and the reaction of ferricytochrome *c* with model outer-sphere reductants is that electron transfer occurs *via* the exposed heme edge.[8,12,13] The present experiments on the oxidation of ferrocytochrome *c* from both horse heart and *Candida krusei* by tris(1,10-phenanthroline)-cobalt(III) are also most easily reconciled with a mechanistic model featuring outer-sphere electron transfer utilizing contact between the heme edge and one of the phenanthroline rings. Indeed, given an edge–edge mechanism for the self-exchange reaction, edge transfer to $Co(phen)_3^{3+}$ must be the path of choice in order to understand the excellent Marcus-theory correlation. It is also important to note that the measured activation parameters and the ionic strength dependence of the protein reaction with $Co(phen)_3^{3+}$ provide very little evidence of any unusual features and therefore are entirely consistent with an ordinary adiabatic electron transfer process. In view of all of the results on model systems, then, it is reasonable to propose that the remote attack reactions utilize a common heme-edge site for both oxidation and reduction of cytochrome *c*. This model is in contrast to the proposal that electron transfer takes place *in vivo* at separate oxidase and reductase binding sites.[16–20] However, it is difficult to understand why a common heme-edge pathway should not also be employed *in vivo*, unless access to the edge is blocked as a consequence of binding to the membrane or to the oxidase or reductase.

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Mechanism for Chiral Recognition of a Prochiral Center and for Amino Acid Complexation to a Cobalt(III) Tetramine. The Crystal Structure, Absolute Configuration, and Circular Dichroism of $\Lambda(-)_{436}$-β_2-[(2*S*,9*S*)-2,9-Diamino-4,7-diazadecanecobalt(III) aminomethylmalonate] Perchlorate Monohydrate

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Abstract: The crystal structure of $\Lambda(-)_{436}$-β_2-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt(III) aminomethylmalonate] perchlorate monohydrate, cell dimensions $a = 13.001$ (2), $b = 14.656$ (3), and $c = 10.601$ (1) Å, space group $P2_12_12_1$, has been determined and refined, with all hydrogen atoms included, to $R = 0.075$. The results of the X-ray determination have shown that the complex has the conformation Λ-β-*R* with the *pro-S* carboxyl group of the malonate coordinated to Co(III). All of the Λ-β-complex is in the *R* conformation, presumably because in this conformation three-point attachment of the malonate *via* an internal hydrogen bond occurs. On decarboxylation of the pure Λ-β- complex, 65% (*S*)-alanine and 35% (*R*)-alanine are formed. The CD spectra of these complexes are analyzed as Gaussian sums as an aid in spectral determination of absolute configuration. Since Λ-α-, trans-, or Δ-β- starting complexes all give similar yields of Λ-β- and Δ-β- products on treatment with amino acids, we suggest a common trans intermediate which gives β_1 complexes at high pH when the amino group attacks first and β_2 complexes at low pH when the carboxylate group attacks first.

The crystal structure of the Λ-β- complex formed between α,α-aminomethylmalonate and $\Lambda(-)_{436}$-α-dichloro-(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt-(III) chloride (**1**) is described here. The α,α-aminomethylmalonate dianion is an example of a prochiral ion since it has two equivalent carboxyl groups. When it interacts with the cobalt complex (**1**) the primary product was shown to be the Λ-β- complex with some Δ-β- product but no Λ-α- product. A comparison of the circular dichroism curve of the Λ-β- complex, with those of corresponding Λ-β- complexes with (*R*)- or (*S*)-alanine, suggested that the malonate moiety was bound in a fixed configuration so that only the *pro-S* carboxyl group (and not the *pro-R* group) was directly coordinated to the Co(III) ion[2] (eq 1). This differentiation between the carboxyl groups occurs in spite of the fact that the binding of an asymmetric tetradentate ligand on the Co(III) ion leaves only two octahedral positions available for coordination of the malonate ion instead of the three positions which have been proposed as a condition[3] for significant chiral recognition of a prochiral center. A specific differentiation between prochiral functional groups is common to enzyme reactions (eq 2)[3–5] but has not been previously observed

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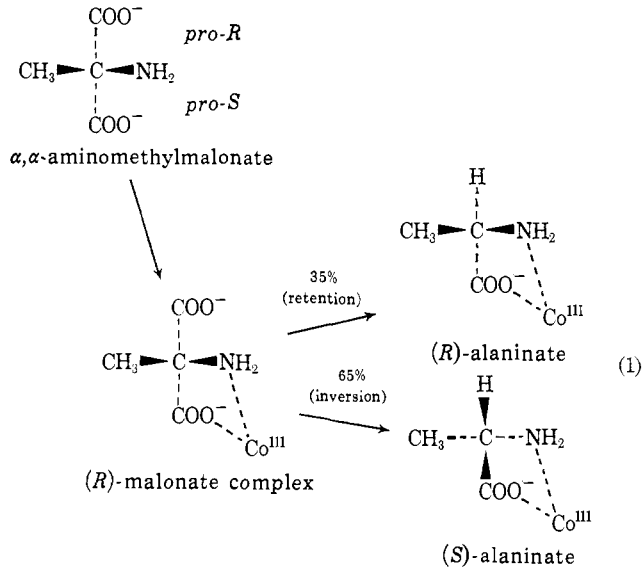
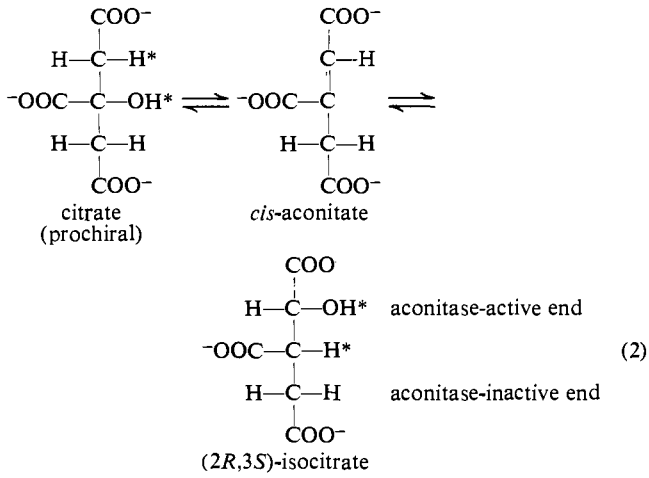


(1)



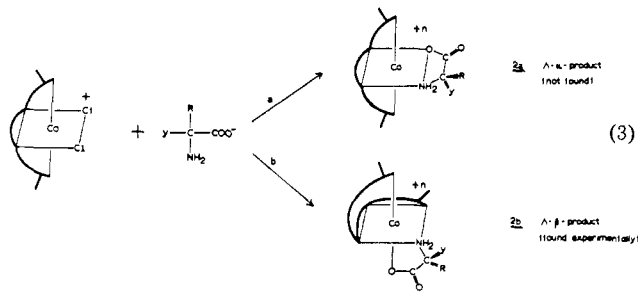
(2)

in small molecule systems. Thus, in these studies we could well have a chemical model equivalent to an enzyme [Co(III) with an asymmetric tetradentate ligand] and a prochiral substrate (α,α-aminomethylmalonate).

It has been shown[2] that the complex just described yields, on decarboxylation, 65% (*S*)-alaninate but only 35% (*R*)-alaninate. Thus, inversion of configuration at the asymmetric carbon atom occurs more readily than retention of configuration on decarboxylation.

The positive principal Cotton effect exhibited by the CD curves near 500 nm for the major component of the reaction mixture of **1** with methylaminomalonate indicates that this tetraminecobalt aminoacidate complex possesses the Λ-configuration. Either Λ configuration (eq 3) presents an interesting possibility: (a) Λ-α-product (**2a**) represents retention of configuration about the cobalt center, previously unobserved in reactions of (α-trien)$CoCl_3$ with amino acids[6,7] and (b) Λ-β- product (**2b**) represents isomerization of the tetramine complex, surprising in that it requires rearrangement of two tetramine chelate rings.

Our purpose in undertaking the X-ray structure determination was threefold: to gain insight into the factors which cause such extreme selectivity, to ascertain the ligand arrangement and absolute configuration about the cobalt center, and to confirm relationships



(3)

substituents for **2b** (Λ-β-product)

3, R = CH_3; y = COO^-
4, R = H; y = H
5, R = CH_3; y = H
6, R = $CH(CH_3)_2$; y = H
7, R = C_6H_5; y = H
8, R = CH_3; y = H with the methyl groups on the tetramine replaced by $-CH(CH_3)_2$

between CD curves and configurations at asymmetric centers. It will be shown that **2b** (the Λ-β-malonate complex **3**), and not the Λ-α- complex (**2a**), is formed (when R = CH_3 and y = COO^-) and that all of the malonate found in the Λ-β- complex has the *pro-S* and not the *pro-R* carboxyl group coordinated to the Co(III) ion. The complex, **3**, will be referred to in this paper as the "(*R*)-malonate complex" in the sense that if the uncoordinated carboxyl group were replaced by a proton with retention of configuration, (*R*)-alanine would result (eq 1). The structures studied will be considered in terms of a mechanism involving a common trans intermediate for substitution reactions of cobalt(III) triethylenetetramine complexes.

Experimental Section

A. Preparation of Complexes. 1. General Preparations from 1 and Its Analogs. The following complexes were prepared as described elsewhere[2]: $\Lambda(-)_{436}$-β$_2$-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt(III) AA]$^{n+}$ where AA = α,α-aminomethylmalonate (**3**), glycine (**4**), (*R*)-alanine (**5**$_R$), (*S*)-alanine (**5**$_S$), (*R*)-valine (6$_R$), (*S*)-valine (6$_S$), (*R*)-phenylalanine (7$_R$), and (*S*)-phenylalanine (7$_S$), $\Lambda(-)_{436}$-β$_2$[(3*S*,10*S*)-3,10-diamino-5,8-diaza-2,11-dimethyldodecanecobalt(III) AA]$^{2+}$ where AA = (*R*)-alanine (8$_R$) and (*S*)-alanine (8$_S$).

2. Alternate Synthesis of 3 from 9. *trans*-[(2*S*,9*S*)-2,9-Diamino-4,7-diazadecanecobalt(III) dichloride] perchlorate (**9**) (0.403 g, 1.0 mmol) and dipotassium α,α-aminomethylmalonate (1.0 mmol) were placed in 100 ml of methanol and heated to reflux. After 5 min of reflux both reactants had dissolved completely to give an orange solution, and orange crystals had begun to precipitate. After 3 hr of reflux the mixture was removed from the heat and allowed to stand at room temperature overnight. The orange crystals were collected, washed with ethanol and ether, then air dried. The rotations were identical with authentic **3**,[2] yield 0.290 g (72.5%).

We had previously synthesized **3** by treatment of **1** with α,α-aminomethylmalonate in refluxing methanol.[2] The preparation presented here, treatment of **9** with α,α-aminomethylmalonate, proceeds as cleanly but more rapidly (minutes instead of hours).

3. Preparation of 9 from 1 *via* 10. $\Lambda(-)_{436}$-α-[(2*S*,9*S*)-2,9-Diamino-4,7-diazadecanecobalt(III) dichloride] chloride monohydrate (**1**) (0.358 g, 1.0 mmol) and sodium chloroacetate (0.35 g, 3.0 mmol) were refluxed overnight in methanol to give a burgundy colored solution. After cooling in an ice bath the solution was treated with sodium perchlorate (0.5 g) then saturated with HCl gas. After 0.5 hr the mixture was filtered to remove a white precipitate, then the solvent evaporated on a steam bath to yield a mixture of green and violet crystals. The residue was weighed, then taken up in 12 *M* HCl. From the absorbance at two wavelengths the yield of **9** was calculated to be 65%. The product was crystallized, from a 50:50 mixture of 12 *M* HCl and methanol, as green needles with rotations identical with authentic **9**.[2]

B. X-Ray Data Collection for Compound 3. The crystal data

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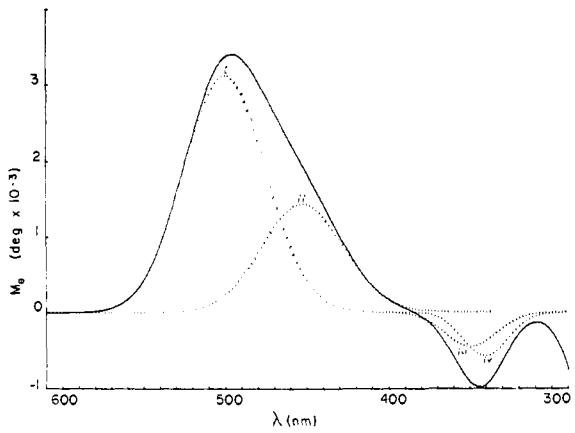

Figure 1. The circular dichroism spectrum of $\Lambda(-)_{436}$-β_2-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt(III) (*R*)-aminomethylmalonate]$^+$ and its component Cotton effects.

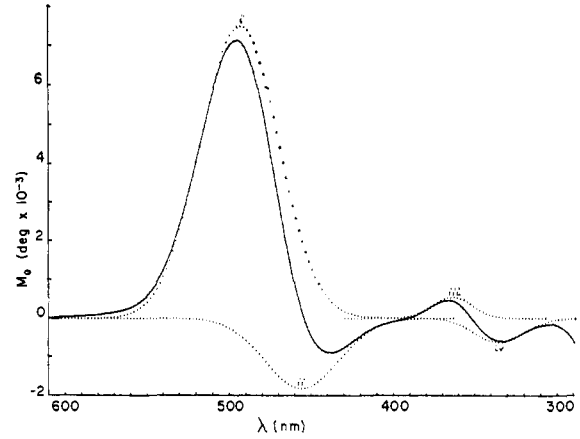

Figure 2. The circular dichroism spectrum of $\Lambda(-)_{436}$-β_2-[(2S,9S)-2,9-diamino-4,7-diazadecanecobalt(III) (*S*)-alanine]$^{2+}$ and its component Cotton effects.

Table I. Crystal Data for $CoClO_9N_5C_{12}H_{29}$ (3)

Formula: $CoO_4N_5C_{12}H_{27}^+ \cdot ClO_4^- \cdot H_2O$	
Formula weight: 481.78	
Crystal system: orthorhombic	
a = 13.001 (2) Å	λ(Cu Kα) 1.5418 Å
b = 14.656 (3) Å	μ(Cu Kα) = 83.2 cm^{-1}
c = 10.601 (1) Å	$F(000)$ = 1008
V = 2019.9 (6) Å^3	Z = 4
D_{calcd} = 1.585 g cm^{-3}	Space group = $P2_12_12_1$
D_{measd} = 1.577 g cm^{-3} (by flotation in tetrachloroethylene and trichloroethylene)	Systematic absences: *h*00, *h* odd; 0*k*0, *k* odd; 00*l*, *l* odd
Crystal size: 0.025 × 0.025 × 0.025 cm^3	

for the Λ-β- complex (**3**) are listed in Table I. Three-dimensional data were collected on a Syntex automated diffractometer with monochromatic Cu Kα radiation using the θ-2θ scan technique. Intensities were measured for two octants (*hkl* and −*hkl*) of the reciprocal lattice up to sin θ/λ = 0.61. The intensity loss of 27% over 112 hr for the four standard reflections measured was corrected for. Values for $\sigma(I)$ were derived from counting statistics and measured instrumental uncertainties. If the intensity I was less than $2.33\sigma(I)$ the reflection was considered to be below the threshold of measurement. Values of $\sigma(F)$ were computed from the expression $(F/2)\{(\sigma^2(I)/I^2) + \delta^2\}^{1/2}$, where δ, the measured instrumental uncertainty, was found to be 0.017. The intensity data were converted to structure amplitudes by application of Lorentz and polarization factors and a spherical absorption correction and placed on an absolute scale with a Wilson plot.

C. Structure Determination and Refinement. The cobalt atom position was found from a Patterson map at which stage the R value was 0.47. The resulting Fourier map revealed the structure which was refined, first isotropically then anisotropically to R = 0.104. Hydrogen atoms were located from a difference map, and refinement was continued alternating the heavy atom and hydrogen atoms in the least-square cycles to give R = 0.075. The weights, w, used in the refinement were $1/[\sigma^2(F_o)]$ with zero weights for reflections below the threshhold of measurement. The quantity minimized was $\Sigma w\{|F_o| - |F_c|\}^2$. Final atomic parameters are given in Table II.

Atomic scattering factors for cobalt, chlorine, oxygen, nitrogen, and carbon atoms were those given in International Tables[8] and for hydrogen atoms those of Stewart, Davidson, and Simpson.[9] Anomalous dispersion corrections for cobalt and chlorine are listed by Cromer and Liberman.[10] Computer programs used in this determination were the X-ray 72 system[11] and UCLALS4.[12]

The absolute configuration of the structure was determined by comparing reflections *hkl*[13] and −*hkl*. The Bijvoet pairs of reflections are compared with calculated values in Table III. The coordinates listed in Table II give the same sign to both calculated and experimental values of $[|F(hkl)| - |F(-hkl)|]$ for all reflections with $F^2(hkl) - F^2(\bar{h}kl) > 12\sigma(F^2)$.

D. CD Spectra. Circular dichroism spectra were obtained over the range of 610–290 nm, at concentrations near 5 × 10^{-3} *M* in 1 *M* HCl on a Cary Model 60 spectrometer thermostated at 26°. The CD curves were fitted by a summation of Gaussian curves with the aid of a Hewlett-Packard 9820 desk calculator with a plotter attachment.

Results

A. CD Spectra. The CD spectrum of $\Lambda(-)_{436}$-β_2-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt(*R*)-aminomethylmalonate]$^+$ (**3**) is presented in Figure 1 (solid line) along with the smallest number of Gaussian component Cotton effects (dotted lines) which fit the experimental curve. All of the (*R*)-amino acid complexes ($\mathbf{5}_R$, $\mathbf{6}_R$, $\mathbf{7}_R$, $\mathbf{8}_R$) have similar CD spectra which can be fit (nonuniquely) by a summation of five or six Gaussian curves (see Tables IV and V) generated by eq 4 where C is the amplitude of the Cotton effect in

$$M_\theta = C \exp\left[-\frac{(x-a)^2}{b^2}\right] \quad (4)$$

degrees, a is the location of the Cotton effect in nanometers, and b is the half width at $1/e$ of the maximum value. The molar ellipticity (M_θ) is further defined by eq 5 where[14] θ is the ellipticity in degrees, c is the concentration in moles/liter, and l is the cell length in centimeters. The parameters for the Cotton effects necessary to generate the composite CD curve for each (*R*)-amino acid complex are presented in Table IV. The CD curve of $\Delta(-)_{436}$-β_2-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt (*S*)-alanine]$^{2+}$ is presented in Figure 2 (solid line) along with its component Cotton effects

$$M_\theta = \frac{100\theta}{cl} \quad (5)$$

(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, pp 201–207.

(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* 42, 3175 (1965.

(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(11) J. M. Stewart, "The X-Ray System—version of 1972," Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972.

(12) P. K. Gantzel, R. A. Sparks, R. E. Long, and K. N. Trueblood UCLALS4 Program in Fortran IV (modified by H. L. Carrell), 1969.

(13) See paragraph at end of paper regarding supplementary material.

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Table II. Final Atomic Parameters for $CoClO_9N_5C_{12}H_{29}$[a]

	x	y	z
Co	638 (1)	756 (1)	2395 (1)
Cl	4648 (3)	1438 (2)	3121 (3)
O(1)	113 (4)	−427 (3)	2601 (7)
O(2)	549 (5)	−1899 (3)	2882 (7)
O(3)	2235 (6)	−146 (4)	4821 (6)
O(4)	2612 (6)	−1614 (5)	4596 (7)
O(5)	4295 (9)	708 (11)	2502 (17)
O(6)	4362 (13)	1229 (8)	4388 (13)
O(7)	4214 (12)	2274 (10)	2874 (16)
O(8)	5698 (9)	1470 (8)	3027 (12)
O(W)	1281 (8)	3231 (7)	−180 (11)
N(1)	403 (7)	678 (6)	582 (7)
N(2)	−768 (6)	1198 (4)	2417 (9)
N(3)	596 (8)	980 (6)	4183 (8)
N(4)	1284 (6)	1951 (5)	2216 (8)
N(5)	2015 (6)	160 (4)	2369 (8)
C(1)	−584 (12)	1146 (8)	251 (12)
C(2)	−1340 (11)	934 (10)	1298 (14)
C(3)	−1266 (8)	903 (10)	3683 (13)
C(4)	−375 (11)	714 (8)	4695 (10)
C(5)	787 (11)	1962 (7)	4410 (10)
C(6)	1672 (9)	2246 (7)	3510 (12)
C(7)	−1009 (11)	851 (11)	−1027 (15)
C(8)	1942 (10)	3249 (8)	3540 (14)
C(9)	760 (10)	−1076 (8)	2732 (10)
C(10)	1900 (7)	−808 (7)	2812 (9)
C(11)	2292 (9)	−842 (8)	4200 (11)
C(12)	2581 (8)	−1446 (7)	1984 (9)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	3.8 (1)	2.2 (1)	3.0 (1)	0.1 (1)	−0.1 (1)	−0.1 (1)
Cl	8.4 (2)	7.1 (1)	9.7 (2)	−1.8 (1)	0.4 (1)	0.9 (1)
O(1)	3.9 (3)	2.3 (2)	6.1 (3)	0.3 (2)	0.6 (3)	0.7 (3)
O(2)	5.7 (3)	1.6 (2)	6.4 (4)	−0.3 (3)	−1.3 (4)	0.1 (2)
O(3)	6.3 (5)	3.1 (3)	3.6 (3)	0.8 (3)	−1.2 (3)	−0.8 (2)
O(4)	8.3 (4)	3.7 (3)	5.7 (4)	2.0 (4)	−4.0 (4)	0.0 (3)
O(5)	13.9 (8)	20.8 (11)	33.8 (17)	−3.8 (10)	−8.8 (14)	−11.2 (14)
O(6)	23.5 (12)	11.7 (7)	13.9 (8)	−0.8 (9)	6.8 (11)	4.0 (8)
O(7)	23.2 (12)	17.7 (9)	27.1 (15)	11.6 (11)	7.3 (14)	12.7 (13)
O(8)	8.8 (6)	14.8 (9)	17.4 (11)	−2.8 (7)	3.1 (10)	−1.8 (9)
O(W)	11.3 (6)	8.8 (6)	11.7 (8)	3.2 (5)	2.1 (7)	−0.2 (7)
N(1)	5.0 (4)	3.1 (3)	4.5 (4)	−0.4 (4)	−1.8 (4)	0.1 (4)
N(2)	5.5 (4)	2.6 (3)	7.4 (5)	1.7 (3)	3.4 (6)	0.5 (4)
N(3)	5.7 (5)	3.3 (4)	4.1 (4)	1.0 (4)	1.0 (5)	0.8 (3)
N(4)	4.4 (4)	2.2 (3)	3.2 (5)	0.0 (3)	−0.9 (4)	0.0 (3)
N(5)	4.7 (4)	2.3 (2)	2.3 (4)	−0.1 (3)	−0.1 (4)	0.3 (3)
C(1)	3.6 (6)	4.2 (6)	6.3 (7)	0.6 (6)	−2.6 (7)	−0.5 (6)
C(2)	4.9 (8)	4.1 (7)	6.5 (8)	0.4 (7)	−0.9 (7)	−1.6 (7)
C(3)	3.2 (5)	10.6 (8)	6.8 (8)	−0.7 (6)	3.7 (6)	4.0 (8)
C(4)	6.4 (7)	4.2 (5)	4.6 (6)	1.4 (7)	1.9 (6)	0.3 (6)
C(5)	7.6 (8)	3.0 (5)	3.4 (5)	0.8 (6)	−0.7 (7)	−1.0 (4)
C(6)	5.4 (6)	2.6 (4)	4.7 (6)	0.8 (5)	−2.0 (6)	−0.2 (5)
C(7)	8.4 (9)	8.4 (8)	9.0 (11)	3.2 (8)	−4.8 (8)	0.1 (10)
C(8)	6.1 (7)	3.8 (5)	8.4 (9)	−0.8 (6)	−1.9 (8)	−2.8 (7)
C(9)	4.5 (6)	3.9 (4)	3.1 (5)	−0.3 (5)	−1.0 (6)	−0.7 (4)
C(10)	3.5 (4)	2.4 (3)	3.3 (6)	0.0 (4)	−0.3 (4)	−0.1 (5)
C(11)	4.1 (6)	3.2 (5)	3.9 (6)	0.5 (5)	−0.6 (5)	−0.1 (5)
C(12)	5.5 (6)	4.3 (5)	2.0 (4)	0.9 (5)	−0.1 (4)	−0.5 (4)

	x	y	z	B
H(Wa)	100 (9)	348 (8)	−119 (10)	17 (3)
H(Wb)	164 (9)	264 (8)	26 (10)	22 (3)
H(N1a)	92 (7)	97 (6)	5 (8)	1 (3)
H(N1b)	14 (7)	6 (6)	21 (9)	4 (3)
H(N2)	−98 (7)	153 (6)	274 (9)	2 (3)
H(N3)	123 (8)	47 (7)	418 (9)	9 (3)
H(N4a)	178 (7)	175 (6)	163 (10)	7 (3)
H(N4b)	84 (7)	247 (6)	162 (9)	12 (3)
H(N5a)	193 (7)	28 (6)	142 (10)	3 (3)
H(N5b)	287 (9)	34 (8)	190 (10)	16 (3)
H(Cl)	−48 (8)	204 (6)	37 (10)	13 (3)
H(C2a)	−164 (8)	13 (7)	147 (10)	6 (3)
H(C2b)	−212 (8)	135 (7)	179 (10)	5 (3)
H(C3a)	−196 (8)	42 (8)	354 (9)	15 (3)
H(C3b)	−157 (9)	90 (7)	459 (12)	16 (3)

Table II (*Continued*)

	x	y	z	B
H(C4a)	−75 (9)	−2 (6)	469 (9)	10 (3)
H(C4b)	−68 (8)	100 (6)	558 (9)	9 (3)
H(C5a)	45 (8)	247 (6)	448 (9)	8 (3)
H(C5b)	103 (8)	214 (6)	540 (10)	8 (3)
H(C6)	217 (7)	186 (6)	356 (9)	4 (3)
H(C7a)	−23 (7)	98 (6)	−189 (9)	16 (3)
H(C7b)	−183 (9)	123 (7)	−85 (10)	3 (3)
H(C7c)	−114 (9)	33 (8)	−85 (11)	17 (3)
H(C8a)	265 (7)	316 (6)	245 (9)	15 (3)
H(C8b)	219 (7)	339 (6)	425 (10)	1 (3)
H(C8c)	132 (7)	350 (6)	358 (10)	7 (3)
H(C12a)	240 (8)	−139 (7)	110 (9)	5 (3)
H(C12b)	254 (7)	−232 (6)	206 (11)	11 (3)
H(C12c)	345 (7)	−97 (6)	202 (9)	14 (3)

[a] Positional parameters are given as fractions of cell edges $\times 10^4$ ($\times 10^3$ for hydrogen). Anisotropic temperature factors are expressed as $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$ and isotropic temperature factors as $\exp(-B \sin^2\theta/\lambda^2)$ with B values given in Å^2. The standard deviations for each parameter, determined from the inverted full matrix, are given in parentheses and apply to the last specified digits.

Table III. Comparison of Bijvoet Pairs to Give the Absolute Configuration of $CoClO_3N_3C_{12}H_{23}$[a]

hkl	$\lvert F_o(hkl)/F_o(\bar{h}kl)\rvert$	$\lvert F_c(hkl)/F_c(\bar{h}kl)\rvert$
144	1.28	1.22
211	1.35	1.15
222	1.35	1.17
223	0.47	0.49
224	1.45	1.25
231	1.36	1.13
232	1.39	1.25
234	1.26	1.18
243	0.57	0.53
251	2.30	1.83
273	1.41	1.33
311	1.24	1.06
323	1.26	1.11
324	1.41	1.23
333	0.58	0.54
352	0.52	0.43
362	1.30	1.18
372	1.23	1.08
413	2.10	1.61
415	1.59	1.41
432	1.24	1.09
453	1.42	1.24
514	1.41	1.18
533	1.32	1.21
561	1.29	1.21
622	0.66	0.67
722	2.41	2.04

[a] Reflections included in this table are those for which $F^2(hkl) - F^2(\bar{h}kl) > 12\sigma(F^2)$.

(dotted lines). All of the (*S*)-amino acid complexes (**5**$_S$, **6**$_S$, **7**$_S$, **8**$_S$) have similar CD spectra. The parameters for the Cotton effects necessary to generate the composite curves for each (*S*)-amino acid complex are presented in Table V. It can be seen that the signs of ii and iii, but not iv, are reversed when an *R* configuration is changed to an *S* configuration.

B. Crystal Structure of the Malonate Complex (3). The structure and absolute configuration of the complex, found in this X-ray study, are shown in Figures 3, 4, and 5[15] and diagrammatically in Figure 6. The CD spectrum of this same complex in solution is shown in Figure 1. It can be seen from Figures 3–6 that the malonate ion is chelated to the cobalt through its atoms N(5) and O(1), and that there is also an internal hydrogen bond from O(3) of malonate to N(3) of the tetradentate ligand. Thus these three atoms, O(1), O(3), and

(15) Figures 3, 4, 5, and 7 were drawn with computer program ORTEP. C. K. Johnson, ORTEP Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Table IV. Parameters[a] of the Component Cotton Effects for the (*R*)-Amino Acid Complexes

Complex[b]		i	ii	iii	iv	v	vi
3	*a*	500	452.5	350	341	252	
	b	35.4	35.4	22.6	19.8	28.3	
	C	3100	1425	−450	−575	−4,500	
4	*a*	496	435	360	342	256	575
	b	36.0	32.0	18.0	23.0	21.0	30.0
	C	5267	443	329	−694	−4,170	130
5$_R$	*a*	501	454	352	337	235	560
	b	35.4	36.8	17.0	19.0	28.3	42.4
	C	4550	2650	−460	−700	−4,000	150
6$_R$	*a*	502.7	455.5	347	330	240	575
	b	36.8	36.8	14.1	21.2	36.8	42.4
	C	4925	2425	−290	−450	2,500	125
7$_R$	*a*	497.5	453.5	350	340	260	560
	b	35.4	36.1	14.1	19.1	28.3	42.4
	C	6230	2850	−100	−700	10,000	150
8$_R$	*a*	499.5	452.5	350	334	245	565
	b	36.8	36.8	17.7	19.1	24.0	35.4
	C	5400	3975	−700	−700	−10,000	225

[a] As defined in eq 4. [b] *a* and *b* units are in nanometers, and *C* units are in degrees.

Table V. Parameters[a] for the Component Cotton Effects for the (*S*)-Amino Acid Complexes

Complex[b]		i	ii	iii	iv	v	vi
5$_S$	*a*	494	456	365	336	254	550
	b	33.0	31.8	17.0	21.2	25.5	42.4
	C	7500	−1815	550	−625	−4500	150
6$_S$	*a*	493.7	463	366	336.5	260	
	b	31.4	37.2	18.4	21.2	25.5	
	C	7625	−3100	600	−370	−4500	
7$_S$	*a*	493.5	453.5	365	337	237	548
	b	31.8	32.0	19.1	21.2	38.2	36.8
	C	7710	−1710	425	−750	−10500	200
8$_S$	*a*	491.5	457	365	337	262	550
	b	33.5	32.0	19.1	21.2	22.6	42.4
	C	9200	−1550	675	−760	−4000	275

[a] As defined in eq 4. [b] *a* and *b* units are in nanometers, and *C* units are in degrees.

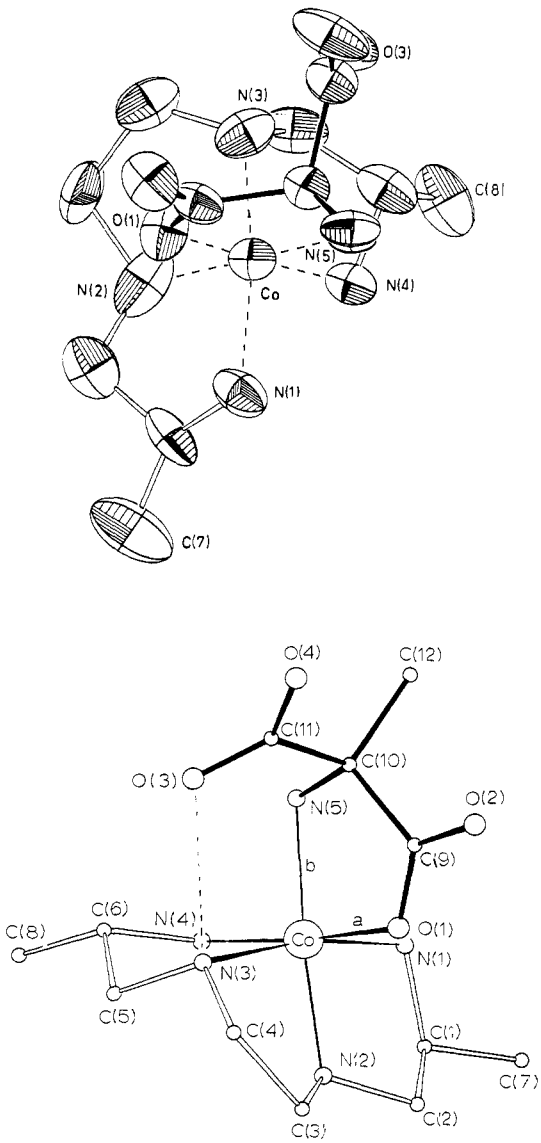


Figure 3. View of the complex showing thermal ellipsoids (above) and the three-point attachment of methylaminomalonate (below). In these and all other diagrams the methylaminomalonate bonds are black and those of the tetramine are unshaded.

Table VI. Some Torsion Angles (deg) in $CoClO_9N_5C_{12}H_{29}$

(a) Malonate Ion	
O(1)-C(9)-C(10)-N(5)	−15 (2)
O(1)-C(9)-C(10)-C(11)	103 (1)
O(1)-C(9)-C(10)-C(12)	−136 (1)
O(2)-C(9)-C(10)-N(5)	169 (1)
O(2)-C(9)-C(10)-C(11)	−73 (1)
O(2)-C(9)-C(10)-C(12)	49 (2)
O(4)-C(11)-C(10)-N(5)	−155 (1)
O(4)-C(11)-C(10)-C(9)	86 (1)
O(4)-C(11)-C(10)-C(12)	−37 (2)
O(3)-C(11)-C(10)-N(5)	27 (2)
O(3)-C(11)-C(10)-C(9)	−91 (1)
O(3)-C(11)-C(10)-C(12)	146 (1)
(b) Tetradentate Ligand	
N(4)-C(6)-C(5)-N(3)	54 (1)
C(8)-C(6)-C(5)-N(3)	176 (1)
C(6)-C(5)-N(3)-C(4)	−164 (1)
C(5)-N(3)-C(4)-C(3)	86 (1)
N(3)-C(4)-C(3)-N(2)	7 (2)
C(4)-C(3)-N(2)-C(2)	149 (1)
C(3)-N(2)-C(2)-C(1)	−170 (1)
N(2)-C(2)-C(1)-C(7)	176 (1)
N(2)-C(2)-C(1)-N(1)	52 (1)

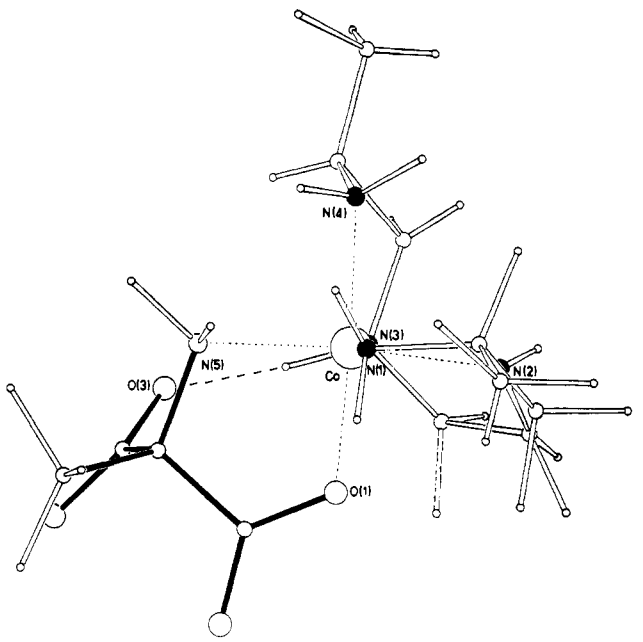


Figure 4. View of the complex onto the plane Co-N(5)-O(1). Note the different disposition of hydrogen atoms for possible hydrogen bonding to a carboxyl group on N(3) (below Co) and N(1) (above Co).

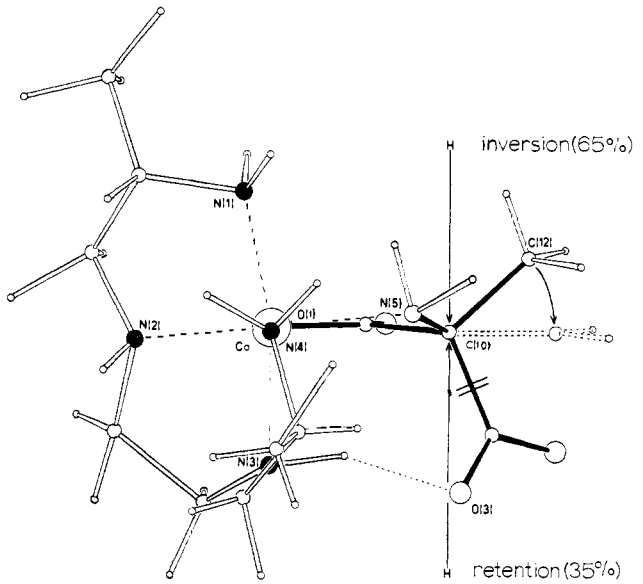
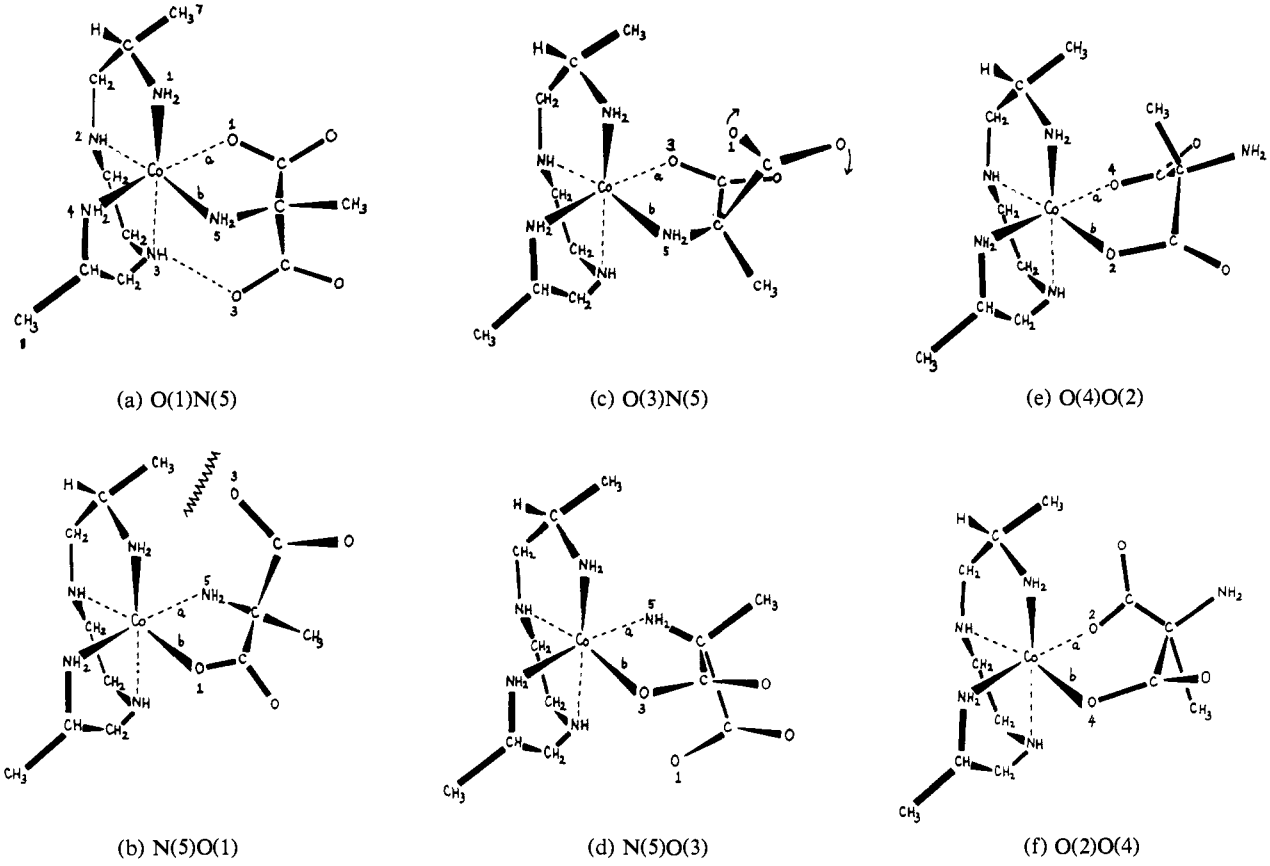


Figure 5. View down the plane Co-O(1)-N(5) showing the decarboxylation.

N(5) of malonate are attachment points to the asymmetric Co(III) complex.

The malonate ion is, in fact, a fairly rigid structure, since an $-NH_2$ (or $-OH$) group[16] adjacent to a carboxyl group tends to lie in the plane of the latter group. This can be seen by the small torsion angles listed in Table VI and by Figure 3, in which the malonate ion is viewed down the plane involving C(12)C(10)N(5). Thus, the torsion angles O(1)C(9)C(10)N(5) and O(3)C(11)C(10)-N(5) are both small (−15 (2) and 27 (2)°, respectively), the value being lower for O(1) which is in the group coordinated to the Co(III). As a result the malonate di-

(16) G. A. Jeffrey and G. S. Parry, *Nature (London)*, **169**, 1105 (1952).



(a) O(1)N(5) (c) O(3)N(5) (e) O(4)O(2)

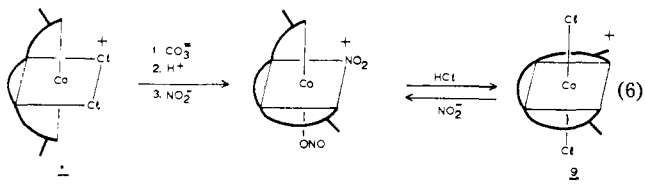
(b) N(5)O(1) (d) N(5)O(3) (f) O(2)O(4)

Figure 6. Different modes of binding of malonate to the cobalt(III) tetramine (**3**). (Compare with Table IX.)

anion does not have much rotational freedom about the bond C(10)–C(11) or C(10)–C(9) in order to accommodate to the Co(III).

It can be seen from Figure 3 that the tetramine ligand has undergone a rearrangement from its configuration in the dichloro precursors **1** and **9** to a structure not observed in acid–base isomerizations in the absence of amino acid (eq 6, Scheme I).[2] The absolute configura-

Scheme I



(6)

tion determined crystallographically has shown that the aminomethylmalonate is bound in a configuration which would be *R* if the unchelated carboxyl group were replaced by a proton with retention of configuration.

The bond distances and interbond angles are given in Table VII. As found in other such Co(III) complexes[17] the large effect of the heavier cobalt ion and the high anisotropy of some light atoms mean that the bond distances and angles are subject to considerable error. There is, as shown in Table II, considerable thermal motion for the perchlorate ion [B = 23, 20, 23, and 14 for O(5) to O(8)], indicative of probable disorder. Such disorder reduces the general accuracy of the structure determination, as indicated by the estimated standard deviations, but does not affect the general findings of this study.

(17) J. W. Turley and R. G. Asperger, *Inorg. Chem.*, **10**, 558 (1971).

All hydrogen atoms were found from a difference map and refined, with results shown in Table II, but those with high B values may be questionable. There were no high peaks in the final difference map except for a few near the cobalt ion position indicating that there are errors in the scattering factor curve used for this ion as a result of an oversimplified treatment of thermal motion and some problems with ionic charge.

The geometry of the Co(III) coordination octahedron is given in Table VII. The average Co···N distance is 1.95 Å. The angles around the cobalt are all near 90°. The angles between Co–N bonds spanned by a ligand are less than 90°, unlike the case for a trans-dichloro complex[17] in which one such angle is 103–108°. The outer rings of the tetradentate ligand complex have the δ conformation but the central ring has an envelope rather than puckered conformation.

The nonbonded O···N and O···O distances in the malonate ion, listed in Table VII, which are 2.63–2.65 and 3.27 Å, respectively, indicate that the O···N distances in the malonate ion are better for the spanning ($2^{1/2} \times 1.95 = 2.73$ Å) of adjacent positions on a Co···N or Co···O octahedron (to give no strain) than the O···O distances which are longer.

The packing in the unit cell is shown in Figure 7 and the hydrogen bonding is described in Table VIII. All hydrogen atoms attached to nitrogen or oxygen atoms take part in hydrogen bonding. The two carboxyl groups of the malonate ion are apparently ionized. The hydrogen bond from N(3) to O(3) has already been discussed and is an important part of the three-point attachment of the malonate dianion to the cobalt(III) complex.

Table VII. Some Angles (deg) and Distances (Å) in the Crystalline Complex

(a) Interatomic Distances

Co-N(4)	1.951 (7)	O(1)-C(9)	1.28 (1)	N(1)-C(1)	1.50 (2)
Co-N(3)	1.925 (17)	O(2)-C(9)	1.25 (1)	C(1)-C(7)	1.53 (3)
Co-N(2)	1.940 (8)	C(9)-C(10)	1.54 (2)	C(1)-C(2)	1.51 (3)
Co-N(1)	1.949 (15)	C(10)-N(5)	1.50 (1)	C(2)-N(2)	1.45 (3)
Co-N(5)	1.992 (8)	C(10)-C(12)	1.56 (2)	N(2)-C(3)	1.55 (2)
Co-O(1)	1.877 (5)	C(10)-C(11)	1.56 (2)	C(3)-C(4)	1.60 (2)
Cl-O(5)	1.34 (2)	C(11)-O(4)	1.28 (1)	C(4)-N(3)	1.43 (2)
Cl-O(6)	1.43 (3)	C(11)-O(3)	1.22 (2)	N(3)-C(5)	1.48 (1)
Cl-O(7)	1.37 (2)			C(5)-C(6)	1.55 (2)
Cl-O(8)	1.37 (1)			C(6)-C(8)	1.51 (2)
				C(6)-N(4)	1.52 (2)

(b) Intracomplex O···O and N···O Distances

O(1)···O(2)	2.25 (1)
O(3)···O(4)	2.22 (1)
O(1)···N(5)	2.63 (1)
O(3)···N(5)	2.65 (1)
O(4)···O(2)	3.27 (1)
O(2)···N(5)	3.61 (1)
O(4)···N(5)	3.60 (1)
O(1)···O(3)	3.65 (1)
O(2)···O(3)	3.95 (1)
O(1)···O(4)	4.25 (1)

(c) Angles

N(1)-Co-O(1)	90.2 (3)	O(5)-Cl-O(6)	102 (1)	N(5)-C(10)-C(11)	107 (1)
N(2)-Co-O(1)	88.0 (3)	O(5)-Cl-O(7)	119 (1)	N(5)-C(10)-C(12)	110 (1)
N(3)-Co-O(1)	91.8 (4)	O(5)-Cl-O(8)	110 (1)	C(11)-C(10)-C(12)	109 (1)
N(4)-Co-O(1)	175.7 (3)	O(6)-Cl-O(7)	105 (1)	C(9)-C(10)-C(12)	111 (1)
N(5)-Co-O(1)	85.6 (3)	O(6)-Cl-O(8)	110 (1)		
N(1)-Co-N(2)	83.3 (4)	O(7)-Cl-O(8)	111 (1)	N(4)-C(6)-C(8)	112 (1)
N(1)-Co-N(3)	167.6 (4)			N(4)-C(6)-C(5)	103 (1)
N(1)-Co-N(4)	91.4 (4)	O(1)-C(9)-O(2)	126 (1)	C(8)-C(6)-C(5)	115 (1)
N(1)-Co-N(5)	95.8 (4)	O(1)-C(9)-C(10)	117 (1)	C(6)-C(5)-C(3)	107 (1)
N(2)-Co-N(3)	84.5 (4)	O(2)-C(9)-C(10)	117 (1)	C(5)-N(3)-C(4)	111 (1)
N(2)-Co-N(4)	96.2 (3)	O(3)-C(11)-O(4)	126 (1)	N(3)-C(4)-C(3)	110 (1)
N(2)-Co-N(5)	173.5 (3)	O(3)-C(11)-C(10)	118 (1)	C(4)-C(3)-N(2)	109 (1)
N(3)-Co-N(4)	87.4 (4)	O(4)-C(11)-C(10)	117 (1)	C(3)-N(2)-C(12)	101 (1)
N(3)-Co-N(5)	96.5 (4)	C(9)-C(10)-C(11)	111 (1)	N(2)-C(2)-C(1)	102 (1)
N(4)-Co-N(5)	90.3 (3)	C(9)-C(10)-N(5)	109 (1)	C(2)-C(1)-C(7)	111 (1)
				C(7)-C(1)-N(1)	113 (1)

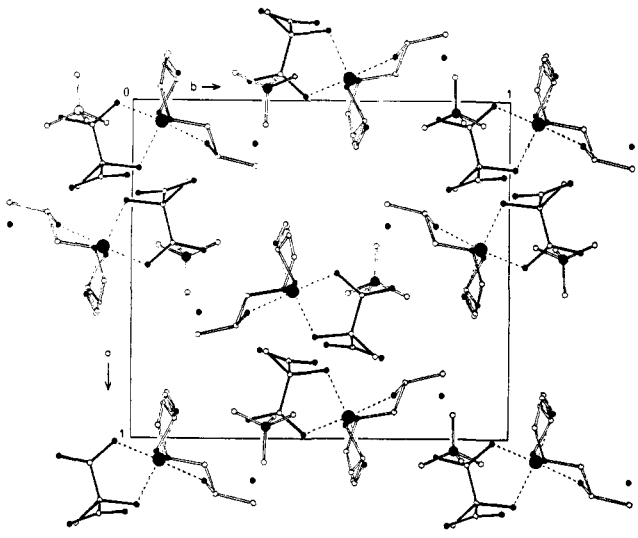


Figure 7. Packing in the unit cell. View down *c*.

Table VIII. Hydrogen Bonding (Å) and Close Interatomic Distances[a]

N(1)-H(N1a)···O(4^{i})	3.11	O(1) none	
N(1)-H(N1b)···O(6^{i})	3.08	O(2)···H(N2^{iv})-N(2^{iv})	2.82
N(1) O(3^{i})	3.27	O(2)···H(N4b^{iv})-N(4^{iv})	2.92
N(2)-H(N2) ···O(2^{ii})	2.82	O(2) O(W^{iv})	3.41
N(3)-H(N3) ···O(3)	2.78[b]	O(3)···H(N3)-N(3)	2.78[b]
N(4)-H(N4a)···O(4^{i})	3.17	O(3)···H(N5a^{iii})-N(5^{iii})	2.87
N(4)-H(N4b)···O(2^{ii})	2.92	O(3) N(1^{iii})	3.27
N(4) O(W)	3.16	O(4)···H(Wb^{iii})-O(W^{iii})	2.78
N(5)-H(N5a)···O(3^{i})	2.87	O(4)···H(N1a^{iii})-N(1^{iii})	3.10
N(5)-H(N5b)···O(5)	3.07	O(4)···H(N4a^{iii})-N(4^{iii})	3.16
		O(5)···H(N5b)-N(5)	3.07
		O(6)···H(N1b^{iii})-N(1^{iii})	3.08
		O(7) none	
		O(8)···H(Wa^{vi})-O(W^{vi})	3.14
		O(W)-H(Wb^{i})···O(4^{i})	2.78
		O(W)-H(Wa)···O(8^{v})	3.14
		O(W) N(4)	3.16
		O(W) O(2^{ii})	3.41

[a] Code: i, $^1/_2 - x, -y, z - ^1/_2$; ii, $-x, ^1/_2 + y, ^1/_2 - z$; iii, $^1/_2 - x, -y, ^1/_2 + z$; iv, $-x, y - ^1/_2, ^1/_2 - z$; v, $-x - 1, ^1/_2 + y, ^1/_2 - z$; vi, $^1/_2 + x, ^1/_2 - y, -z$. [b] Intracomplex hydrogen bond.

Discussion

A. Analysis of CD Spectra. In order to clarify the observation that the signs of peaks ii and iii (Figures 1 and 2) invert on going from (*R*)- to (*S*)-amino acid, we investigated the so-called "vicinal effect" of the amino acid ligands. The vicinal effect of an (*S*)-amino acid, ideally the contribution to the CD curve from the complexed amino acid ligand alone, can be found by taking half the sum of the CD curves of Λ-β-[(*S*,*S*)-diaminodiazadecanecobalt (*S*)-amino acid]$^{2+}$ and Δ-β-[(*R*,*R*)-diaminodiazadecanecobalt (*S*)-amino acid]$^{2+}$. Since

Table IX. Binding of the Malonate Ion to Co(III) Complex

Location of ligand[a]	a [trans to N(4)]	b [trans to N(2)]	Other possible interactions	Remarks
a	O(1)	N(5)	O(3) → N(3)	Experimentally found. Three-point attachment
b	N(5)	O(1)	O(3) → N(1)	O(3) close to methyl C(7). Two-point attachment
c	O(3)	N(5)	O(1) → N(1)	O(1) cannot hydrogen bond. Two-point attachment
d	N(5)	O(3)	O(1) → N(3)	O(1) cannot hydrogen bond. Two-point attachment
e	O(4)	O(2)		N(1) near malonate methyl C(12). O(4)···O(2) long, causes strain. Two-point attachment
f	O(2)	O(4)		O(2)···O(4) long, causes strain. Two-point attachment

[a] See Figure 6.

Δ-β-[(*R*,*R*)-diaminodiazadecanecobalt (*S*)-amino acid]$^{2+}$ is the mirror image of Λ-β-[(*S*,*S*)-diaminodiazadecanecobalt (*R*)-amino acid]$^{2+}$, the same result obtains by taking the difference between the CD curves of the latter and Λ-β-[(*S*,*S*)-diaminodiazadecanecobalt (*S*)-amino acid]$^{2+}$. The vicinal effect curves obtained in this way for (*S*)-alanine and (*R*)-alanine are shown in Figure 8. The vicinal effect for (*S*)-phenylalanine (obtained from the data in Tables IV and V) compares favorably[18] with that observed by Liu and Douglas for phenylalanine in $(NH_3)_4$Co-(*S*)-phenylalaninate^{2+}.[20] Figure 8 also contains the CD curve of Λ-β-[(*S*,*S*)-diaminodiazadecanecobalt glycinate]$^{2+}$, which would be expected to exhibit no vicinal effect from the amino acid ligand. Upon examination of the curves of Figure 8 it becomes readily apparent that addition of the vicinal effect curves of either (*S*)- or (*R*)-alanine to the CD curve of the glycinate complex (to give the CD curve of the (*S*)- or (*R*)-alanine complex, respectively) would cause a dramatic change only in the region of peaks III and IV (Figure 8) where the tetramine moiety has no strong peaks. A less notable effect would occur in the region of I and II which are beneath the large principal Cotton effect.

The signs of the component Cotton effects for **3** were identical with those of the (*R*)-amino acid series. We therefore were led to the conclusion that the aminomethylmalonate moiety is bound in the *R* configuration (in the sense that if the free carboxyl group were replaced by a proton, (*R*)-alanine would result).[21]

Since the effect on the CD spectra of replacing the α-proton of an amino acid with a carboxylate chromophore was uncertain, it became necessary to substantiate this conclusion by an X-ray structure determination. Furthermore, even though CD established the Λ-configuration for the tetramine ligand, spectral evidence was not sufficiently conclusive to allow differentiation between an α or β structure.

B. Chiral Recognition of a Prochiral Center. The structure of **3**, shown by this X-ray crystallographic study to be the Λ-β_2 isomer, reveals a hydrogen bond between one carboxylate group of the aminomethylmalonate moiety and the proton on a secondary nitrogen of the 2,9-diamino-4,7-diazadecane ligand. It becomes evident that, in actuality, there exists three-point binding of the malonate moiety. This is shown in Figure 6a.

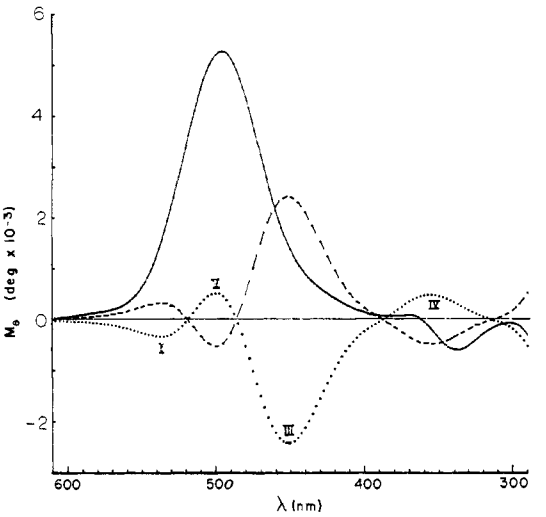


Figure 8. The "vicinal effect" curve for (*S*)-alanine (···) and (*R*)-alanine (– – –). The CD spectrum of Λ(−)$_{436}$-β_2-[(2*S*,9*S*)-2,9-diamino-4,7-diazadecanecobalt(III) glycinate]$^{2+}$ (——) is also shown.

The methyl groups of the tetradentate ligand are both in equatorial positions in the five-membered rings. As a result they may block bulkiness in substituents at the two Co(III) coordination positions (O(1) and N(2)). The methyl group, C(7), affects the manner in which a ligand is added in the coordination position occupied by O(1) of the aminomethylmalonate ion (a in Table IX and Figure 3b). The methyl group, C(8), blocks the position occupied by N(2) of the tetramine. Thus, while there are, in theory, several ways in which the malonate can bind (since N(1) as well as N(3) can accept a hydrogen bond from a carboxylate group), the binding with positions N(5) and O(1) reversed results in a complex with O(3) too near the methyl group C(7) (see Table IX and Figure 6b). This situation cannot be remedied by rotation about C(10)–C(11) since the amino group of the aminomethylmalonate tends to lie in the planes of both carboxyl groups and therefore free rotation about C(10)–C(11) cannot occur. It would also be expected that hydrogen bonding of a carboxyl group to a secondary nitrogen atom, N(3), would be preferred over that to a primary nitrogen atom, N(1), because of the greater basicity of secondary *vs.* primary amines as indicated by higher p*K* values for secondary amines and by shorter hydrogen bond distances to secondary nitrogen atoms (Table VIII), thus favoring the arrangement in Figure 6a over that in Figure 6b. Other modes of binding of the aminomethylmalonate

(18) Since the tetramine will perturb the amino acid and *vice versa*, we would expect to observe a different vicinal effect for each Co(III) tetramine moiety (*i.e.*, the shape of the differential CD curve which comprises the vicinal effect for an optically active ligand is determined by the total molecular symmetry[19]).

(19) Y. Shimura, *Bull. Chem. Soc. Jap.*, 31, 315 (1958).

(20) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 3, 1356 (1964).

(21) Note that although the sets of component Gaussian Cotton effects are not unique, the same result obtains from any sets that fit the experimental data.

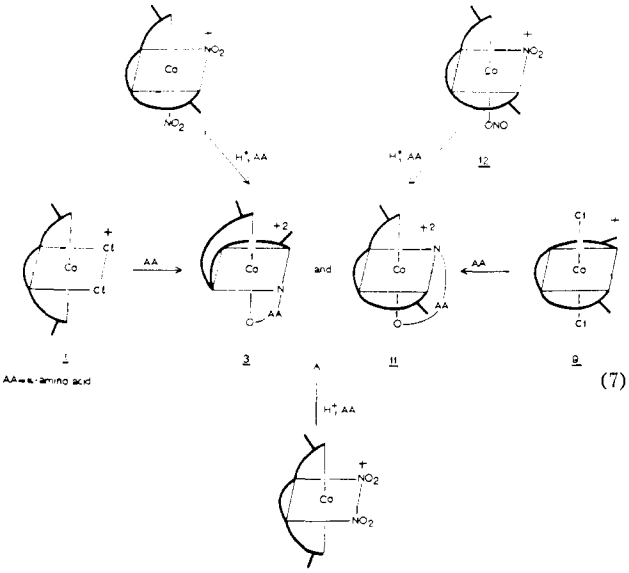
(Figure 6c–f) result in only two-point attachment. The Co(III) complex with the diaminodiazadecane ligand bound as in **1** presents a situation which has *greater blockage by methyl groups so that three-point* attachment of the aminomethylmalonate is not possible.

Thus, the metal with the tetradentate asymmetric ligand has provided a template which can differentiate between the two carboxyl groups of the prochiral aminomethylmalonate (as suggested by Ogston in his three-point hypothesis for enzyme systems).[3] Under these circumstances it is not surprising that such a high degree of chiral recognition should exist. (It is estimated[2] that the presence of 0.5% **3**$_S$ could have been detected but was not.)

In the case of aconitase it is also believed[5] that metal (Fe(II)) chelation aids in the chiral recognition of the two prochiral $-CH_2COO^-$ groups of the citrate ion. In this case only one mode of binding brings the carboxymethylene group in the correct position in the active site for dehydration or isomerization to occur.

C. Mechanism for Amino Acid Complexation to Co(III) Tetramines *via* a Trans Intermediate. The observation here and in an earlier paper,[2] that Λ-α-, trans-, and Δ-β- starting complexes all give similar yields of Λ-β- and Δ-β- product upon treatment with amino acids (eq 7, Scheme II), would seem to require the

Scheme II

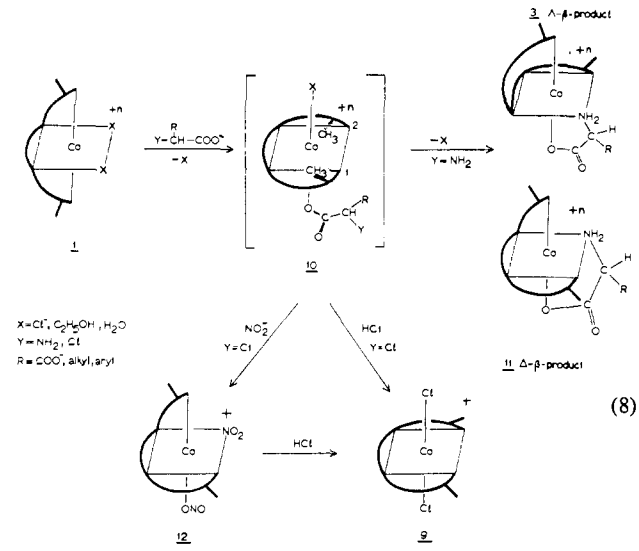


(7)

existence of a common intermediate. A trans intermediate (among others[22]) adequately explains our results.

When **1** is treated, at pH 5–7, with an amino acid (eq 8) an oxygen bound trans intermediate (**10**) results. The amino group of the amino acid may then attack at position 1 (of **10**) with elimination of X to produce Λ-β- product (**3**) or at position 2 to produce Δ-β- product (**11**). Steric hindrance at position 2 (of **10**), due to the tetramine methyl group, causes the Λ-β- complex to predominate (74.2% in the case of aminomethylmalonate). In order to further substantiate this hypothesis, **1** was treated with a monodentate carboxylate ligand (chloroacetate) which should yield **10** only. Upon treatment with nitrite ion the resulting solution

(22) A. M. Sargeson, *Pure Appl. Chem.*, 33, 527 (1973).

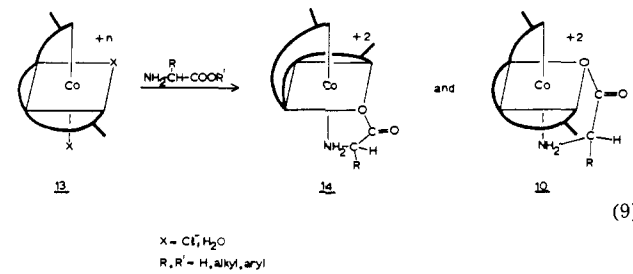


(8)

yielded Δ-β-[2,9-diamino-4,7-diazadecanecobalt (ONO)-$(NO_2)]^+$ (**12**) which upon acidification with hydrochloric acid yielded *trans*-[2,9-diamino-4,7-diazadecanecobalt dichloride]$^+$ (**9**).[2] Only a Δ-β or trans intermediate could have yielded **12**.[2] The possibility of **1** as a Δ-β isomer was eliminated by the presence of a strong positive Cotton effect at 546 nm. Quenching of **10** with HCl would be expected to yield **9** directly as well as some **1**. This expectation was realized when, upon treatment of the chloroacetate solution with gaseous HCl, **9** was obtained in 65% yield. Thus, we conclude that a trans intermediate (**10**) is formed as **1** is converted to **3** or **11**.

This mechanism would lead us to predict that treatment of *trans*-[2,9-dimethyl-4,7-diazadecanecobalt dichloride]$^+$ (**9**) with α,α-aminomethylmalonate would give the same yield of **3** as would treatment of **1** with the same reagent. This prediction is borne out in the experimental results where **3** results in 72.5% yield from **9** (*vs.* 74.2% from **1**).[2]

The corresponding β complexes (**13**) may also proceed *via* the same trans intermediate upon treatment with amino acids. Regardless of which X is displaced first, if conditions are such that the carboxylate group attacks first (lower pH), a β_2 complex will always result (**3** and **11**). If conditions are such that the amino group attacks first (higher pH or ester), a β_1 complex will result (eq 9). This obviates the necessity of rationalizing why



(9)

one X should be eliminated at a much higher rate than the other.

D. Decarboxylation of the Methylaminomalonate Chelate. It has been shown[2] that decarboxylation of C(4) from the pure (*R*)-malonate complex (**3**) in acid solution results in 65% (*S*)-alaninate and 35% (*R*)-alaninate. It is assumed that decarboxylation involves

an enolate intermediate to which a proton is added. It would be presumed that this protonation would result in racemization in the absence of any steric hindrance.

An inspection of Figure 5 shows that there is no steric hindrance to the approach of a proton to C(10), although experimental results indicate a proton adds preferentially from the top of this figure, inverting the configuration. It might be thought that either O(3) of the decarboxylation product (CO_2) is slow to leave (compared to the time for protonation) or that another molecule, perhaps water, is hydrogen bonded to N(3) at this site, partially blocking rapid protonation. Figure 5 shows that pathway of a proton to give inversion of configuration is less obstructed.

E. Summary. In conclusion we have found (1) that three-point attachment provides a sufficient condition for chiral recognition of "equivalent" groups in a symmetrical, prochiral molecule, (2) that the product distribution upon addition of α,α-aminomethylmalonate (or any α-amino acid) to a Co(III) tetramine can be explained by invoking a trans intermediate, and (3) that resolution of CD spectra into component Cotton effects can provide useful information as to the chirality of asymmetric centers induced on complexation. The fact that complexing to an agent with two open binding sites may derive stereospecific recognition *via* the presence of a third, hydrogen bonding, site opens new avenues for the creative design of template molecules.

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Supplementary Material Available. A listing of structure factor amplitudes for the α,α-aminomethylmalonate complex will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5741.

Stereochemical Rigidity in ML_5 Complexes. II. Preparations and Intermolecular Exchange of Cationic ML_5 Complexes of Cobalt(I), Rhodium(I), Iridium(I), Nickel(II), Palladium(II), and Platinum(II)

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Abstract: A series of complexes of the form $ML_5^{n+}(X^-)_n$ have been synthesized (M = Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II); L = phosphite). The Pd(II) and Pt(II) species are novel in that they represent the first ML_5 compounds for these metals; complexes in this class have been described previously for the other four metals. We report new preparative techniques for Co(I) and Ir(I) and extend the scope of known complexes for several of the metals. The steric range within which ML_5 species may be prepared is defined in connection with the equilibrium $ML_5 \rightleftharpoons ML_4 + L$ and the steric size of L. Intermolecular exchange effects associated with the above equilibrium are analyzed. Preparative problems associated with transesterification are discussed.

The question of stereochemistry and fluxional behavior in five-coordinate transition metal complexes has been a problem of considerable interest since the early nmr experiments of Cotton, *et al.*[1] Recently we have reported the first nmr evidence for stereochemical rigidity and trigonal bipyramidal equilibrium stereochemistry for complexes of the form $RhL_5^+X^-$ (L = phosphite)[2,3] together with a detailed line shape analysis indicating that the permutational nature of the exchange process[2] is consistent with the Berry mechanism.[4] As a continuing part of this investigation a substantial number of ML_5 complexes of Co(I), Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II) have been prepared; some preliminary results with regard to stereochemistry and stereochemical rigidity in these complexes have been communicated.[5] The present paper describes the preparation of the $ML_5^{n+}(X^-)_n$ complexes together with an analysis of intermolecular exchange in $Rh[P(OCH_3)_3]_5^+B(C_6H_5)_4^-$.

Prior to this work, the only well-established five-coordinate species of the type ML_5 for platinum was $Pt(SnCl_3)_5^{3-}$;[6] there appeared to be no well-characterized ML_5 species for Pd. The PtL_5^{2+} and PdL_5^{2+} phosphite complexes described here are therefore signif-

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(2) J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, **95**, 1344 (1973).
(3) P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, **95**, 7272 (1973).
(4) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).
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