Comparison with data published for analogous complexes shows that the averaging process at the high-temperature limit may be attributed to inversion at the tricoordinate sulfur atoms: $[Fe_2(CO)_5L(\mu\text{-}S\text{-}t\text{-}Bu)_2]_2$,[25] L = CO, ΔG = 77 kJ mol^{-1} and L = Ph_3P, ΔG = 66 kJ mol^{-1}; *trans*-$[Ru(CO)(\mu\text{-}SCH_2Ph)(C_5H_5)]_2$,[26] ΔG = 58.7 kJ mol^{-1}. For these complexes the inversion barriers may be correlated with the angles subtended at the bridging sulfur. Thus in strongly metal-metal-bonded structures, the very acute M-S-M angles appear to impede inversion as expected if the process requires a trigonal-planar transition state at sulfur.[27] So that this hypothesis could be tested, the complex $W_2Cl_4(\mu\text{-}S\text{-}i\text{-}Bu)_2(\mu\text{-}S)(SMe_2)_2]$[28] has been synthesized. It is isoelectronic and isostructural with $W_2Cl_4(\mu\text{-}SEt)_2(\mu\text{-}S)(C_4H_8S)_2$ for which the W—S(Et)—W bond angles are ca. 62°, due to the short W═W bond.[12] For this complex, which differs from **1** in the smaller W-S-W angle, one would predict a higher barrier to inversion at sulfur. Consistent with this prediction, only one isomer can be detected in solution over the accessible range of temperatures.

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Registry No. 1, 80288-48-8; $WCl_4(Me_2S)_2$, 53922-82-0.

Supplementary Material Available: A listing of observed and calculated structure factors and $\sigma(F)$ values and Tables S1 and S2 containing the coordinates of the phenyl carbon and hydrogen atoms, respectively (28 pages). Ordering information is given on any current masthead page.

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Structural and Kinetic Trans Influence in (Amino acidato)cobalt(III) Complexes? α-Hydrogen Exchange and Crystal and Molecular Structure of *mer*-Tris(glycinato)cobalt(III) Dihydrate

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The rate of the α-hydrogen-exchange reaction of glycinato ligands in *mer*-tris(glycinato)cobalt(III) has been found to be different for the three stereochemically different glycinato ligands. This rate difference is interpreted as resulting from the trans influence; the carboxyl oxygen ligand is more effective than the amino nitrogen ligand in labilizing the trans α-hydrogen. The relevance of the trans influence to the α-hydrogen-exchange reaction has been tested and seems to be substantiated for several (glycinato)cobalt(III) chelates. To see if the above reactivity difference is reflected in the molecular structure, we performed the single-crystal X-ray analysis of *mer*-$[Co(H_2NCH_2CO_2)_3]\cdot 2H_2O$ to R_F = 0.047 and R_{wF} = 0.062 for 2101 reflections with $|F| > 3[\sigma(|F|)]$. The crystal is orthorhombic, $Pna2_1$, with a = 15.331 (2) Å, b = 13.205 (2) Å, c = 11.606 (2) Å, and Z = 8. The three glycinato ligands are coordinated in the meridional geometry to complete a nearly octahedral cobalt center. The Co-N bond trans to oxygen is shortened relative to the average length of mutually trans Co-N bonds by 0.022 (3) Å. This structural feature correlates with the rate data, and it seems probable that the kinetic trans influence as found for the α-hydrogen-exchange reaction results, at least partially, from the structural trans influence.

The activation of α-hydrogens of amino acids[2] and peptides[3] through coordination to metal ions has been studied by several workers. The works in this area have been reviewed recently by Pasini and Casella.[4] Previously, we have found,[5] and recently Norman and Phipps[6] confirmed, that the exchange reaction of the α-hydrogens of three stereochemically different glycinato ligands in *mer*-tris(glycinato)cobalt(III), *mer*-[Co(gly)$_3$], proceeds at unequal rates. At that time we could give no explanation to it nor an assignment to the proton NMR spectrum of this compound in deuterium oxide. Similarly, as we will show here, Norman and Phipps could not make a correct assignment.

On the other hand, we have subsequently shown that the chemical shift of α-hydrogens of amino acids and α-aminocarboxylates coordinated to cobalt(III) can be explained quantitatively, in the absence of valence angle distortion, by the effect of the magnetic anisotropy of the central cobalt ion.[7]

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The effect on proton chemical shifts can be assessed quantitatively by the use of either ^{59}Co chemical shifts or visible absorption spectral data.[8] The theory based on this effect has been applied to several cobalt(III) complexes successfully.[8,9] More recently, the result of the magnetic susceptibility measurements on $[Co(NH_3)_5Cl]Cl_2$ by Bramley et al.[10] confirmed the dominance of this effect upon the chemical shift of ammine hydrogens. Juranic et al.[8] refined the theory advanced by us so as to be suitable for practical applications. These works have enabled us to assign firmly the proton resonances of *mer*-$[Co(gly)_3]$. The assignment and the reactivity of stereochemically different glycinato ligands in *mer*-$[Co(gly)_3]$ have led us to assume the participation of the trans influence in such hydrogen-exchange reactions. Additionally, the X-ray structure analysis on *mer*-$[Co(gly)_3]\cdot 2H_2O$ has suggested that the trans influence in such reactions results, at least partially, from the structural trans influence. This paper describes the results of α-hydrogen-exchange reactions of glycinato ligands chelated to cobalt(III), as well as the crystal and molecular structure of *mer*-$[Co(gly)_3]\cdot 2H_2O$ and its implication in such reactions.

Experimental Section

Materials. *mer*-$[Co(gly)_3]\cdot 2H_2O$,[11] C_1-*cis*(*N*),*cis*(*O*)-$[Co(gly)_2(acac)]$,[12] and C_1-*cis*(*N*),*cis*(*O*)-$Na[Co(gly)_2(ox)]$[13] were prepared by the literature methods, where acac = 2,4-pentanedionate ion and ox = oxalate ion.

Nuclear Magnetic Resonance. The NMR spectra were obtained either on a JEOL PS-100 spectrometer (100 MHz) or on a Varian T-60 spectrometer (60 MHz). Chemical shifts are referenced to internal sodium 4,4-dimethyl-4-silapentane-1-sulfonate. The hydrogen-exchange reaction of *mer*-$[Co(gly)_3]$ was measured for basic deuterium oxide solution (pD 10.77 with Na_2CO_3) containing 2.06 mg/mL of the complex. The exchange rates were determined from the plots of ln (intensity) vs. time, where intensity refers to the integrated intensity of the glycine peak relative to that of the external reference, (polyethylene glycol)-2000 in 35% HCl.

The exchange reactions of the C_1 isomers of $[Co(gly)_2(acac)]$ and $Na[Co(gly)_2(ox)]$ were followed similarly. Though accurate rates for these two complexes could not be obtained owing to very small rate constants and possible decomposition, it was confirmed that in both compounds the glycine methylene hydrogens resonating at higher magnetic fields were exchanged with deuterium more rapidly than those resonating at lower fields.

X-ray Data Measurements of *mer*-$[Co(H_2NCH_2CO_2)_3]\cdot 2H_2O$. From Weissenberg photographs taken with Ni Kα radiation (λ = 1.6591 Å), the crystals were orthorhombic and the systematic absences $h = 2n + 1$ for ($h0l$) and $k + l = 2n + 1$ for ($0kl$) indicated the space group C_{2v}^{9}-$Pna2_1$ (No. 33) or D_{2h}^{16}-$Pnam$ (No. 62 with an alternate setting). It was estimated from crystal-packing considerations ($c/2$ = 5.803 Å) that the space group is $Pna2_1$, because the *mer*-$[Co(gly)_3]$ complex should possess neither $\bar{1}$ nor m symmetry. The crystal used for the data collection had the dimension of 0.30 × 0.21 × 0.09 mm. The cell constants were obtained by a least-squares method using 25 independent reflections on a Rigaku AFC-5 automated four-circle diffractometer with Mo Kα radiation (λ = 0.71069 Å) monochromated by a graphite plate. The cell constants were determined to be a = 15.331 (2) Å, b = 13.205 (2) Å, c = 11.606 (2) Å, and V = 2349.6 (6) Å^3. The measured density of 1.791 g/cm^3 obtained by a flotation technique using a $CHCl_3$–$CHBr_3$ mixed solution agrees well with the calculated value of 1.793 g/cm^3 for $Z = 8$. The intensity data were collected by the ω–2θ scan technique to a maximum 2θ value of 55° at a scan rate of 8°/min (50 kV, 170 mA). Out of 3120 independent reflections measured, 2101 reflections of $|F| > 3[\sigma(|F|)]$ were selected and used in the structure determination. No absorption correction was made since the linear absorption coefficient of μ = 15.61 cm^{-1} was low.

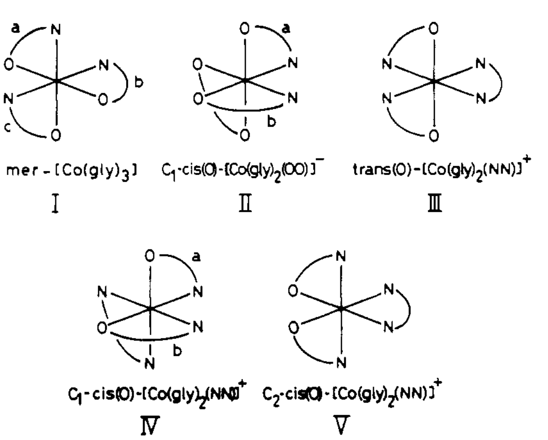

Figure 1. Glycinato ligand positions in the cobalt(III) complexes examined here; OO = acac$^-$ or ox^{2-} and NN = en or tn.

Structure Determination and Refinement. The positions of the two crystallographically independent cobalt atoms were determined from the three-dimensional Patterson map. The amino and carboxyl groups of glycinato ligands around the cobalt atoms were revealed in subsequent Fourier maps. Four cycles of the block-diagonal least-squares refinement, using anisotropic thermal parameters for individual atoms without hydrogen atoms, reduced an R_F value, $\sum||F_o| - |F_c||/\sum|F_o|$, to 0.072. The anomalous dispersion corrections for the cobalt atoms for Mo Kα radiation were included; $\Delta f'$ = 0.30 and $\Delta f''$ = 0.97. Further refinement using both positional and anisotropic thermal parameters for Co, O, N, and C atoms and isotropic thermal parameters for H atoms converged an R_F value to 0.047 and an R_{wF} value, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, to 0.062. Equivalent refinement of the enantiomeric model (obtained by changing the sign of all coordinates) converged with R_F = 0.048, but abnormal bond distances and angles around the cobalt atoms were noted.[14] A final difference Fourier map revealed no peaks higher than 0.6 e/Å^3. The quantity minimized was $\sum w(|F_o| - k|F_c|)^2$. The weighting scheme used was $w = (\sigma_{cs}{}^2 + (a|F_o|)^2 + b|F_o|)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics for each reflection and the values of a and b used in the final refinement are 0.03 and 0.3, respectively. All the atomic scattering factors were taken from ref 15. The final atomic parameters and final anisotropic thermal parameters are given in Tables I and II (Table II is supplementary material). The computer programs used were FOUR-MMM (Fourier synthesis) and HBLS-IV (least-squares calculation) with slight modification.[16,17] ORTEP drawing was carried out by the computer system XTL in a Syntex R3 automated four-circle diffractometer. A table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

The proton NMR spectrum of *mer*-$[Co(gly)_3]$ (I of Figure 1) in deuterium oxide exhibits two resonances at δ 3.68 and 3.42 due to glycinato methylene hydrogens with an intensity ratio of 2:1, when measured at 60 MHz. The low-field peak is split, at 100 MHz, into two marginally resolved peaks. The amino hydrogens are exchanged with deuterium rapidly. Application of the theory of chemical shift based on the

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Table I. Final Atomic Parameters for *mer*-[Co(gly)$_3$]·2H$_2$O

atom	x	y	z	$B^{a,b}$
Co(A)	0.92893 (6)	0.73964 (6)	0.76250 (9)	
O(A1)	1.0207 (4)	0.7638 (4)	0.6553 (6)	
O(A2)	0.9405 (4)	0.5963 (4)	0.7406 (5)	
O(A3)	0.8362 (4)	0.7169 (4)	0.8654 (5)	
O(A4)	1.0884 (4)	0.8860 (5)	0.5586 (6)	
O(A5)	1.0037 (4)	0.4573 (4)	0.8068 (6)	
O(A6)	0.6928 (4)	0.7052 (6)	0.8773 (7)	
N(A1)	0.9241 (4)	0.8839 (5)	0.7828 (6)	
N(A2)	1.0117 (4)	0.7214 (5)	0.8881 (6)	
N(A3)	0.8406 (5)	0.7404 (5)	0.6428 (6)	
C(A1)	0.9796 (7)	0.9333 (7)	0.6946 (11)	
C(A2)	1.0360 (6)	0.8578 (6)	0.6307 (8)	
C(A3)	1.0299 (6)	0.6139 (7)	0.9044 (9)	
C(A4)	0.9905 (5)	0.5511 (6)	0.8120 (8)	
C(A5)	0.7554 (5)	0.7205 (7)	0.6920 (9)	
C(A6)	0.7597 (5)	0.7166 (7)	0.8200 (8)	
Co(B)	0.82105 (6)	0.25046 (7)	0.74070 (9)	
O(B1)	0.7306 (4)	0.2707 (4)	0.8499 (5)	
O(B2)	0.8184 (3)	0.1071 (4)	0.7634 (5)	
O(B3)	0.9145 (3)	0.2388 (4)	0.6344 (5)	
O(B4)	0.6599 (4)	0.3877 (5)	0.9500 (6)	
O(B5)	0.7534 (4)	−0.0323 (4)	0.7045 (7)	
O(B6)	1.0551 (4)	0.2033 (5)	0.6218 (7)	
N(B1)	0.8202 (4)	0.3948 (5)	0.7200 (6)	
N(B2)	0.7379 (4)	0.2296 (5)	0.6166 (6)	
N(B3)	0.9088 (4)	0.2559 (5)	0.8616 (6)	
C(B1)	0.7654 (6)	0.4422 (6)	0.8098 (8)	
C(B2)	0.7146 (5)	0.3631 (6)	0.8757 (7)	
C(B3)	0.7047 (5)	0.1247 (6)	0.6277 (8)	
C(B4)	0.7618 (5)	0.0589 (6)	0.7014 (7)	
C(B5)	0.9913 (5)	0.2131 (6)	0.8113 (8)	
C(B6)	0.9895 (5)	0.2189 (6)	0.6801 (8)	
O(W1)	0.7813 (5)	0.9573 (5)	1.0184 (7)	
O(W2)	0.8517 (5)	0.5986 (5)	0.4431 (7)	
O(W3)	0.6131 (5)	0.9105 (5)	0.5488 (7)	
O(W4)	0.9414 (6)	0.0592 (6)	0.4530 (10)	
H(NA11)	0.873 (7)	0.910 (8)	0.765 (10)	0.2 (23)
H(NA12)	0.934 (5)	0.898 (6)	0.848 (8)	0.1 (16)
H(NA21)	1.055 (7)	0.746 (7)	0.872 (11)	0.1 (24)
H(NA22)	0.985 (6)	0.752 (6)	0.953 (9)	0.8 (19)
H(NA31)	0.851 (6)	0.789 (7)	0.613 (9)	1.1 (20)
H(NA32)	0.863 (6)	0.695 (7)	0.591 (8)	0.5 (18)
H(CA11)	0.938 (7)	0.987 (8)	0.629 (11)	2.7 (26)
H(CA12)	1.011 (9)	0.998 (12)	0.723 (12)	3.9 (30)
H(CA31)	1.096 (8)	0.613 (10)	0.899 (13)	5.1 (36)
H(CA32)	1.022 (9)	0.585 (9)	0.992 (13)	4.7 (35)
H(CA51)	0.707 (8)	0.760 (8)	0.676 (12)	3.4 (30)
H(CA52)	0.729 (10)	0.655 (11)	0.636 (15)	5.8 (39)
H(NB11)	0.845 (7)	0.440 (8)	0.714 (9)	1.7 (23)
H(NB12)	0.794 (7)	0.412 (8)	0.639 (11)	2.2 (24)
H(NB21)	0.689 (7)	0.289 (9)	0.613 (11)	3.1 (28)
H(NB22)	0.767 (7)	0.239 (8)	0.548 (10)	0.4 (24)
H(NB31)	0.926 (6)	0.327 (7)	0.882 (9)	1.4 (21)
H(NB32)	0.891 (6)	0.208 (7)	0.928 (9)	0.9 (19)
H(CB11)	0.777 (7)	0.476 (8)	0.855 (11)	2.5 (25)
H(CB12)	0.730 (7)	0.472 (7)	0.778 (10)	1.9 (23)
H(CB31)	0.647 (7)	0.124 (8)	0.683 (11)	2.6 (25)
H(CB32)	0.729 (8)	0.091 (9)	0.555 (11)	3.4 (29)
H(CB51)	1.035 (7)	0.243 (7)	0.839 (9)	1.2 (21)
H(CB52)	0.994 (5)	0.154 (6)	0.838 (8)	0.1 (17)

[a] Isotropic temperature factor, in units of Å^2. [b] Anisotropic parameters are listed in Table II (supplementary material).

magnetic anisotropy of cobalt(III), coupled with the crystallographically determined geometry of glycinato chelates, predicts that the a hydrogens of I should resonate at a higher magnetic field (about δ 3.34) and the chemical shifts of the b and c hydrogens should be close (both at about δ 3.60).[7,8]

The methylene hydrogens of C_1-*cis*(*N*),*cis*(*O*)-[Co(gly)$_2$(acac)] (II) appear at δ 3.35 and 3.55,[12] and they are assigned to the a and b glycines, respectively. The assignment for the C_1 isomer of [Co(gly)$_2$(ox)]$^-$ (II) follows similarly; the a glycine is assigned to the peak at a higher magnetic field (δ 3.43) and the b glycine to the low-field peak (δ 3.58[13]).

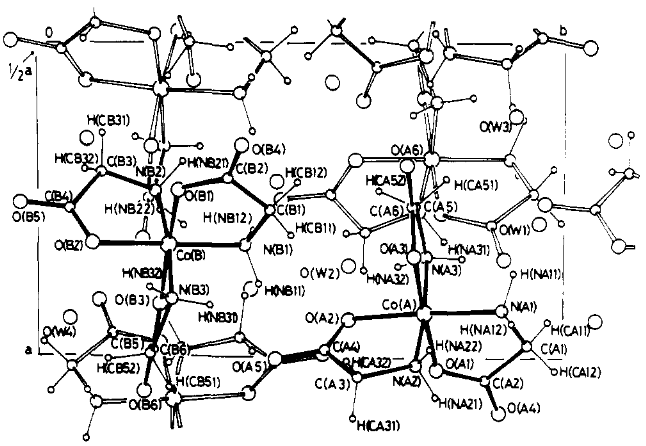

Figure 2. Crystal packing in *mer*-[Co(gly)$_3$]·2H$_2$O.

Hydrogen-Exchange Reaction. The rate constants for the exchange of the α-hydrogens of *mer*-[Co(gly)$_3$] (I) were found to be $k_a = 1.6 \times 10^{-5}$ s^{-1}, $k_b \simeq k_c = 4.1 \times 10^{-6}$ s^{-1} at pD 10.77 and 25 °C, where k_a, for example, is the pseudo-first-order rate constant for the a hydrogens of I. For compounds II with OO = acac$^-$ and ox^{2-}, both a hydrogens were exchanged with deuterium more rapidly than the b hydrogens. We are here concerned only with the relative lability of methylene hydrogens in a complex. Factors that may affect the rate of α-hydrogen exchange of coordinated α-aminocarboxylates are solution pH,[2b] temperature,[2b] overall charge on the complex,[18] valence angle distortion,[19] and the relative efficiencies in stabilizing the carbanion intermediates.[18] All these factors seem, however, to be irrelevant to the relative ease of hydrogen exchange of several types of glycinato ligands in a complex.

In this context, it seems pertinent to recall that in monosubstituted cobalt(III) pentaammines, [Co(NH$_3$)$_5$X]$^{n+}$, the ammine hydrogens trans to X were activated to different degrees depending upon the substituent X.[10,20] This phenomenon has been rationalized in terms of the trans bond strengthening or weakening effect of the X ligand.[21,22] This line of reasoning leads us to note the trans-ligating atoms of each glycinato chelate. For the a glycinato ligand of I, the ligating atom trans to its carboxyl group is oxygen and that trans to the amino group is also oxygen. Thus, the stereochemical difference among the three glycinato ligands of I is that the a glycinate has two oxygens as the trans ligators, whereas the b and c glycinates have either two nitrogens or one nitrogen and one oxygen at their trans positions. Since the amino nitrogen is a stronger ligand than the carboxyl oxygen,[13] these stereochemical differences, along with the observation on [Co(NH$_3$)$_5$X]$^{n+}$, suggest that the glycinato–cobalt bond in the a chelate is stronger than either of the b and c chelate bonds. This would result in the least electron densities on the methylene carbon atom of the a glycinate, because the electron-withdrawing effect exerted by the positively charged cobalt(III) ion is transmitted most effectively to this carbon atom, hence the highest degree of activation of the a chelate. Experimentally this is what we have observed

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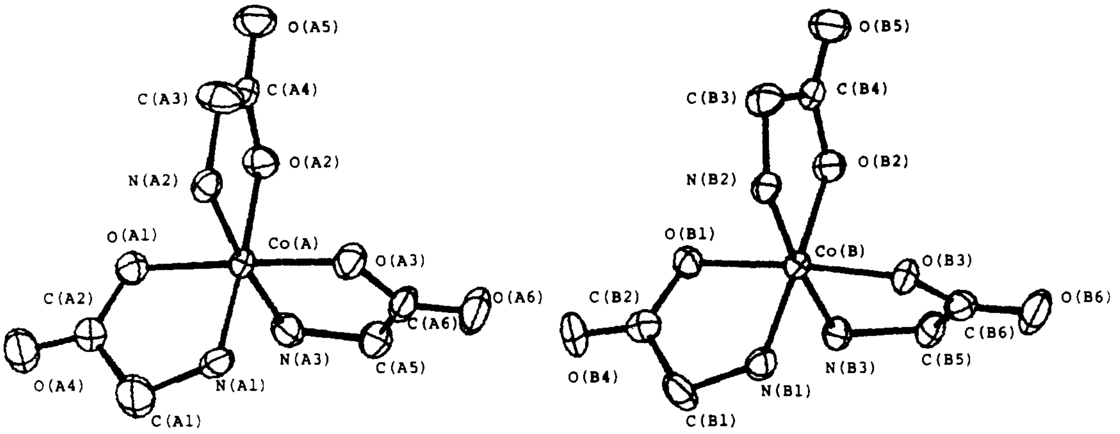

Figure 3. ORTEP drawings of the two crystallographically independent *mer*-[Co(gly)$_3$] complexes.

for I. The greater rate of the a glycinates of compounds II with OO = acac$^-$ and ox^{2-} is also consistent with this inference.

The pertinence of the above postulate can be tested for other (glycinato)cobalt(III) complexes. Since the overall charge on the complex is reported to have an effect on the rate of the α-hydrogen-exchange reaction,[18] we should compare the rates of complexes with the same charge. For the three geometrical isomers of $[Co(gly)_2(en)]^+$ (en = ethylenediamine) of Figure 1, the following second-order rate constants (in dm^3/(mol s) at 50 °C) are reported:[23] 2.1 for the trans(O) isomer (III), 1.4 for the a glycinate of the C_1-cis(O) isomer (IV), 0.30 for the b glycinate of the C_1-cis(O) isomer (IV), and 0.325 for the C_2-cis(O) isomer (V). Thus, it will be noted that the first two hydrogens have larger rate constants than the others and the ligating atoms trans to these two chelates are oxygen and nitrogen, while in the latter two chelates they are two nitrogens. This trend can also be observed for the three geometrical isomers of $[Co(gly)_2(tn)]^+$ (tn = 1,3-propanediamine).[23] Though the rate differences are small indeed in all the cases examined, we are inclined to conclude that the relative efficiency in activating the trans α-hydrogens of glycinato chelates is greater for oxygen than for amino or amine nitrogen.

Description of the Structure of *mer*-[Co(gly)$_3$]·2H$_2$O. The molecular packing in *mer*-[Co(gly)$_3$]·2H$_2$O is illustrated in Figure 2. Interatomic distances and angles and possible intermolecular hydrogen bonds are given in Tables III and IV (Table IV is supplementary material). All hydrogen atoms of amino groups take part in the N—H···O type hydrogen bonding. It is found that one hydrogen atom of the methylene group C(A1) apparently hydrogen bonds to one water molecule, the distances C(A1) to O(W4) and H(A11) to O(W4) being 3.31 (2) and 2.25 (14) Å, respectively. The persepctive drawings of the two crystallographically independent complexes are shown in Figure 3. The least-squares planes of the six glycinato chelates including the cobalt atoms are presented in Table V (supplementary material). The displacement from the plane 6 formed by Co(B), N(B3), O(B3), C(B5), C(B6), and O(B6) is large compared with that in the other chelates. This may be due to the short contact O(A5)···C(B5)(3.23 (1) Å) as shown in Figure 2. This distortion does not seem to affect the coordination bondings in complex B, as indicated by their bond distances and bond angles being quite normal.[24-26]

Table III. Interatomic Bond Distances (Å) and Angles (Deg) with Least-Squares Estimated Standard Deviations in Parentheses

(a) Bond Distances

Co(A)–O(A1)	1.905 (6)	Co(A)–O(A2)	1.919 (6)
Co(A)–O(A3)	1.881 (6)	Co(A)–N(A1)	1.922 (7)
Co(A)–N(A2)	1.948 (7)	Co(A)–N(A3)	1.940 (7)
O(A1)–C(A2)	1.30 (1)	O(A2)–C(A4)	1.28 (1)
O(A3)–C(A6)	1.29 (1)	O(A4)–C(A2)	1.22 (1)
O(A5)–C(A4)	1.26 (1)	O(A6)–C(A6)	1.23 (1)
N(A1)–C(A1)	1.48 (2)	N(A2)–C(A3)	1.46 (1)
N(A3)–C(A5)	1.45 (1)	C(A1)–C(A2)	1.52 (2)
C(A3)–C(A4)	1.48 (1)	C(A5)–C(A6)	1.49 (1)
Co(B)–O(B1)	1.898 (6)	Co(B)–O(B2)	1.913 (6)
Co(B)–O(B3)	1.897 (6)	Co(B)–N(B1)	1.922 (7)
Co(B)–N(B2)	1.943 (7)	Co(B)–N(B3)	1.945 (7)
O(B1)–C(B2)	1.28 (1)	O(B2)–C(B4)	1.29 (1)
O(B3)–C(B6)	1.29 (1)	O(B4)–C(B2)	1.25 (1)
O(B5)–C(B4)	1.21 (1)	O(B6)–C(B6)	1.23 (1)
N(B1)–C(B1)	1.48 (1)	N(B2)–C(B3)	1.48 (1)
N(B3)–C(B5)	1.50 (1)	C(B1)–C(B2)	1.51 (1)
C(B3)–C(B4)	1.50 (1)	C(B5)–C(B6)	1.53 (1)

(b) Bond Angles

O(A1)–Co(A)–N(A1)	86.7 (3)	O(A2)–Co(A)–N(A2)	85.2 (3)
O(A3)–Co(A)–N(A3)	85.9 (3)	Co(A)–O(A1)–C(A2)	116.0 (6)
Co(A)–O(A2)–C(A4)	115.5 (6)	Co(A)–O(A3)–C(A6)	115.4 (6)
Co(A)–N(A1)–C(A1)	109.3 (7)	Co(A)–N(A2)–C(A3)	110.0 (6)
Co(A)–N(A3)–C(A5)	110.3 (6)	O(A1)–C(A2)–O(A4)	124.3 (9)
O(A2)–C(A4)–O(A5)	121.8 (9)	O(A3)–C(A6)–O(A6)	122.6 (9)
O(A4)–C(A2)–C(A1)	120.8 (9)	O(A5)–C(A4)–C(A3)	121.3 (9)
O(A6)–C(A6)–C(A5)	120.4 (9)	N(A1)–C(A1)–C(A2)	112.1 (10)
N(A2)–C(A3)–C(A4)	111.9 (8)	N(A3)–C(A5)–C(A6)	111.0 (8)
C(A1)–C(A2)–O(A1)	114.8 (9)	C(A3)–C(A4)–O(A2)	116.9 (8)
C(A5)–C(A6)–O(A3)	116.8 (8)		
O(B1)–Co(B)–N(B1)	86.5 (3)	O(B2)–Co(B)–N(B2)	87.0 (3)
O(B3)–Co(B)–N(B3)	87.1 (3)	Co(B)–O(B1)–C(B2)	115.5 (5)
Co(B)–O(B2)–C(B4)	115.1 (5)	Co(B)–O(B3)–C(B6)	115.0 (5)
Co(B)–N(B1)–C(B1)	109.6 (6)	Co(B)–N(B2)–C(B3)	107.1 (5)
Co(B)–N(B3)–C(B5)	106.7 (5)	O(B1)–C(B2)–O(B4)	122.7 (8)
O(B2)–C(B4)–O(B5)	122.9 (8)	O(B3)–C(B6)–O(B6)	122.4 (9)
O(B4)–C(B2)–C(B1)	121.1 (8)	O(B5)–C(B4)–C(B3)	122.0 (8)
O(B6)–C(B6)–C(B5)	121.7 (9)	N(B1)–C(B1)–C(B2)	110.9 (7)
N(B2)–C(B3)–C(B4)	113.0 (7)	N(B3)–C(B5)–C(B6)	110.7 (7)
C(B1)–C(B2)–O(B1)	116.3 (7)	C(B3)–C(B4)–O(B2)	115.0 (7)
C(B5)–C(B6)–O(B3)	115.9 (8)		

The most noteworthy feature in Table III is that the Co–N bond trans to oxygen is shorter than the average length of mutually trans Co–N bonds. The difference is $\Delta = 0.022$ (3) Å, where the error in the difference is computed by using the formula $\sigma_\Delta = (\sigma_1^2 + \sigma_2^2)^{1/2}$ (σ_1 and σ_2 are the errors in the Co–N bond lengths trans to oxygen and nitrogen, respectively).[27,28]

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Kinetic and Structural Trans Influence in (Glycinato)cobalt(III) Complexes? The above structural feature correlates nicely with the α-hydrogen-exchange rates of this compound, if we recall that the chelate rings Co(A)–N(A1)–C(A1)–C(A2)–O(A1) and Co(B)–N(B1)–C(B1)–C(B2)–O(B1) of Figure 3 correspond to the a chelate of I of Figure 1. Since the Co(A)–N(A1) and Co(B)–N(B1) bond distances are the shortest among the Co–N bonds, the electron-withdrawing effect of the central metal ion should be transmitted most effectively to these chelates, hence the greatest exchange rate at C(A1) or equivalently C(B1). Though this structure–reactivity correlation may be just fortuitous, it seems probable that the different exchange rates result, at least partially, from the structural trans influence.

It is often pointed out[22] that it is rather difficult to decide whether any bond-length variation is significant and therefore whether this can be attributed to effects of the lattice and the counteranion(s). The sample complex analyzed here crystallographically is a nonelectrolyte and carried no counteranions, and as such the lattice effects should be minimal. The possible occurrence of the structural trans influence in chelated glycinates seems to be found also in the recently reported crystal structure of *mer-cis*(*N*),*cis*(*O*)-$[Co(gly)_2(eta)]$,[25] where eta = $H_2NCH_2CH_2O^-$. To avoid the lattice effects, we refer to only the electrically neutral complex. In this complex, the Co–N(glycinate) bond trans to oxygen is 1.924 (4) Å and that trans to nitrogen is 1.955 (5) Å.

To confirm the existence of structural trans influence and its correlation with the hydrogen-exchange rates, we are making the crystal structure analysis of the diastereoisomer formed by Λ-C_1-*cis*(*O*)-$[Co(gly)_2(en)]^+$ (complex IV of Figure 1) and the monohydrogen *d*-tartrate ion.[29]

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Registry No. *mer*-$[Co(H_2NCH_2CO_2)_3]\cdot 2H_2O$, 80340-08-5.

Supplementary Material Available: Final anisotropic thermal parameters (Table II), intermolecular hydrogen bonds (Table IV), least-squares planes formed by the glycinato ligands (Table V), and a listing of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic and Magnetic Properties of Mixed-Ligand Complexes of Copper(II) with Imidazole and N-Protected Amino Acids. Crystal and Molecular Structure of Bis(hippurato)bis(imidazole)copper(II)

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Mixed-ligand complexes of the type $CuL_2(Im)_2$ (L = N-protected amino acidate = benzoylglycinate (hippurate), acetylglycinate (aceturate), *N*-acetyl- and *N*-benzoyl-DL-alaninate, *N*-acetyl- and *N*-benzoyl-β-alaninate and -leucinate; Im = imidazole) were synthesized and characterized by means of electronic, infrared, and EPR spectroscopies. For one of them, bis(hippurato)bis(imidazole)copper(II), the crystal structure was also determined by the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 10.4863$ (4) Å, $b = 11.4758$ (3) Å, $c = 10.3410$ (4) Å, and $\beta = 102.234$ (1)°. Least-squares refinement of the 217 variables led to a value of the conventional R index of 0.041 for 1932 independent reflections having $I > 2\sigma(I)$. The structure consists of copper atoms lying on the center of symmetry, square-planar coordinated via two centrosymmetric imidazole nitrogens and carboxylic oxygens; two weak interactions (2.736 (4) Å) with uncoordinated carboxylic oxygens in the "out-of-plane" positions complete the coordination to a very distorted tetragonal bipyramid. Electronic and infrared spectra are consistent with this type of structure for all the complexes. The EPR spectra on finely ground polycrystalline samples are also consistent with an essentially $d_{x^2-y^2}$ ground state, except those of bis(amino acidato)bis(imidazole)copper(II) (amino acidate = hippurate and *N*-acetyl-β-alaninate), which are discussed in the light of the structural properties as due to the presence of magnetically unequivalent sites.

Introduction

So that the importance of mixed-ligand complexes in biological fluids could be understood, the mutual influence of two ligands bound to the same metal ion was investigated. In particular the ternary 2,2′-bipyridyl–Cu^{2+}–O and imidazole–Cu^{2+}–O ligand complexes[2-5] were found more stable than the corresponding binary complexes, Cu^{2+}–O ligand, since bipyridyl and imidazole enhance the affinity of Cu(II) for the oxygen donor sites of anionic ligands.[4] These studies have only been performed in solution and are lacking in respect of the disposal of the ligands around the metal ion and of the co-

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