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## Structural and Spectroscopic Studies of Diamminocobalt(III) Complexes of Tripeptides

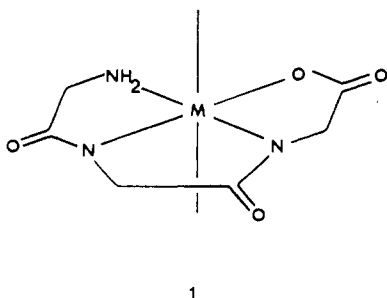
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Received February 8, 1982

The crystal structure of  $[\text{Co}(\text{NH}_3)_2(\text{L-ala-gly-gly})]\cdot 2\text{H}_2\text{O}$  has been determined by X-ray structure analysis. The crystals are triclinic with the space group  $P1$  ( $C_1^1$ ; No. 1), with  $Z = 2$ , and with  $a = 7.2913$  (3) Å,  $b = 8.7373$  (15) Å,  $c = 10.7212$  (8) Å,  $\alpha = 85.930$  (9)°,  $\beta = 77.169$  (6)°, and  $\gamma = 84.253$  (9)°. The structure has been refined by least-squares methods to an  $R$  value of 0.0627 (2056 reflections). The N-terminal chelate ring adopts a nonplanar structure with the methyl group in an equatorial orientation. The absorption and circular dichroism spectra of this complex and analogous complexes with other N- and C-terminal substituted peptides are reported. The effects of the different substituents are compared with those for similar divalent metal complexes and are discussed in terms of different contributions to the chirality of the complexes including the side-group rotamer populations and the above nonplanarity of the chelate ring system.

### Introduction

The circular dichroism (CD) spectra of labile complexes of tripeptides with structure **1** have been reported previously for



copper(II), nickel(II), and palladium(II).<sup>1-8</sup> Inert diamminocobalt(III) tripeptide complexes with this structure have recently been synthesized,<sup>9</sup> and their CD spectra are reported here. The molecular structure of one of these compounds, diammine(L-alanyl-glycylglycine)cobalt(III), has been determined to confirm the mode of coordination and to examine whether any special structural features exist that might influence the circular dichroism.

This is the first structure reported for a cobalt(III) tripeptide complex and the first structure in which the tripeptide complex has structure **1** although there are a number of structures of copper(II) tripeptides in the literature in which the tripeptide does not function as a quadridentate chelate.<sup>10-17</sup>

### Experimental Section

The preparation of the complexes has been described previously.<sup>9</sup> The CD and UV-visible spectra were recorded on a Jobin-Yvon Mark III Dichrograph and Cary 17 spectrophotometer, respectively.

**Crystal Structure Analysis.** The red-brown crystals of  $[\text{Co}(\text{NH}_3)_2(\text{L-ala-gly-gly})]\cdot 2\text{H}_2\text{O}$  were examined by precession film techniques and showed the crystal system to be triclinic. Unit-cell parameters were obtained by least-squares refinement of  $2\theta$  values for 25 automatically centered reflections ( $\theta > 15^\circ$ ).

Intensity data for one hemisphere of reciprocal space were collected on an Enraf-Nonius CAD-4/F automatic diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation. Profile analysis of a representative reflection indicated that the conditions for the measurement of integrated intensities would be obtained by  $\omega$ -( $1/n$ ) $2\theta$  scans, where  $n = 1$ . The  $\omega$  scan and the horizontal counter aperture were  $(0.54 + 0.13 \tan \theta)^\circ$  and  $(1.0 + 0.5 \tan \theta)$  mm, respectively. The scan speeds were determined by a required precision,  $\sigma(I) < 0.015I$ , subject to a maximum scan time of 50 s/reflection. Each reflection was scanned over 96 steps. The peak count  $P$  was recorded over the central 64 steps, with 16 steps at each end to measure the backgrounds  $B_1$  and  $B_2$ . The intensity  $I$  was calculated as  $I = x[P - 2(B_1 + B_2)]$  with standard deviation  $\sigma(I) = \{x[P + 4(B_1 + B_2)]\}^{1/2}$ , where  $x$  is a factor to account

for the differences in scan speeds.

Two standard reflections were measured at regular intervals of X-ray exposure time (3600 s). The percentage decrease in intensities averaged over 2 reflections was plotted against X-ray exposure time. The plot of 36 data points was approximately linear, showing no decomposition or crystal movement.

A total of 2748 reflections were collected in the range  $1^\circ < \theta < 70^\circ$ . Lorentz and polarization corrections were applied by using the program SUSCAD.<sup>18</sup> Of these 2748 reflections, 201 were omitted since they had negative or zero values for  $F_o$ , giving 2547 unique reflections. No absorption corrections were applied as the crystal was of regular shape ( $0.30 \times 0.30 \times 0.30$  mm<sup>3</sup>).

### Results

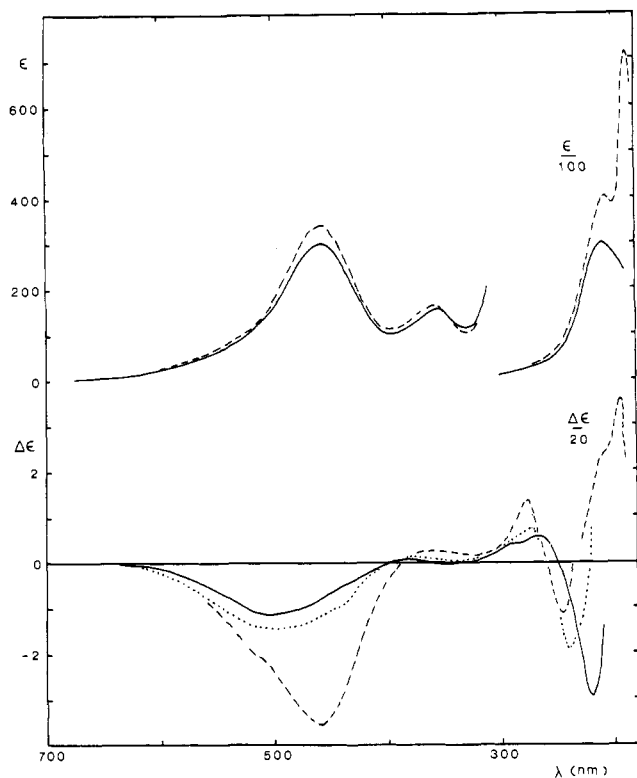
**CD and UV-Visible Spectra.** The spectra are presented in Figures 1 and 2.

**Structure Analysis.** The following unit-cell parameters were obtained at 25 °C: crystal system, triclinic; space group,  $P1$  ( $C_1^1$ ; No. 1);  $Z$ , 2;  $a$ , 7.2913 (3) Å;  $b$ , 8.7373 (15) Å;  $c$ , 10.7212 (8) Å;  $\alpha$ , 85.930 (9)°;  $\beta$ , 77.169 (6)°;  $\gamma$ , 84.253 (9)°;  $V$ , 661.7 Å<sup>3</sup>;  $\mu$ , 107.27 cm<sup>-1</sup>; mol wt, 329.22;  $\rho$ (measd), 1.657 g cm<sup>-3</sup>;  $\rho$ (calcd), 1.652 g cm<sup>-3</sup>;  $F(000)$ , 284 electrons.

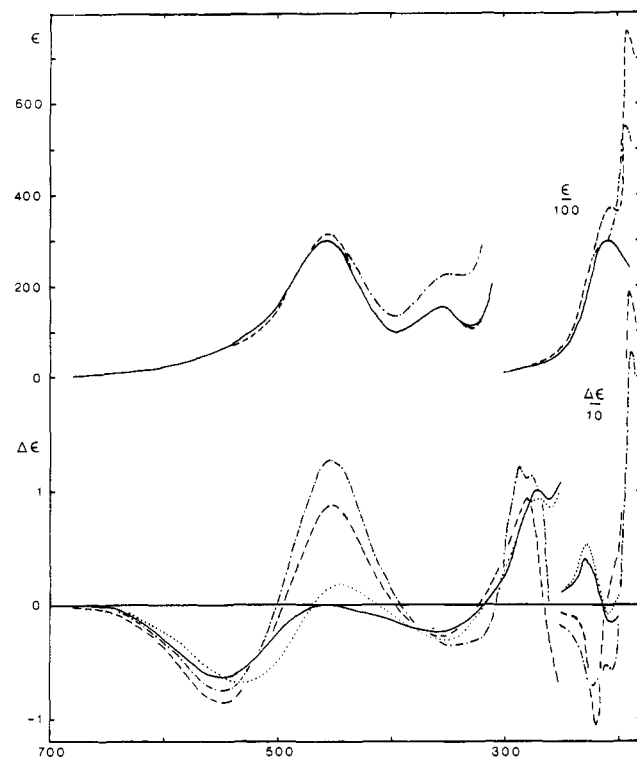
The coordinates of Co(1) were fixed at (0.0, 0.0, 0.0), and a subsequent difference Fourier revealed all the remaining non-hydrogen atoms. The structure was then refined by block-matrix least-squares techniques,<sup>19</sup> first isotropically and then anisotropically, to give  $R = 9.2\%$ . At this stage a few

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**Figure 1.** Absorption spectra (upper) and circular dichroism spectra (lower) of aqueous solutions of the diamminocobalt(III) complexes of gly-gly-L-ala (—), gly-gly-L-leu (---), and gly-gly-L-phe (-·-). The absorption spectra for the two alkyl-substituted peptides are almost superimposable.



**Figure 2.** Absorption spectra (upper) and circular dichroism spectra (lower) of aqueous solutions of the diamminocobalt(III) complexes of L-ala-gly-gly (—), L-leu-gly-gly (---), L-phe-gly-gly (-·-), and L-tyr-gly-gly (-··). The absorption spectra for the two alkyl-substituted peptides are almost superimposable.

of the hydrogen atoms appeared. All hydrogen atom positions, except those for the water molecules, were calculated by using standard geometry with C-H and N-H distances fixed at

**Table I.** Atomic Coordinates ( $\times 10^4$ ) for  $[\text{Co}(\text{NH}_3)_2(\text{L-ala-gly-gly})]\cdot 2\text{H}_2\text{O}$

	x	y	z
Co(1)	0000	0000	0000
N(1)	-9348 (12)	-9935 (10)	-8317 (8)
N(2)	-10633 (11)	-9917 (9)	-11675 (8)
N(3)	-11761 (13)	-8080 (10)	-9655 (9)
C(1)	-13441 (15)	-8533 (11)	-8693 (11)
C(2)	-13699 (14)	-10255 (11)	-8705 (10)
O(1)	-15172 (10)	-10843 (10)	-8131 (9)
N(4)	-12126 (11)	-11025 (9)	-9240 (8)
C(3)	-11828 (15)	-12677 (13)	-9169 (12)
C(4)	-9653 (15)	-13177 (13)	-9702 (13)
O(2)	-9046 (13)	-14550 (10)	-9697 (10)
N(5)	-8756 (12)	-11976 (10)	-10206 (9)
C(5)	-6738 (16)	-12076 (14)	-10746 (11)
C(6)	-6272 (16)	-10418 (14)	-11172 (10)
C(7)	-15226 (16)	-7526 (15)	-8843 (16)
O(3)	-4609 (11)	-10191 (11)	-11720 (8)
O(6)	-7517 (10)	-9302 (9)	-10866 (9)
Ow(1)	-209 (13)	-6537 (10)	-7714 (8)
Ow(3)	-6567 (17)	-13739 (12)	-7464 (11)
Co(2)	-7142 (2)	-6082 (2)	-3535 (2)
N(1')	-7848 (13)	-6155 (12)	-5202 (10)
N(2')	-6619 (12)	-6118 (12)	-1819 (10)
N(3')	-5462 (11)	-7940 (10)	-3881 (9)
C(1')	-3405 (14)	-7517 (14)	-4198 (12)
C(7')	-2167 (16)	-8685 (14)	-5029 (15)
C(2')	-3419 (16)	-5912 (15)	-4688 (11)
O(1')	-1868 (10)	-5348 (8)	-5298 (8)
N(4')	-5041 (11)	-5016 (10)	-4345 (9)
C(3')	-5376 (16)	-3382 (12)	-4488 (12)
C(4')	-7381 (16)	-2972 (11)	-3850 (10)
O(2')	-8066 (12)	-1570 (8)	-3890 (9)
N(5')	-8346 (11)	-4128 (10)	-3373 (8)
C(5')	-10379 (13)	-4034 (13)	-2751 (11)
C(6')	-10898 (13)	-5620 (12)	-2399 (9)
O(3')	-12475 (10)	-5839 (9)	-1715 (9)
O(6')	-9594 (9)	-6774 (8)	-2707 (7)
Ow(2)	-6830 (13)	-9478 (9)	-5818 (9)
Ow(4)	-10544 (16)	-12445 (13)	-6199 (12)

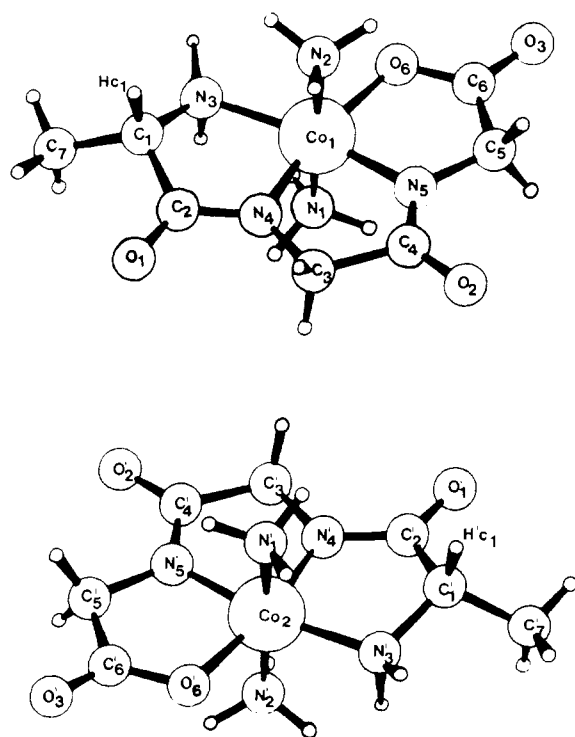
**Table II.** Bond Lengths (Å)

N(1)-Co(1)	1.971 (10)	N(2)-Co(1)	1.946 (9)
N(3)-Co(1)	2.011 (8)	N(4)-Co(1)	1.866 (3)
N(5)-Co(1)	1.872 (8)	O(6)-Co(1)	1.976 (7)
C(1)-N(3)	1.483 (13)	C(2)-C(1)	1.536 (14)
C(7)-C(1)	1.529 (16)	O(1)-C(2)	1.252 (12)
N(4)-C(2)	1.305 (12)	C(3)-N(4)	1.437 (14)
C(4)-C(3)	1.589 (15)	O(2)-C(4)	1.237 (14)
N(5)-C(4)	1.312 (14)	O(5)-N(5)	1.453 (14)
C(6)-C(5)	1.536 (17)	O(3)-C(6)	1.252 (13)
O(6)-C(6)	1.272 (13)	N(1')-Co(2)	1.973 (12)
N(2')-Co(2)	1.958 (11)	N(3')-Co(2)	1.939 (8)
N(4')-Co(2)	1.883 (8)	N(5')-Co(2)	1.841 (9)
O(6')-Co(2)	1.945 (7)	C(1')-N(3')	1.539 (14)
C(7')-C(1')	1.496 (16)	C(2')-C(1')	1.462 (17)
O(1')-C(2')	1.299 (13)	N(4')-C(2')	1.345 (14)
C(3')-N(4')	1.427 (14)	C(4')-C(3')	1.490 (15)
C(2')-C(4')	1.277 (12)	N(5')-C(4')	1.298 (13)
C(5')-N(5')	1.482 (12)	C(6')-C(5')	1.475 (15)
O(3')-C(6')	1.244 (11)	O(6')-C(6')	1.321 (12)

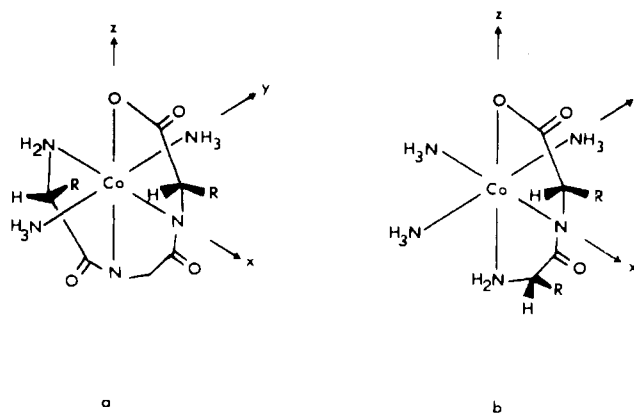
0.965 Å. In subsequent refinements the hydrogen atoms were allowed to ride on the associated C or N atoms such that their geometry was constrained. All hydrogen atoms were given an overall temperature factor, which was refined after each least-squares cycle. The final  $R$  value of 6.27% for unit weights was obtained by using 2056 reflections for  $I \geq 2.5\sigma(I)$ . The largest residuals in the final difference map were in the vicinity of the cobalts with magnitude  $1.3 \text{ e } \text{Å}^{-3}$ . Scattering factors ( $\text{Co}^{2+}$  or  $\text{Co}^{3+}$ ) were taken from ref 20. Table I shows the final atomic coordinates, Table II bond lengths, and Table III

Table III. Valence Angles (Deg)

N(2)-Co(1)-N(1)	176.2 (4)	N(3)-Co(1)-N(1)	90.5 (4)
N(3)-Co(1)-N(2)	86.7 (4)	N(4)-Co(1)-N(1)	90.2 (4)
N(4)-Co(1)-N(2)	92.1 (4)	N(4)-Co(1)-N(3)	84.5 (3)
N(5)-Co(1)-N(1)	90.4 (4)	N(5)-Co(1)-N(2)	92.8 (4)
N(5)-Co(1)-N(3)	169.5 (4)	N(5)-Co(1)-N(4)	85.1 (4)
O(6)-Co(1)-N(1)	90.6 (4)	O(6)-Co(1)-N(2)	87.7 (4)
O(6)-Co(1)-N(3)	106.1 (3)	O(6)-Co(1)-N(4)	169.4 (3)
O(6)-Co(1)-N(5)	84.3 (3)	C(1)-N(3)-Co(1)	106.6 (6)
C(2)-C(1)-N(3)	112.0 (8)	C(7)-C(1)-N(3)	111.7 (9)
C(7)-C(1)-C(2)	111.8 (10)	O(1)-C(2)-C(1)	123.1 (9)
N(4)-C(2)-C(1)	111.2 (9)	N(4)-C(2)-O(1)	125.1 (9)
C(2)-N(4)-Co(1)	120.6 (7)	C(3)-N(4)-Co(1)	115.3 (6)
C(3)-N(4)-C(2)	123.8 (8)	C(4)-C(3)-N(4)	109.1 (9)
O(2)-C(4)-C(3)	120.8 (10)	N(5)-C(4)-C(3)	110.4 (9)
N(5)-C(4)-O(2)	128.5 (10)	C(4)-N(5)-Co(1)	119.5 (7)
C(5)-N(5)-Co(1)	117.0 (7)	C(5)-N(5)-C(4)	122.8 (9)
C(6)-C(5)-N(5)	105.6 (9)	O(3)-C(6)-C(5)	118.4 (10)
O(6)-C(6)-C(5)	119.9 (9)	O(6)-C(6)-O(3)	121.4 (11)
C(6)-O(6)-Co(1)	112.6 (7)	N(2')-Co(2)-N(1')	175.1 (4)
N(3')-Co(2)-N(1')	90.4 (4)	N(3')-Co(2)-N(2')	89.6 (4)
N(4')-Co(2)-N(1')	89.6 (4)	N(4')-Co(2)-N(2')	95.2 (4)
N(4')-Co(2)-N(3')	85.8 (4)	N(5')-Co(2)-N(1')	89.1 (4)
N(5')-Co(2)-N(2')	91.9 (4)	N(5')-Co(2)-N(3')	169.0 (4)
N(5')-Co(2)-N(4')	83.2 (4)	O(6')-Co(2)-N(1')	88.6 (4)
O(6')-Co(2)-N(2')	86.7 (3)	O(6')-Co(2)-N(3')	105.7 (3)
O(6')-Co(2)-N(4')	168.4 (3)	O(6')-Co(2)-N(5')	85.3 (3)
C(1')-N(3')-Co(2)	109.2 (7)	C(7')-C(1')-N(3')	110.2 (10)
C(2')-C(1')-N(3')	107.3 (9)	C(2')-C(1')-N(7')	117.1 (10)
O(1')-C(2')-C(1')	120.7 (10)	N(4')-C(2')-C(1')	117.1 (9)
N(4')-C(2')-O(1')	121.8 (11)	C(2')-N(4')-Co(2)	114.8 (8)
C(3')-N(4')-Co(2)	116.1 (6)	C(3')-N(4')-C(2')	129.1 (9)
C(4')-C(3')-N(4')	107.1 (8)	O(2')-C(4')-C(3')	119.6 (9)
N(5')-C(4')-C(3')	115.4 (9)	N(5')-C(4')-O(2')	124.8 (10)
C(4')-N(5')-Co(2)	118.1 (7)	C(5')-N(5')-Co(2)	115.9 (7)
C(5')-N(5')-C(4')	125.9 (9)	C(6')-C(5')-N(5')	107.5 (8)
O(3')-C(6')-C(5')	119.7 (9)	O(6')-C(6')-C(5')	118.6 (8)
O(6')-C(6')-O(3')	121.4 (9)	C(6')-O(6')-Co(2)	112.7 (6)

Figure 3. Structures of  $[\text{Co}(\text{NH}_3)_2(\text{L-ala-gly-gly})]$ .

the valence angles. The structure of the complex and the atom identification are given in Figure 3. Final observed and calculated structure factors, hydrogen parameters, thermal parameters, and deviations of the atoms from the metal and ligand atom planes for the two complex ions are available as supplementary material.

Figure 4. Structures of (a)  $[\text{Co}(\text{NH}_3)_2(\text{L-tripeptide})]$  and (b)  $[\text{Co}(\text{NH}_3)_3(\text{L-dipeptide})]$ .

## Discussion

The presence of two independent molecules in the cell provides an interesting opportunity to check on the influence of packing forces on the molecular geometry. Bond lengths and valence angles are in their normal ranges and are very similar. The deviations from the metal-donor atom plane are consistent for the two molecules. The main distortion from planarity is centered in the alanine moiety where both molecules show significant deviations for the methyl carbon C(7) (-0.23, -0.18 Å), the  $\alpha$ -carbon C(1) (+0.39, +0.40 Å), and the carbonyl carbon C(2) (+0.12, -0.07 Å). This is the expected result of the alanine methyl group adopting an equatorial conformation. A similar distortion from planarity is seen in one ring of *cis*-bis(D-alaninato)copper(II) where the methyl carbon is -0.63 Å and the  $\alpha$ -carbon +0.21 Å from the plane of the other amino acid atoms.<sup>21</sup> The other ring of this complex has an axial methyl conformation. The complex (glycyl-L-alaninato)copper(II) hydrate also has the methyl axial, and 1.5 Å from the average plane of the other atoms of the complex.<sup>22</sup> This peptide is generally less planar than the cobalt peptide complex reported here. The only other major deviations (>0.1 Å) from planarity are found for the three peptide carbonyl oxygens: O(1), +0.174, +0.01 Å; O(2), +0.15, -0.15 Å; O(3), -0.03, +0.17 Å.

The metal chromophore has a rhombic symmetry under which the triply degenerate cubic d-d transitions,  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ , are each split into three components. The splitting depends on the spectrochemical parameters,  $\Delta$ , for the donor groups. Although it was originally thought that  $\Delta$  for the peptide  $\text{N}^-$  is less than that for the amino group,<sup>23</sup> Billo has shown that for copper(II) the reverse is true.<sup>24</sup> Support for the generality of this latter order can be obtained from a comparison of the  $\lambda_{\text{max}}$  values for the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transitions for the following complexes:  $[\text{Co}(\text{NH}_3)_5(\text{gly-O})]^{3+}$ , 501 nm;<sup>25</sup>  $[\text{Co}(\text{NH}_3)_4(\text{gly})]^{2+}$ , 493 nm;<sup>26</sup>  $[\text{Co}(\text{NH}_3)_3(\text{gly-gly})]^+$ , 489 nm;<sup>27</sup>  $[\text{Co}(\text{NH}_3)_2(\text{gly-gly-gly})]$ , 456 nm;  $[\text{Co}(\text{NH}_3)_2(\text{gly-gly-gly-gly})]$ , 433 nm.<sup>28</sup> Although the differences in the low-symmetry splitting of this band complicate a quantitative comparison of these complexes, the data support the following order for the spectrochemical parameters for the peptide

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chelates:  $\Delta_{N^-} > \Delta_{NH_2R} > \Delta_{NH_3} > \Delta_{CO_2}$ . The fact that the Co-N bond length for the peptide  $N^-$  (1.86 Å) is much shorter than for the amino N (1.98 Å) is also consistent with the proposal that  $\Delta_{N^-}$  is greater than  $\Delta_{NH_2R}$ . With this order of parameters and according to the concepts of low-symmetry splittings developed by Schäffer and Jørgensen,<sup>29</sup> the  ${}^1T_{1g}$  level is split in the rhombic holohedrized ( $D_{2h}$ ) field into three levels with symmetries  ${}^1B_{3g}$ ,  ${}^1B_{1g}$ , and  ${}^1B_{2g}$  that transform as rotations about the  $N^-$ ,  $NH_3$  ( $x$ ), the  $NH_3$ ,  $NH_3$  ( $y$ ), and the  $N^-$ ,  $O^-$  ( $z$ ) axes (Figure 4) and that have energies in the order given with the  ${}^1B_{3g}$  level at lowest energy. Because the  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition is magnetic dipole forbidden for an octahedral complex, its CD will not be considered in detail.

The visible absorption spectra of the diamminocobalt(III) tripeptide complexes have maxima at 456 nm ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ) and at 356 nm ( ${}^1A_{1g} \rightarrow {}^1T_{2g}$ ) with a shoulder at about 540 nm, which is most apparent in the phe-gly-gly complex. From the shape of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  band it would appear that the transition at 540 nm is the lowest of the three components and hence is assigned to  ${}^1A_{1g} \rightarrow {}^1B_{3g}$ . The positions of the other two components cannot be gauged from the absorption spectra.

The CD spectra of the gly-gly-ala and gly-gly-leu complexes have negative Cotton effects centered at 500 nm, with the leucyl complex possessing a negative shoulder about 440 nm. The maximum intensity of the negative Cotton effect in the gly-gly-phe complex is shifted to higher energy occurring at 460 nm, with a shoulder now on the high-wavelength side at about 520 nm. A similar shift in the position of the predominant negative Cotton effect has also been observed for the analogous nickel(II)<sup>4</sup> and palladium(II)<sup>7</sup> complexes. It is not clear for these C-terminal substituted peptides whether the small positive Cotton effect that occurs at 360–380 nm is associated with the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  or  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions because cancellation by the predominant negative Cotton effects under the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  could move the observed high-energy positive component toward the  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  region. Although it is not possible to determine unambiguously the signs of the three components of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  absorption band, it can be concluded that, for the C-terminal substituted tripeptides with the L configuration, the total rotational strength of the d-d bands is negative. This has also been found for the nickel(II),<sup>4</sup> palladium(II),<sup>7</sup> and copper(II)<sup>2,5</sup> complexes.

The asymmetric field in the C-substituted tripeptide complex relative to the three axes of the complex closely resembles that for the corresponding triamminocobalt(III) complex of C-substituted dipeptides (Figure 4). The sizes of the low-symmetry splitting of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  band for the two types of complexes would differ, but some similarity in their CD spectra would be expected. The CD spectrum of  $[Co(NH_3)_3(gly-L-ala)]^2$  has been published,<sup>27</sup> and as expected, it is very similar to that for  $[Co(NH_3)_2(gly-gly-L-ala)]$ .

For the N-terminal substituted tripeptides with the L configuration a negative Cotton effect occurs at about 540 nm and a positive, except for the alanyl peptide, at about 450 nm under the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  absorption band, and a negative peak occurs under the  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  band. The observed rotational strength for the negative band with  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  parentage is markedly less than for the corresponding Cotton effect for the C-terminal substituted tripeptides. This reduction in the negative Cotton effect has also been observed for the analogous nickel(II),<sup>4</sup> palladium(II),<sup>7</sup> and copper(II)<sup>2,5</sup> complexes. This is associated with an increase in the rotational strength of the higher energy positive Cotton effect. For the L-phe-gly-gly complexes of the above divalent metal ions only the positive band is observed.<sup>2,4,5,7</sup> However, for the diamminocobalt(III) complexes, the total rotational strength for the d-d transitions

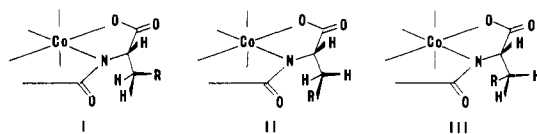


Figure 5. Side-group rotamers for peptide complexes, shown for C-terminal substituted peptide.

is negative for the four N-terminal substituted L peptides included in this study.

The rotational strength induced in the d-d transitions is derived from the so-called vicinal effect of the asymmetric center and from any chiral puckering of the chelate ring system. In the crystalline state  $[Co(NH_3)_2(L-ala-gly-gly)]$  shows marked nonplanarity in the N-terminal chelate ring, with the methyl group occupying an equatorial orientation. The atoms in the rest of the peptide backbone are constrained to be close to the coordination plane, although the peptide oxygen in the middle chelate lies about 0.15 Å from the coordination plane. NMR studies have shown that the electrons from the peptide groupings are delocalized around the chelate rings.<sup>9</sup> The fact that this delocalized system is twisted as a result of the substitution would lead to the introduction of rotational strength in the peptide transitions and also in the d-d transitions via the charge-transfer transitions.

The chirality introduced to the force field around the metal chromophore by the asymmetric center is dependent on the positions of the various groups relative to the metal and is therefore influenced by the side-group rotamer populations (Figure 5). These populations have been determined previously by  ${}^1H$  NMR spectroscopy.<sup>9</sup> In rotamer III the substituent R lies below the peptide ring in contrast to the other two rotamers in which the substituent is oriented away from the metal. Rotamer III is the most populated rotamer for the phenylalanyl, tyrosyl, and leucyl peptides.<sup>9</sup> In  $[Co(NH_3)_2(gly-gly-L-phe)]$  rotamer III has a mole fraction of about 0.9, and the phenyl group interacts strongly with one of the  $NH_3$  ligands.<sup>9</sup> In this orientation the phenyl group should have a marked influence on the CD induced in the d-d bands, and this could account for the observed shift in the position of the predominant negative Cotton effect relative to that of the alkyl peptides and for the relatively large size of the CD bands. In the N-terminal substituted peptide complexes the mole fraction of rotamer III is 0.6 for the phenylalanyl and 0.75 for the tyrosyl compound. This positioning of the aromatic group would again contribute to the differences observed between the aromatic- and alkyl-substituted peptides.

In the UV region all the diamminocobalt(III) L-tripeptide complexes studied gave a positive Cotton effect at about 270 nm, which would be associated with a ligand  $\rightarrow$  metal charge-transfer transition. The aromatic groups'  ${}^1L_b \pi \rightarrow \pi^*$  transitions also occur in this region, and the positive Cotton effect at 286 nm observed for the L-tyr-gly-gly complex is probably associated with this transition. For the C-terminal substituted peptides, a negative Cotton effect is observed at about 240 nm, which is followed by a positive effect for gly-gly-L-phe occurring as a shoulder at about 210 nm. Both these bands could originate from the absorption band at 208 nm. For the N-terminal substituted peptides, L-ala-gly-gly and L-leu-gly-gly, the signs of these Cotton effects are reversed. For L-phe-gly-gly and L-tyr-gly-gly a more complicated pattern of bands occurs in this region possibly due to the superposition of bands from the  ${}^1L_a \pi \rightarrow \pi^*$  transitions in the aromatic rings and from charge-transfer transitions. The three peptides with aromatic side groups also have an intense absorption at 190 nm with an associated very large Cotton effect, which is positive for the L peptides. This absorption band, which was not observed for the alkyl-substituted peptides, could be the  ${}^1B_a$  band for the aromatic ring.

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**Acknowledgment.** The authors gratefully acknowledge financial support from the Australian Research Grants Committee.

**Registry No.** [Co(NH<sub>3</sub>)<sub>2</sub>(L-ala-gly-gly)]·2H<sub>2</sub>O, 83351-01-3; Co(NH<sub>3</sub>)<sub>2</sub>(gly-gly-L-ala), 74808-51-8; Co(NH<sub>3</sub>)<sub>2</sub>(gly-gly-L-leu), 74808-52-9; Co(NH<sub>3</sub>)<sub>2</sub>(gly-gly-L-phe), 74808-53-0; Co(NH<sub>3</sub>)<sub>2</sub>(L-

leu-gly-gly), 83351-02-4; Co(NH<sub>3</sub>)<sub>2</sub>(L-phe-gly-gly), 74808-55-2; Co(NH<sub>3</sub>)<sub>2</sub>(L-tyr-gly-gly), 74808-56-3.

**Supplementary Material Available:** Listings of observed and calculated structure factors, atomic coordinates, thermal parameters, and deviations of the atoms from the metal and ligand atom planes for [Co(NH<sub>3</sub>)<sub>2</sub>(L-ala-gly-gly)]·2H<sub>2</sub>O (15 pages). Ordering information is given on any current masthead page.

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## The Molybdenum-Molybdenum Triple Bond. 12.<sup>1</sup> Preparation and Characterization of Bis(*tert*-butyl mercaptido)tetrakis(dimethylamido)dimolybdenum(M≡M)

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Received March 17, 1982

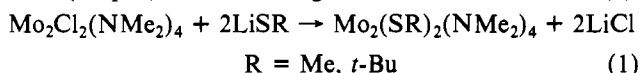
From the reaction between Mo<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> and LiSR (≥2 equiv) in hexane, yellow-orange crystalline compounds of Mo<sub>2</sub>(SR)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> have been isolated, where R = Me and *t*-Bu. Crystal data for Mo<sub>2</sub>(S-*t*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> are *a* = 14.322 (4) Å, *b* = 17.514 (5) Å, *c* = 9.865 (2) Å, β = 101.39 (1)°, *V* = 2425.7 (1) Å<sup>3</sup>, *Z* = 4, *d*<sub>calcd</sub> = 1.497 g cm<sup>-3</sup>, and space group *P*2<sub>1</sub>/*n*. The solid-state molecular structure reveals an unbridged Mo≡Mo bond of distance 2.217 (1) Å and an antirotameric conformation for the Mo<sub>2</sub>S<sub>2</sub>N<sub>4</sub> skeleton, which has virtual C<sub>2h</sub> symmetry. The important averaged bond distances and bond angles are Mo-S = 2.363 (3) Å, Mo-N = 1.95 (1) Å, Mo-Mo-S = 95 (1)°, and Mo-Mo-N = 104 (1)°. These observations are compared with related findings for compounds having a central (Mo≡Mo)<sup>6+</sup> moiety. Mo<sub>2</sub>(S-*t*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> reacts with excess *t*-BuSH to give Mo<sub>2</sub>(μ-S)<sub>2</sub>(S-*t*-Bu)<sub>4</sub>(HNMe<sub>2</sub>)<sub>2</sub> as the only characterizable molybdenum-containing compound. Mo<sub>2</sub>(S-*t*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> reacts with excess ROH (R = *t*-Bu, *i*-Pr) to give Mo<sub>2</sub>(OR)<sub>6</sub> compounds with the elimination of HNMe<sub>2</sub> and HS-*t*-Bu.

### Introduction

Molybdenum and tungsten are now well-known to form an extensive series of dinuclear compounds with a central (M≡M)<sup>6+</sup> unit.<sup>2,3</sup> The simplest members of this series are the homoleptic compounds X<sub>3</sub>M≡MX<sub>3</sub>, where X = CH<sub>2</sub>SiMe<sub>3</sub>, NMe<sub>2</sub>, OR (R = *t*-Bu, *i*-Pr), and the closely related compounds of formula M<sub>2</sub>X<sub>2</sub>Y<sub>4</sub>, where X = Cl, Br and Y = NMe<sub>2</sub>, CH<sub>2</sub>SiMe<sub>3</sub>. As part of a general program aimed at elucidating the coordination chemistry of the (Mo≡Mo)<sup>6+</sup> unit, we investigated reactions between Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and bulky thiols RSH (R = *t*-Bu, *i*-Pr, CH<sub>2</sub>Ph). The products of these reactions were not, however, Mo<sub>2</sub>(SR)<sub>6</sub> compounds that could have been formed by simple exchange reactions but rather were Mo<sub>2</sub>(μ-S)<sub>2</sub>(SR)<sub>4</sub>(HNMe<sub>2</sub>)<sub>2</sub> compounds.<sup>4</sup> We now describe further reactions aimed at attaching mercaptido groups to the (Mo≡Mo)<sup>6+</sup> unit.

### Results and Discussion

**Synthesis.** Hydrocarbon solutions of Mo<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub><sup>5</sup> and LiSR (2 equiv) react according to the metathetic reaction (1).



The new mercaptido compounds are yellow-orange crystalline solids that are exceedingly air and moisture sensitive. When heated under vacuum, they sublime at 90–100 °C (10<sup>-4</sup> torr), though this is accompanied by some decomposition. They are

soluble in hydrocarbon solvents at room temperature, but only sparingly so at low temperatures. Elemental analyses and other characterization data are given in the Experimental Section.

**Solid-State Structure of Mo<sub>2</sub>(S-*t*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>.** Final atomic positional parameters are given in Table I. Bond distances and angles are given in Tables II and III, respectively. An ORTEP view of the molecule giving the atomic numbering scheme used in the tables is given in Figure 1, and a view of the molecule down the Mo-Mo bond is shown in Figure 2.

The Mo-Mo distance of 2.217 (1) Å is typical of the distances found in Mo<sub>2</sub>X<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>-containing compounds; cf. Mo-Mo = 2.201 (2) Å, which is found for the compounds where X = Cl<sup>5</sup> and Me,<sup>6</sup> both of which also crystallize from hydrocarbon solvent in the antirotamer. The Mo-N distances, 1.95 (1) Å (averaged), and the planar arrangement of the NMe<sub>2</sub> groups with respect to the Mo≡Mo bond are also typical of M<sub>2</sub>X<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> compounds. The Mo-N distances, 1.95 (1) Å (averaged), are somewhat shorter, however, than those found in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>, which span a range from 1.97 (1) to 2.00 (1) Å and average 1.98 Å.<sup>7</sup> This is consistent with the view that substitution of a less π-donating group, SR for NMe<sub>2</sub>, would enhance N-to-Mo π bonding in the remaining Mo-NMe<sub>2</sub> groups. The Mo-N distance, 1.95 (1) Å (averaged), is, however, greater than that in Mo<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>, 1.93 (1) Å (averaged). Again, this is consistent with the further replacement of a more electronegative group and a weaker π-donating ligand, Cl for SR.

One might wonder whether the Mo-S distances 2.362 (2) and 2.363 (2) Å provide any indication of sulfur-to-molybdenum π bonding. Indeed, what Mo-S distance might one

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