), −3.2 (2 C), −4.5, −21.9 (2 C), −22.9 (tren CH_2), −20.9 (glycine CH_2). Anal. Calcd for $[CoC_8N_5H_{22}O_{10}Cl_2]$: Co, 12.33; C, 20.08; H, 4.64; N, 14.64; Cl, 14.83. Found: Co, 12.2; C, 19.9; H, 4.9; N, 14.3; Cl, 15.1.

β_2-$[Co(trien)(gly)](ClO_4)_2{\cdot}2H_2O$ was obtained from β-$[Co(trien)(CO_3)]ClO_4$ (15 g)[12] and glycine:[13] yield, 11 g (66%); $\epsilon_{max}{}^{479} = 128$, $\epsilon_{max}{}^{347} = 141$ (H_2O); ^{13}C NMR spectrum (D_2O) δ +117.6 (COO), −13.0, −14.2, −16.4, −17.7, −19.0, −20.1 (trien CH_2), −25.2 (glycine CH_2). Anal. Calcd for $[CoC_8N_5H_{26}O_{12}Cl_2]$: Co, 11.46; C, 18.68; H, 5.10; N, 13.62; Cl, 13.79. Found: Co, 10.7; C, 18.6; H, 4.7; N, 12.8; Cl, 13.5.

Vilsmeier–Haack Acylations. The following general procedure was employed. The Co(III) complex (5 g) in DMF (50 mL) was cooled to −10 °C (salt/ice), and $POCl_3$ (20 mL) was added dropwise over 40 min with stirring, while maintaining the temperature below 5 °C. Following the addition, the solution was stirred at 25 °C for 20 min, then cautiously poured into a mixture of ice (40 g) and water (400 mL), and finally sorbed on a column (100 × 40 mm) of H^+ resin and washed well (H_2O).

(1) **(p)-$[Co(tren)(gly)](ClO_4)_2$**: eluting the column with HCl (3 M, 4 L) yielded first mauve (p)-$[Co(tren)(glyH)(Cl)]^{2+}$ (this was crystallized as the dichloride salt from HCl/H_2O and characterized by its ^1H and ^{13}C NMR spectra and elemental analysis). Anal. Calcd for $[CoC_3N_5H_{23}O_2Cl_3]$: Co, 15.25; C, 24.84; H, 6.00; N, 18.11; Cl, 27.55. Found: Co, 15.2; C, 24.7; H, 5.8; N, 18.0; Cl, 27.7. The major species eluted from the column (orange 3+ ion) was taken to dryness and crystallized twice from H_2O by using excess $ZnCl_2/HCl$ (3 M), to yield golden orange needles of (p)-[Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]$Cl{\cdot}ZnCl_4{\cdot}H_2O$ (5.2 g, 81%): $\epsilon_{max}{}^{468} = 146$ (H_2O); ^1H NMR spectrum (D_2O) δ 2.6–3.6 (br, 12 H, tren CH_2); 3.26, 3.52 (3 H, 3 H, $N(CH_3)_2$), 4.8–5.1 (br, 2 H, NH_2), 7.64 (s, 1 H, =C(H)–N); ^{13}C NMR spectrum (D_2O) δ +110.1 (COCl), +91.6 (=C—N), +40.1 (NH_2-C=); −16.4, −26.4 (−$N(CH_3)_2$); −4.5 (2 C), −7.5, −20.9 (2 C), −21.6 (tren CH_2). Anal. Calcd for $[CoC_{11}H_{29}N_6O_2ZnCl_6]$: Co, 9.60; C, 21.50; H, 4.76; N, 13.68; Cl, 34.64. Found: Co, 9.5; C, 21.6; H, 5.0; N, 13.6; Cl, 34.6. This complex was also isolated as a mixed chloride perchlorate salt from $H_2O/HClO_4$ (6 M). Anal. Calcd for $[CoC_{11}N_6H_{29}O_{10}Cl_4]$: Co, 9.71; C, 21.75; H, 4.82; N, 13.84; Cl, 23.40. Found: Co, 9.9; C, 22.4; H, 5.0; N, 13.7; Cl, 23.5.

(2) (t)-**$[Co(tren)(gly)](ClO_4)_2$**: eluting the column with HCl (3 M) yielded violet $[Co(tren)(OH_2)Cl]^{2+}$, which was discarded, followed by a deep red-orange 3+ species. This was taken to dryness and crystallized from H_2O by using excess $ZnCl_2/HCl$ (3 M) to yield red needles of (t)-[Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]$ZnCl_4{\cdot}Cl{\cdot}2H_2O$ (4.0 g, 63%): $\epsilon_{max}{}^{474} = 160$ (H_2O); ^1H NMR spectrum (D_2O) δ 2.4–3.2 (br, 12 H, tren CH_2), 2.92, 3.18 (3 H, 3 H, $N(CH_3)_2$), 5.0–5.3 (br, 2 H, NH_2), 6.91 (s, 1 H, =C(H)—N); ^{13}C NMR spectrum (D_2O) δ +110.1 (COCl), +91.6 (=CN), +40.1 (NH_2—C=), −16.5, 26.4 ($N(CH_3)_2$), −3.3 (2 C), −4.5, −21.9 (3 C) (tren CH_2). Anal. Calcd for $[CoC_{11}N_6H_{31}O_3ZnCl_6]$: Co, 9.32; C, 20.89; H, 4.94; N, 13.29; Cl, 33.66. Found: Co, 9.3; C, 21.6; H, 4.9; N, 13.2; Cl, 33.2.

(3) **β_2-$[Co(trien)(gly)](ClO_4)_2{\cdot}2H_2O$**: eluting the column with HCl (3 M) yielded a single orange 3+ species. This was taken to dryness and

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Table I. Crystal Data and Details of Data Collection

a, Å	14.608 (3)
b, Å	15.517 (4)
c, Å	10.562 (2)
β, deg	100.75 (2)
cell vol, $Å^3$	2352.1
Z	4
d_{obsd},[a] g cm^{-3}	1.74 (1)
d_{calcd}, g cm^{-3}	1.73
space group	$P2_1/n$
$\mu_{\mathrm{MoK}\alpha}$, cm^{-1}	24.6
cryst faces with perpendicular dists (mm) between pairs of faces in parentheses	{010}.069, {210}.038, {2–10}.050, {10–1}.263
range of transmission factors[b]	0.854–0.924
radiatn	Mo Kα
wavelength, Å	Kα_1 = 0.7093, Kα_2 = 0.713 59
monochromator	graphite ($2\theta_{\mathrm{m}} = 12.16°$)
takeoff angle, deg	3
cryst counter dist, cm	28.5
scan speed (2θ)	2°/min
scan method	$\theta/2\theta$
scan width[c]	from $(2\theta - 0.5)°$ to $(2\theta + \Delta + 0.5)°$
total background time (t_{b}), s	20
"standard" measurements	3 every 97 reflctns
"standard" indices	(–1,10,–1), (1,0,–7), (–11,0,–1)
cryst stability	<9% isotropic intensity loss
2θ range	3–60°
data collected	$(h,k,\pm l)$
no. of intensities measd	7727
no. of reflctns with $I > 3\sigma(I)$	4631
P^2 [d]	21.5 ± 1
temp, °C	21.5 ± 1
$R_{\mathrm{s}}(=\Sigma\sigma_{\mathrm{s}}\vert(F_{\mathrm{o}})\vert\Sigma\vert F_{\mathrm{o}}\vert)$	0.033

[a] By flotation in bromoform/CCl_4. [b] Applied to $\vert F_{\mathrm{o}}\vert$. [c] Δ is the separation (deg) of the Mo Kα_1 and MoKα_2 peaks at the 2θ value of the reflection. [d] Weights $w = \sigma^{-2}(F_{\mathrm{o}})$ (reflection esd) $= \{[\sigma(I)/(Lp)^2 + P^2\vert F_{\mathrm{o}}\vert^4\}^{1/2}/2\vert F_{\mathrm{o}}\vert$ where $\sigma(I) = [\mathrm{CT} + (t_{\mathrm{p}}/t_{\mathrm{b}})^2(B_1 + B_2)]^{1/2}$ with the intensity, I, $= [\mathrm{CT} - (t_{\mathrm{p}}/t_{\mathrm{b}})(B_1 + B_2)]$ where CT is the total peak count in t_{p} (s), B_1 and B_2 are individual background counts in $t_{\mathrm{b}}/2$ (s), and Lp (Lorentz–polarization correction) $= (\cos^2 2\theta + \cos^2 2\theta_{\mathrm{m}})/2 \sin 2\theta$. $\sigma_{\mathrm{s}}(F_{\mathrm{o}})$ (reflection esd from counting statistics along) $= \sigma(I)/2Lp\vert F_{\mathrm{o}}\vert$.

crystallized from $HClO_4$ (6 M, 20 mL) by the addition of ethanol (80 mL) to yield small blocklike crystals of β_2-[Co(trien)(3-(dimethylamino)-2-aminoacrylyl chloride)]$(ClO_4)_3 \cdot H_2O$: $\epsilon_{\mathrm{max}}^{476} = 132$ (H_2O); ^1H NMR spectrum (D_2O) δ 2.4–3.4 (br, 12 H, trien CH_2), 3.25, 3.54 (3 H, 3 H, $N(CH_3)_2$), 6.6–7.0 (br, 2 H, NH_2), 7.63 (s, 1 H, $=CH-N$); ^{13}C NMR spectrum (D_2O) δ +110.1 (COCl), +91.3 ($=CH-N$), +40.0 ($NH_2-C=$), –16.5, –26.4 ($N(CH_3)_2$), –12.7, –14.0, –16.0, –17.4, –18.7, –24.5 (trien CH_2). Anal. Calcd for $[CoC_{11}N_6H_{29}O_{14}Cl_4]$: Co, 8.80; C, 19.70; H, 4.36; N, 12.54; Cl, 21.19. Found: Co, 9.1; C, 20.4; H, 4.5; N, 12.5; Cl, 21.2.

X-ray Structure Determination of (p)-[Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)]$(ZnCl_4)Cl \cdot H_2O$

Collection and Reduction of X-ray Intensity Data. Preliminary Weissenberg and precession photographs show diffraction symmetry $2/m$ and systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicated the space group $P2_1/n$ (an alternate setting of the space group $P2_1/c$). The accurate cell dimensions and crystal orientation matrix were derived by least-squares refinement, from the optimized 2θ, ω, and χ angles for each of 12 high-angle reflections (Mo Kα radiation, $2\theta > 40°$). Intensities were measured on a Picker FACS-I computer-controlled four-circle diffractometer.[14] Details of the crystal data and data collection techniques are given in Table I. The intensities were corrected for absorption and reduced to $\vert F_{\mathrm{o}}\vert$ as described previously.[15]

Solution and Refinement of the Structure. Scattering factors for the atoms and the real and imaginary parts of the anomalous dispersion corrections were taken from ref 16. The computer programs used are described elsewhere.[15] The MULTAN[17] program package was used to compute normalized structure factors, E_{hkl}, and to determine the phases of the 300 largest normalized structure factors. The E map with the highest figure of merit showed clearly both the tetrachlorozincate ion and the cobalt atom with its first coordination sphere. The remaining atomic positions were determined from successive difference Fourier syntheses. Full-matrix least-squares refinement of atomic positional parameters as well as anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms reduced R $(=\sum\vert\vert F_{\mathrm{o}}\vert - \vert F_{\mathrm{c}}\vert\vert/\sum\vert F_{\mathrm{o}}\vert)$ to the final value of 0.035 ($R_{\mathrm{w}} = {}^1/_2(\sum w(\vert F_{\mathrm{o}}\vert - \vert F_{\mathrm{c}}\vert)^2/\sum w\vert F_{\mathrm{o}}\vert^2) = 0.043$). The function minimized was $\sum w(\vert F_{\mathrm{o}}\vert - \vert F_{\mathrm{c}}\vert)^2$ with weights, w, as defined in ref 15.

In the final cycle no parameter varied by $>0.4\sigma$ for a hydrogen atom or $>0.01\sigma$ otherwise. A difference synthesis calculated at the end of the refinement showed no feature with an absolute value of >0.4 e $Å^{-3}$. The quantity ${}^1/_2[\sum w(\vert F_{\mathrm{o}}\vert - \vert F_{\mathrm{c}}\vert)^2/(n - m)]$ was 1.18. The minimized function was approximately independent of $\lambda^{-1} \sin \theta$ or $\vert F_{\mathrm{o}}\vert$, and a comparison of $\vert F_{\mathrm{o}}\vert$ with $\vert F_{\mathrm{c}}\vert$[18] showed extinction to be unimportant. The final atomic parameters are listed in Table II. Structure factor listings are deposited.[18]

Results and Discussion

(p)-[Co(tren)(gly)]$(ClO_4)_2$ was synthesized stereospecifically from [Co(tren)(OH_2)(OH)]$(ClO_4)_2$ and glycine. The p and t isomers were readily separated chromatographically from a ~40:60 p/t mixture derived from the hydroxaqua complex and glycine ethyl ester.[11] The glycinato complexes were characterized by elemental analyses, ^1H and ^{13}C NMR, and electronic spectroscopy. The orange p and red t isomers have been described previously;[11] their configurations are known from single-crystal X-ray studies.[19]

The Vilsmeier–Haack reaction was performed on the p isomer by using excess $POCl_3$ in dimethylformamide, yielding an orange complex which eluted from cation-exchange resin as a 3+ ion. The reaction was complete in minutes at -10 °C. The product crystallized in good yield (~80%) as tetrachlorozincate chloride hydrate, triperchlorate, or chloride diperchlorate salts, and elemental analysis indicated the cation stoichiometry $[CoC_{11}N_6H_{27}OCl]^{3+}$. The ^1H NMR spectrum showed a low-field singlet (1 H) at δ 6.64, attributable to an α-enamine proton $-CH=N$, and two field independent (60, 100 MHz) singlets at δ 3.26 (3 H) and 3.52 (3 H), consistent with diastereotopic methyl groups of a $=N^+(CH_3)_2$ moiety. These assignments were confirmed by the ^1H coupled and decoupled ^{13}C NMR spectra. The singlet at δ 91.6 was split into a doublet (J_{CH} = 174.5 Hz) in the coupled spectrum, characteristic of a one-proton α coupling, $-CH=N$. The singlets at δ -16.4 (1 C) and -26.4 (1 C) each split into a quartet (J_{CH} = 125 Hz), consistent with inequivalent methyl groups. Further, a weakly coupled carbon signal was located at δ 40.1 (d, J_{CH} = 6 Hz). This was indicative of a fully substituted unsaturated carbon β to a methine, i.e., $=C-CH$. Finally, the ^{13}C signal observed at δ 110.1 was in the region expected for O-bound carboxylate. It appeared ~8 ppm upfield from its usual position (~118 ppm) which implied some delocalization of the C=O π electrons. The Vilsmeier reaction had clearly taken place, but the location of the covalently bound Cl atom in the cation was not unequivocally defined by the preliminary data. The Cl atom was obviously rather kinetically inert. Both the visible spectrum and the lack of reactivity with Ag^+ indicated that it was not bound to Co(III), and an X-ray crystallographic study was therefore undertaken to establish its structure.

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Table II. Final Atomic Parameters with Estimated Standard Deviations in Parentheses[a]

ATOM	X/A	Y/B	Z/C	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
CO	0.88573(3)	0.83264(3)	0.18502(4)	0.00212(2)	0.00176(1)	0.00377(4)	0.00013(1)	0.00075(2)	0.00020(2)
CL(1)	1.15418(6)	0.82375(6)	0,07136(10)	0.00340(4)	0.00349(4)	0.01059(11)	-0.00012(3)	0.00339(5)	0.00087(5)
O(1)	0.0954(1)	0.8661(1)	0.1188(2)	0.0026(1)	0.0023(1)	0.0060(2)	0.0000(1)	0.0015(1)	0.0005(1)
N(1)	0.8180(2)	0.9368(2)	0.1253(2)	0.0029(1)	0.0020(1)	0.0049(2)	0.0003(1)	0.0007(1)	0.0005(1)
N(2)	0.7774(2)	0.7971(2)	0.2545(3)	0.0023(1)	0.0026(1)	0.0056(3)	0.0001(1)	0.0010(1)	0.0004(2)
N(3)	0.9386(2)	0.8985(2)	0.3400(3)	0.0028(1)	0.0024(1)	0.0049(3)	0.0001(1)	0.0006(2)	-0.0001(1)
N(4)	0.8372(2)	0.7842(2)	0.0146(3)	0.0032(1)	0.0024(1)	0.0044(2)	0.0000(1)	0.0009(2)	0.0001(1)
N(5)	0.9545(2)	0.7269(2)	0.2404(3)	0.0025(1)	0.0021(1)	0.0040(2)	0.0004(1)	0.0009(1)	0.0001(1)
N(6)	1.0862(2)	0.5743(2)	0.2073(3)	0.0028(1)	0.0023(1)	0.0083(3)	0.0003(1)	0.0015(2)	-0.0004(2)
C(1)	0.7232(2)	0.9346(2)	0.1629(3)	0.0027(2)	0.0028(1)	0.0068(3)	0.0008(1)	0.0007(2)	-0.0001(2)
C(2)	0.7229(2)	0.8750(2)	0.2751(3)	0.0026(2)	0.0031(1)	0.0060(3)	0.0005(1)	0.0006(2)	-0.0003(2)
C(3)	0.8756(3)	1.0102(2)	0.1860(4)	0.0035(2)	0.0020(1)	0.0081(4)	0.0002(1)	0.0012(2)	0.0001(2)
C(4)	0.9084(3)	0.9904(2)	0.3268(4)	0.0033(2)	0.0024(1)	0.0075(4)	0.0000(1)	0.0008(2)	-0.0010(2)
C(5)	0.8085(3)	0.9370(2)	-0.0186(3)	0.0039(2)	0.0031(2)	0.0049(3)	0.0009(1)	0.0009(2)	0.0012(2)
C(6)	0.7779(3)	0.8488(2)	-0.0669(3)	0.0036(2)	0.0038(2)	0.0043(3)	0.0007(1)	0.0005(2)	0.0005(2)
C(7)	1.0534(2)	0.8047(2)	0.1296(3)	0.0024(1)	0.0028(1)	0.0051(3)	-0.0002(1)	0.0012(2)	-0.0002(2)
C(8)	1.0383(2)	0.7260(2)	0.1845(3)	0.0023(1)	0.0023(1)	0.0046(3)	0.0001(1)	0.0008(2)	0.0001(1)
C(9)	1.0906(2)	0.6537(2)	0.1678(3)	0.0026(1)	0.0029(1)	0.0059(3)	0.0000(1)	0.0012(2)	-0.0003(2)
C(10)	1.1401(4)	0.5068(3)	0.1565(6)	0.0060(3)	0.0028(2)	0.0167(7)	0.0007(2)	0.0052(4)	-0.0011(3)
C(11)	1.0265(3)	0.5436(3)	0.2943(5)	0.0048(2)	0.0030(2)	0.0116(5)	0.0009(2)	0.0030(3)	0.0012(3)
ZN	0.44323(3)	0.76465(3)	0.13146(4)	0.00315(2)	0.00257(2)	0.00451(3)	-0.00013(1)	0.00108(2)	-0.00011(2)
CL(2)	0.48174(7)	0.80432(7)	0.33729(8)	0.00525(5)	0.00476(5)	0.00453(7)	-0.00070(4)	0.00132(5)	-0.00037(5)
CL(3)	0.35802(6)	0.85844(6)	-0.00864(8)	0.00375(4)	0.00337(4)	0.00649(8)	0.00050(3)	0.00107(5)	0.00036(4)
CL(4)	0.57346(6)	0.74306(6)	0.04379(9)	0.00275(4)	0.00469(4)	0.00702(8)	-0.00012(3)	0.00121(4)	-0.00137(5)
CL(5)	0.35679(7)	0.64004(6)	0.11220(10)	0.00554(5)	0.00306(4)	0.00917(10)	-0.00138(4)	0.00337(6)	-0.00102(5)
CL(6)	0.20375(6)	0.40192(5)	0.89251(9)	0.00400(4)	0.00278(4)	0.00745(9)	-0.00087(3)	0.00033(5)	0.00020(4)
O(2)	0.3642(2)	0.4272(3)	0.1417(4)	0.0044(2)	0.0051(2)	0.0100(4)	0.0006(1)	-0.0007(2)	0.0004(2)

ATOM	X/A	Y/B	Z/C	B(A**2)
H(1)	0.708(2)	0.992(2)	0.177(3)	2.1(7)
H(2)	0.684(2)	0.910(2)	0.087(4)	2.8(8)
H(3)	0.754(2)	0.901(2)	0.357(3)	2.3(7)
H(4)	0.664(2)	0.855(2)	0.284(3)	2.4(7)
H(5)	0.793(3)	0.763(2)	0.330(4)	3.3(8)
H(6)	0.743(3)	0.762(3)	0.199(4)	5.0(11)
H(7)	0.837(2)	1.062(2)	0.177(3)	2.5(7)
H(8)	0.931(3)	1.013(2)	0.149(3)	3.3(8)
H(9)	0.959(3)	1.027(2)	0.358(4)	3.8(9)
H(10)	0.857(2)	0.995(2)	0.374(3)	2.5(7)
H(11)	1.005(3)	0.898(2)	0.347(4)	3.4(8)
H(12)	0.925(2)	0.879(2)	0.406(4)	2.6(8)
H(13)	0.767(2)	0.977(2)	-0.050(3)	2.2(7)
H(14)	0.871(2)	0.951(2)	-0.038(3)	2.8(8)
H(15)	0.714(3)	0.837(2)	-0.061(3)	3.0(8)
H(16)	0.785(3)	0.845(2)	-0.152(4)	3.5(9)
H(17)	0.881(3)	0.774(3)	-0.016(4)	3.6(10)
H(18)	0.804(3)	0.738(2)	0.023(4)	3.3(9)
H(19)	0.971(3)	0.725(2)	0.321(4)	3.4(9)
H(20)	0.916(4)	0.681(4)	0.206(5)	8,3(15)
H(21)	1.134(2)	0.664(2)	0.123(3)	2.4(7)
H(22)	1.177(3)	0.466(3)	0.222(5)	6.4(13)
H(23)	1.097(3)	0.468(3)	0.106(4)	5.4(12)
H(24)	1.170(3)	0.529(3)	0.107(5)	4.9(12)
H(25)	0.969(4)	0.527(3)	0.250(5)	7.5(15)
H(26)	1.050(3)	0.493(3)	0.331(4)	3.9(9)
H(27)	1.028(3)	0.584(3)	0.358(4)	5.0(12)
H(28)	0.361(4)	0.472(4)	0.154(6)	7.5(19)
H(29)	0.323(4)	0.406(3)	0.069(6)	7.5(15)

[a] Anisotropic temperature factors take the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

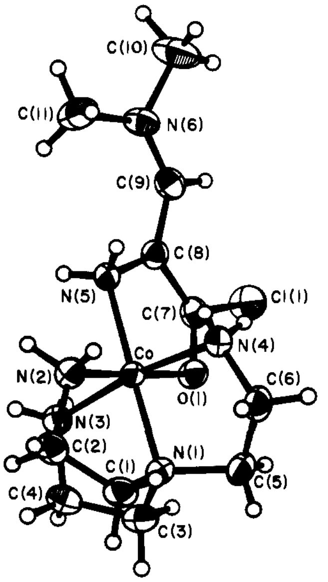


Figure 1. Molecular geometry and atom numbering in the [Co(tren)(3-(dimethylamino)-2-aminoacrylyl chloride)] cation. Hydrogen atoms are unlabeled.

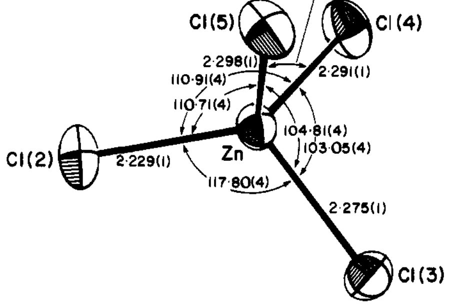


Figure 2. Geometry and atom numbering in the tetrachlorozincate anion.

Single-Crystal X-ray Structure of the Vilsmeier Adduct. The crystal contains discrete molecular and ionic units linked by hydrogen bonding. The molecular geometry of the cation is shown in Figure 1, and bond lengths and angles are listed in Table III. The molecular geometry of the tetrachlorozincate anion is shown in Figure 2.

The Cation. The neutral ligand 3-(dimethylamino)-2-aminoacrylyl chloride is bonded to the Co^{III}(tren) moiety with the bound oxygen atom trans to a primary nitrogen of the tren ligand (p isomer). The geometry at cobalt is very approximately octahedral. Deviations of atoms from the three coordination planes of the

Table III. Bond Lengths (Å) and Angles (Deg) in the Cation[a]

Co-N(1)	1.938 (3)	O(1)-Co-N(1)	93.7 (1)
Co-N(2)	1.944 (3)	O(1)-Co-N(2)	178.6 (1)
Co-N(3)	1.963 (3)	O(1)-Co-N(3)	86.4 (1)
Co-N(4)	1.958 (3)	O(1)-Co-N(4)	87.3 (1)
Co-N(5)	1.955 (3)	O(1)-Co-N(5)	85.4 (1)
Co-O(1)	1.936 (2)	N(1)-Co-N(2)	87.5 (1)
N(1)-C(1)	1.511 (4)	N(1)-Co-N(3)	86.3 (1)
N(1)-C(3)	1.490 (4)	N(1)-Co-N(4)	86.8 (1)
N(1)-C(5)	1.501 (4)	N(1)-Co-N(5)	178.4 (1)
N(2)-C(2)	1.486 (4)	Co-N(4)-C(6)	110.2 (2)
N(3)-C(4)	1.492 (4)	Co-N(3)-C(4)	110.8 (2)
N(4)-C(6)	1.490 (4)	Co-N(2)-C(2)	108.7 (2)
C(1)-C(2)	1.504 (5)	Co-N(1)-C(1)	109.5 (2)
C(3)-C(4)	1.507 (5)	Co-N(1)-C(3)	106.5 (2)
C(5)-C(6)	1.500 (5)	Co-N(1)-C(5)	106.1 (2)
C(7)-O(1)	1.267 (4)	N(2)-C(2)-C(1)	107.7 (3)
C(7)-Cl(1)	1.723 (3)	N(3)-C(4)-C(3)	108.8 (3)
C(7)-C(8)	1.387 (5)	N(4)-C(6)-C(5)	108.2 (3)
C(8)-N(5)	1.456 (4)	N(1)-C(1)-C(2)	111.0 (3)
C(8)-C(9)	1.387 (4)	N(1)-C(3)-C(4)	108.6 (3)
C(9)-N(6)	1.306 (4)	N(1)-C(5)-C(6)	108.0 (3)
N(6)-C(10)	1.470 (5)	Co-O(1)-C(7)	110.5 (2)
N(6)-C(11)	1.461 (5)	O(1)-C(7)-Cl(1)	116.1 (2)
		O(1)-C(7)-C(8)	123.0 (3)
C(8)-C(9)-N(6)	131.4 (3)	C(8)-C(7)-Cl(1)	120.9 (2)
C(9)-N(6)-C(11)	125.4 (3)	C(7)-C(8)-N(5)	111.9 (3)
C(9)-N(6)-C(10)	119.6 (4)	C(7)-C(8)-C(9)	121.6 (3)
C(11)-N(6)-C(10)	114.9 (3)	C(9)-C(8)-N(5)	125.8 (3)
		Co-N(5)-C(8)	108.1 (2)

[a] Estimated standard deviations are given in parentheses.

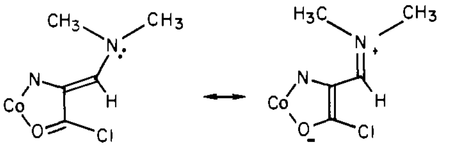
octahedron and dihedral angles between these planes are listed in Table IV. The three Co–N(amine) bonds trans to amino groups do not differ appreciably in length, although the Co–N(2) bond trans to the coordinated acid chloride function is marginally shorter (by ~0.02 Å). N(2) does not appear to be involved in the hydrogen-bonding network (Table V) in contrast to the N(3), N(4), and N(5). The bond length from cobalt to secondary or tertiary nitrogen atoms in multidentate chelating amines is usually shorter than the bond length from cobalt to primary amine nitrogen, and this trend is evident here; Co–N(1) is shorter (by ~0.02 Å) than Co–N(3) and Co–N(4). The Co–O(1) bond length in the acid chloride function (1.936 (2) Å) lies at the higher end of the range, found in previously reported work for carboxylate complexes.[20] Finally, the mean C–N bond length for the tren ligand (1.495 Å) is very similar to equivalent quantities in (tren)Co^{III} [19,21] and (Metren)Co^{III} [22] complexes.

The three five-membered chelate rings of the Co(tren) moiety adopt the enantiomorphic (δλλ) and (δλδ) conformations (Figure 1). This is one of the four energetically distinct enantiomorphic sets.

Strain-energy minimization calculations on the model cation $[Co(tren)(en)]^{3+}$ indicate that the observed set of conformations of the tren ligand is energetically more stable by at least 2.7 kcal mol^{-1} over the next highest energy set. A summary of the results of these calculations is deposited as supplementary material,[18] and the subject is not pursued further here other than to note that this same (δλλ) configuration, or its enantiomorph (δλδ) (or both), is observed in all other octahedral metal tren complexes reported to date, e.g., $[Co(tren)(NCS)_2]NCS$[23] and (p)- and (t)-$[Co(tren)(gly)](ClO_4)_2$.[19] A different situation appears to pertain for five-coordinated complexes, e.g., $[Cu(tren)(SCN)]NCS$[24] and $[Co(Me_6tren)Br]^+$,[25] which adopt the (λλλ) set, but we have not carried out strain-energy calculations for the trigonal-bipyramidal geometry.

The bidentate ligand 3-(dimethylamino)-2-aminoacrylyl chloride is approximately planar. Deviations from the mean coordination planes about N(6), C(9), and C(8) are given in Table IV. Maximum electron delocalization and exact planarity are compromised by steric interactions between the methyl group $C(11)H_3$ (Figure 1) and the amine group $N(5)H_2$ which lead to the distortion observed. However, it is clear that equivalent ligand planarity for the other possible ligand configuration, *E*, where the dimethylamino and amino functions are trans with respect to the C(8)—C(9) bond, is less likely because of an even closer approach of two groups, the methyl group and the chlorine atom of the acid chloride function.

The N(6)—C(10) and N(6)—C(11) bond lengths (mean 1.465 Å) are not significantly different from the usual value for a C—N(sp^2) bond length (1.472 Å).[26] However, the N(6)—C(9) bond length (1.306 Å) approaches more closely that expected for a carbon–nitrogen double bond.[27,28] The C(8)—C(9) and C(7)—C(8) bond lengths do not differ significantly and lie between accepted values for C(sp^2)═C(sp^2) (1.33 Å)[26] and C(sp^3)—C(sp^3) (1.51 Å),[26] being similar to the C—C bond length in benzene (1.395 Å).[26] The C(7)—O(1) bond length (1.267 Å) lies between values observed for the shorter (1.233 Å)[27] and longer (1.358 Å)[26] C—O bonds in carboxylic acids and esters. These observations together with the approximate planarity of the ligand suggest approximately equal contributions from the resonance structures **5**. This structure is stabilized both by coordination to cobalt and



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by the presence of the dimethylamino group. A comparison of bond lengths for the C═C—C(═O)Cl framework with equivalent quantities in acrylyl chloride[29] emphasizes the delocalization. The C(7)—Cl(1) bond length (1.723 Å) is similar to that in acrylyl chloride.

The angles C(9)-N(6)–C(11), C(8)–C(9)–N(6), and N(5)–C(8)-C(9) are all larger than the "ideal" value of 120°. This is probably to avoid too close an approach of the methyl group $C(11)H_3$ to the coordinated amine function $N(5)H_2$. Even with these distortions the N(19)...H(27) contact (2.34 Å) is short (Table V).

The Tetrachlorozincate Anion. The Zn–Cl bond lengths fall within the range reported in other determinations of the geometry of the tetrachlorozincate ion.[22,30-32] The anion exhibits a distorted tetrahedral geometry. The angles Cl(2)-Zn–Cl(4), Cl(2)–Zn–Cl(5), and Cl(4)–Zn–Cl(5) are approximately the tetrahedral value (109°28′), but Cl(2)–Zn–Cl(3) is larger and the remaining two angles are smaller, indicating the major distortion arises from moving Cl(3) away from Cl(2) toward the midpoint of the Cl(4)–Cl(5) vector. It is not possible to relate this distortion, or indeed the significant variation in Zn–Cl bond lengths, to the hydrogen-bonding scheme (Table V). There is, however, a close

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Table IV

Least-Squared Planes and Distances (Å) of Atoms from Those Planes

plane	atoms defining plane	dist of atoms from the plane							
i	Co, N(3), N(4), N(1), N(5)	Co	−0.052	N(3)	0.063	N(4)	0.064		
		N(1)	−0.041	N(5)	−0.033				
ii	Co, N(2), O(1), N(1), N(5)	Co	−0.005	N(2)	−0.014	O(1)	−0.015		
		N(1)	0.017	N(5)	0.017				
iii	Co, O(1), N(2), N(3), N(4)	Co	−0.041	O(1)	−0.067	N(2)	−0.058		
		N(3)	0.083	N(4)	0.083				
iv	O(1), C(7), C(8), N(5)	O(1)	0.016	C(7)	−0.030	C(8)	0.026		
		N(5)	−0.013	Co	0.213	Cl(1)	−0.169		
		C(9)	0.298	N(6)	0.432	C(11)	0.185	C(10)	0.95
v	N(6), C(9), C(10), C(11)	N(6)	−0.020	C(9)	0.008	C(10)	0.006		
		C(11)	0.007	C(8)	0.184				
vi	C(8), C(7), C(9), N(5)	C(8)	−0.052	C(7)	0.017	C(9)	0.019		
		N(5)	0.017	N(6)	0.012	C(11)	−0.212		
		C(10)	0.334						
vii	C(9), C(8), N(6), H(21)	C(9)	0.001	C(8)	0.000	N(6)	0.000		
		H(21)	0.000	C(7)	0.046	N(5)	0.170		
		C(10)	0.236	C(11)	0.139				

Angles (Deg) between Planes

i and ii	80.8	i and iii	86.7	ii and iii	89.0
ii and iv	8.9	v and vii	8.9	vi and vii	4.1
v and vi	12.9				

Table V. Probable Hydrogen-Bonding Interactions and Short Nonbonded Contacts[a]

(a) Hydrogen Bonding Interactions

A···H-B	A···B, Å	A···H, Å	H-B, Å	<A···H-B, deg
Cl(1)···H(17)$^{\text{I}}$-N(4)$^{\text{I}}$	3.37	2.62	0.79 (5)	159
Cl(4)···H(19)$^{\text{II}}$-N(5)$^{\text{II}}$	3.38	2.59	0.84 (4)	157
Cl(5)···H(12)$^{\text{II}}$-N(3)$^{\text{II}}$	3.37	2.58	0.82 (4)	162
Cl(6)···H(18)$^{\text{III}}$-N(4)$^{\text{III}}$	3.14	2.35	0.89 (4)	148
Cl(6)···H(20)$^{\text{III}}$-N(5)$^{\text{III}}$	3.18	2.26	0.94 (5)	166
Cl(5)···H(28)-O(2)	3.32	2.64	0.71 (6)	161
Cl(6)···H(29)$^{\text{IV}}$-O(2)$^{\text{IV}}$	3.21	2.31	0.94 (5)	160
O(2)···H(11)$^{\text{V}}$-N(3)$^{\text{V}}$	2.89	1.95	0.96 (4)	166

angles (deg) around Cl(6)		angles (deg) around O(2)		angles (deg) around Cl(5)	
H(18)···Cl(6)···H(20)	64	H(28)-O(2)···H(19)	109	H(12)···Cl(5)···H(28)	92
H(18)···Cl(6)···H(29)	79	H(29)-O(2)···H(19)	116	Zn-Cl(5)···H(12)	83
H(2)···Cl(6)···H(29)	142	H(28)-O(2)-H(29)	116	Zn-Cl(5)···H(28)	145

(b) The Shorter Nonbonded Interactions (Å)

H(19)···H(27)	2.34	Cl(4)···H(15)	2.90
H(19)···H(28)$^{\text{VI}}$	2.28	Cl(5)···H(16)$^{\text{I}}$	2.89
Cl(1)···Cl(3)$^{\text{VII}}$	3.29	Cl(5)···H(3)$^{\text{II}}$	2.90
Cl(2)···H(23)$^{\text{VI}}$	2.89	Cl(6)···H(10)$^{\text{I}}$	2.79
Cl(2)···H(4)	2.93	Cl(6)···H(1)$^{\text{I}}$	2.82
Cl(3)···H(19)$^{\text{II}}$	2.96	Cl(6)···H(6)$^{\text{III}}$	2.88
Cl(3)···H(26)$^{\text{VI}}$	2.96	Cl(6)···H(25)$^{\text{III}}$	2.91
Cl(3)···H(1)$^{\text{VII}}$	2.97		
Cl(4)···H(6)	2.72		

[a] The superscripts refer to atoms related to those in Table II by the operations: (I) $x - {}^1/_2$, $1{}^1/_2 - y$, ${}^1/_2 + z$; (II) $x - {}^1/_2$, $1{}^1/_2 - y$, $z - {}^1/_2$; (III) $1 - x$, $1 - y$, $1 - z$; (IV) x, y, $1 + z$; (V) $1{}^1/_2 - x$, $-{}^1/_2 + y$, ${}^1/_2 - z$; (VI) $1{}^1/_2 - x$, ${}^1/_2 + y$, ${}^1/_2 - z$; (VII) $1 - x$, $2 - y$, $-z$; (VIII) $1 + x$, y, z.

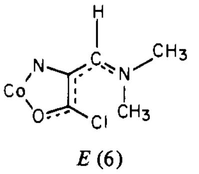
approach of Cl(1) in the cation to Cl(3) of the tetrachlorozincate anion (Table V), and it seems likely that this gives rise to the distortion. The differences in Zn-Cl bond lengths then appear to result from an attempt to equalize Cl···Cl nonbonded contacts within the tetrachlorozincate anion. This is an example of large variations in bond length arising from a spacially anisotropic distribution of nonbonding (van der Waals) contacts.

Crystal Packing. The packing of ions in the crystal lattice (Figure 3) is probably determined by hydrogen-bonding interactions. The more important of these, using the shorter A···B contacts and α···H-B angles approaching 180° as the criteria, are marked by thin lines in Figure 3, and the details are listed in Table V. Although the chloride ion Cl(6) on the basis of the above criteria appears to be involved in three hydrogen-bonding interactions, the angles subtended by the hydrogen atoms at chlorine deviate substantially from those expected for sp^3-hybridized chlorine. The shorter nonbonding contacts (<2.5 Å for H···H, <3.0 Å for Cl···H, and <3.6 Å for Cl···Cl) are also listed in Table V. Only the Cl(1)···Cl(3) contact (3.29 Å) is exceptionally short.

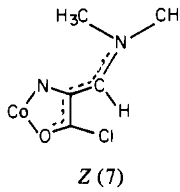
Isomerism and Stability. The visible spectrum of the cation shows its first ligand field band at 471 nm (ϵ = 105 M^{-1} cm^{-1}) consistent with the (p)-[Co(tren)O-N] structure.[19] The t isomers absorb at significantly lower energies ($\lambda_{\text{max}} \approx 500$ nm).[10] Furthermore, the ^{13}C NMR spectrum also appears to be diagnostic of the p configuration. A consistent relationship has been observed between the [Co(tren)O-N] topology and the chemical shifts of the tren methylene carbon atoms in several p and t isomeric pairs where the geometry is known.[21] In the trans isomers, the carbons α to the tertiary amine center absorb at δ -3.3 (2 C) and -5.0 (1 C) and those α to the primary amine at δ -21.9 (2 C) and -22.9 (1 C). For the p isomers, the absorption pattern δ -4.6 (2 C), -7.3 (1 C) and δ -20.9 (2 C), -21.6 (1 C) is distinctly different, and the Vilsmeier products clearly fit into this category. The 2:1 intensity ratios are also consistent with the mirror symmetry of the molecular structure through a plane incorporating the Vilsmeier chelate.

It is clear that neither the chromophore nor the complex topology were affected much by attack from the Vilsmeier-Haack reagent on the glycine ligand.

The delocalization observed should restrict rotation about the C-NMe$_2$ bond and thereby account for the diastereotopic methyl group. It would also accommodate the inertness of the Cl$^-$ ion to hydrolysis since the ligand is now akin to a less reactive chloro vinyl ether rather than a reactive acid chloride. The delocalization therefore raises an additional isomer problem since the ligand can adopt either the *E* (**6**) or *Z* (**7**) configuration. The isolated complex was isomerically pure *Z* although both *Z* and *E* forms



E (**6**)



Z (**7**)

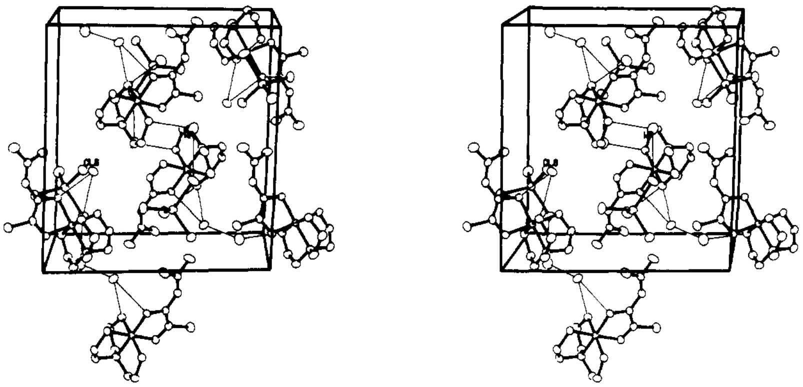


Figure 3. Geometry and atom numbering in the tetrachlorozincate anion. Thin lines represent possible hydrogen-bonding interactions.

appear to have been observed in solution. The ^1H NMR spectrum of the crude product isolated almost quantitatively from the reaction mixture showed two low-field singlets at δ 7.64 and 6.86. There was a corresponding doubling of the $=N^+(CH_3)_2$ signals (δ 3.26, 3.52 and δ 3.86, 3.06). Neither set of signals corresponded to those for free dimethylformamide nor dimethylamine. The relative intensity of the two sets varied somewhat from synthesis to synthesis but was generally ~1:4, the major component being that isolated. The ^1H NMR spectrum of the mixture following elution from an ion-exchange resin with HCl and evaporation to dryness showed only the presence of the isolated isomer along with (p)-$[Co(tren)(NH_2CH(CHO)CO_2)]^{2+}$. These results imply the existence of the less stable *E* isomer which apparently hydrolyzes to the aldehyde complex. All attempts to crystallize or isolate this minor species by chromatography (in neutral or acid solutions) failed. It was clear also that the two isomers do not equilibrate. The addition of the pure major adduct to the isomer mixture yields a corresponding change in the ^1H NMR spectrum of the *Z* isomer but not that of the *E* isomer, and no further change occurs with time in neutral solution. In acid solution, the absorptions ascribed to the minor component are replaced completely by signals attributable to the formyl glycine complex and free dimethylamine; i.e., its hydrolysis is faster than its conversion to the stable *Z* form.

An examination of Dreiding models indicated that the *Z* isomer would be less sterically hindered than the *E* isomer. In the latter, the Cl atom and one of the methyl groups interact significantly. The ligand may be required to distort substantially to alleviate this congestion with consequent loss of energy of delocalization. Such a rationale is consistent with the relative stabilities of the two isomers to hydrolysis.

Other Products. By carrying out the Vilsmeier reaction on (p)-$[Co(tren)(gly)]^{2+}$ at higher temperatures (20–40 °C) and by using excess of the premixed reagents ($DMF/POCl_3$), we obtained a purple side product also (1–10% yield). It chromatographed as a 2+ ion and was crystallized as its dichloride salt. Elemental analysis indicated the cation stoichiometry $[CoC_8N_5H_{23}O_2Cl]$. ^1H, ^{13}C NMR, and visible spectra indicated quite clearly that it was (p)-$[Co(tren)Cl(NH_2CH_2COOH)]Cl_2$, i.e., N-bound unidentate glycine. The proposed mechanism for the Vilsmeier reaction (vide infra) can accommodate its formation, but presently we just note it as another synthetic route to a N-bound unidentate glycinato complex. Usually the N-bound form, e.g., $[Co(NH_3)_5(NH_2CH_2COOH)]^{3+}$, is prepared from glycine ester, which binds initially through nitrogen; subsequent hydrolysis of the ester group gives the acid.[33] This novel aspect of the Vilsmeier procedure has been extended to $[Co(en)_2(NH_2(CH_2)_2S)]^{2+}$ where $POCl_3/DMF$ has been used to open the aminothiol ring to produce *cis*-$[Co(en)_2Cl(NH_2(CH_2)_2SH)]^{2+}$;[21] dangling thiols are generally difficult to prepare in Co(III) chemistry since they readily reduce Co(III) to Co(II) and trigger ligand disproportionation reactions.

Other Vilsmeier Adducts. The Vilsmeier reaction seems generally applicable to $[CoN_4(gly)]^{2+}$ complexes. The anticipated products were obtained from *cis*-β_2-(*RR*,*SS*)-$[Co(trien)(gly)](ClO_4)_2$ and (t)-$[Co(tren)(gly)](ClO_4)_2$ in good yield. By comparison with the (p)-$[Co(tren)(gly)]^{2+}$ adduct of known configuration (*Z*), their spectroscopic properties again indicated the *Z* configuration for the 3-(dimethylamino)-2-aminoacrylyl chloride ligand and retention of the remaining ligand geometry. No *E* isomers were observed, even transiently. Work in progress on the $[Co(en)_2(gly)]^{2+}$ system indicated that routes to chiral complexes of the type Λ-$[Co(en)_2NH_2CH(CHO)CO_2]^{2+}$, derived from the Vilsmeier adduct by hydrolysis, are viable and these appear to be extremely useful synthetic intermediates in the synthesis of some natural products.

Mechanism. Vilsmeier–Haack formylations are believed to occur via an initial reaction between $POCl_3$ and dimethylformamide to form the chlorodimethyliminium salt (**8**)[4,34–37] (Scheme I). There appears to be some debate about the most abundant form of the salt, whether Cl^- or $OPOCl_2^-$ is bound to the C atom for example.[34–37] However, there is agreement that an equilibrium is established relatively slowly ($k \leq 10^{-3}$ M^{-1} s^{-1} at −20 °C) but neither the rates nor the equilibrium constants are consistent.[34,36] The results are dependent on the method of measurement. In one study[34] the kinetics for the Vilsmeier intermediate formation and decay were deduced from the rate of its reaction with the substrate. Depending on the substrate, either the formation of the intermediate or its capture could be made rate determining. In another study,[36] the intermediate's production and supposedly its equilibration were established by NMR techniques and subsequently by infrared and Raman spectroscopy.[37] The discrepancies which exist may reside in the different phenomena which the different strategies essentially measure. It suffices for this study to note that the intermediate is apparently in equilibrium with $POCl_3$ and DMF on a long time scale and that $POCl_3$ is not consumed all that rapidly.

Aliphatic carboxylic acids of the type RCH_2COOH are inert to formylation under these conditions unless R activates the adjacent methylene carbon to electrophilic attack, i.e., R should be an aromatic or heteroatomic group, halogen or carboxylate derivative.[38] Attempts to formylate glycine hydrochloride and its *N*-methyl, *N*-benzyl, and *N*-phenyl derivatives by using **8** (4 h at 80 °C followed by 2 h at 125 °C in excess $DMF)_{39}$ resulted in trimethinium salts of the type depicted in Scheme I. The Vilsmeier intermediate is proposed[39,40] as the electrophile introducing the Cl atom to give the acid chloride (**9**) in the first instance and thereby the lability into the methylene group. The equilibrium

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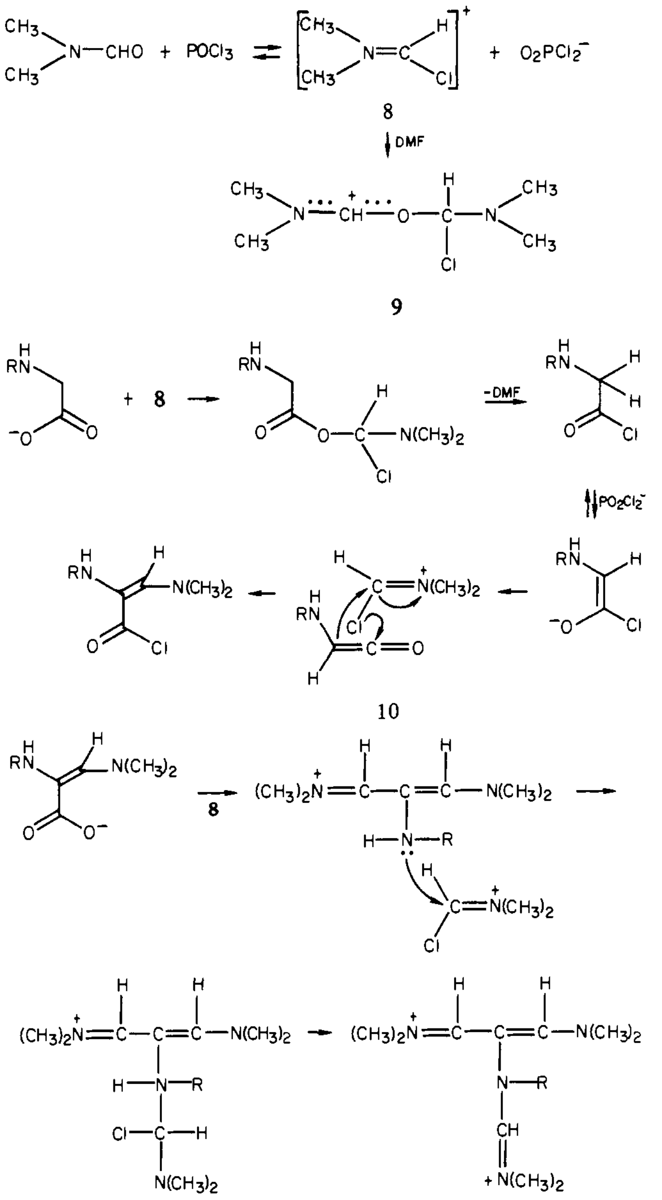
Scheme I

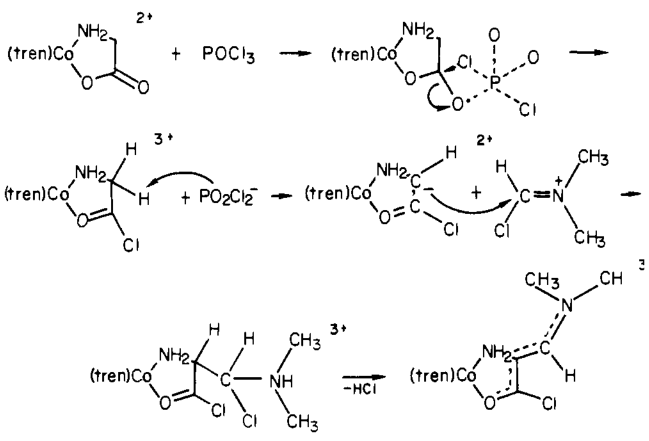


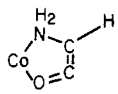
concentration of $POCl_3$ or residual $POCl_3$ alluded to earlier could also accommodate the formation of the acid chloride.

Removal of a proton by the base $PO_2Cl_2^-$ and loss of HCl to give the ketene **10** has also been advanced.[39,40] The ketene is then required to react with the Vilsmeier cation to give the variety of iminium ions displayed in Scheme I.

When glycine is chelated to the Co(III) ion, the course of the Vilsmeier reaction changes. Two centers appear to be attacked (although only one $(CH_3)_2N{=}CH-$ residue is introduced) and no decarboxylation takes place. Binding the lone pair of electrons of the N atom to the metal ion gives the N center some ammonium ion character, and binding the carboxylate ion gives it some ester character. Both effects act to labilize the methylene protons. However, it still requires a good base to effect the proton removal ($t_{1/2}$ (25 °C) $\approx 10^3$–10^4 s for H exchange in 0.01 M OH^-).[7] Preliminary formation of the chelated acid chloride, however, would labilize the protons further, and this could be achieved by addition of free $POCl_3$, present in the reaction mixture, to the exo carboxylate oxygen or possibily by addition of the Vilsmeier intermediate at the same site. Of these two proposals, the former seems the more likely and the reaction Scheme II is couched in these terms. What appears very unlikely indeed is the subsequent formation of the supposed amino ketene intermediate **10** (Scheme I). The geometry required to coordinate such an intermediate through the terminal N and O atoms would lead to a grossly distorted and hence improbable ketene moiety

Scheme II





It follows that if this mechanism applies for the unchelated amino acid derivatives, it is inappropriate at least for the chelated molecules.

Attack of electrophiles at the exo oxygen of chelated amino acids is not without precedent. Chelated amino acid esters can be made this way by using $SOCl_2$ in alcohols presumably via a transient chelated acid chloride.[41] Once the acid chloride is formed, it is more than conceivable that $O_2PCl_2^-$ could remove a proton from the methylene group and create a chelated carbanion which could then readily capture the Vilsmeier cation (Scheme II). Elimination of HCl yields the final Vilsmeier adduct which is unusually stable.

The stability of the chelated aminoacrylyl chloride is one of the most striking features of the chemistry. The cobalt(III) ion clearly has a substantial electron-withdrawing effect since it is this ion which labilizes the methylene protons in the parent chelated glycinate ion. It exerts this effect through both the carboxylate moiety and the coordinated amino group cooperatively. Neither group alone is sufficient to labilize the protons. It can be expected therefore that the same electron-withdrawing effect will exist for the chelated Vilsmeier adduct. Such an effect would be expected to enhance nucleophilic attack by water at this moiety leading to hydrolysis of dimethylamine and Cl^- to yield the chelated aldehyde. Since this is not observed except in concentrated aqueous acids, or base, we presume the difference between the normal behavior expected in organic systems and that observed here lies in the difference between a proton and the Co(III) center in promoting the hydrolysis. Protonation of the oxygen and the amine groups would be expected to be much more effective than the case for the metal ion in activating hydrolysis. Relatively therefore, the metal ion protects the ligand from protonation and thereby relatively stabilizes it. The metal ion must also activate the ligand to hydrolysis relative to the uncoordinated neutral molecule but much less so than a proton.

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Supplementary Material Available: A table of strain-energy minimization calculations, a figure of structures A–F, and a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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