epimerization of *exo*- to *endo*-methyl reactant (**2** $\rightarrow\!\!\!/\!\!\rightarrow$ **3**) occurs in the pyrolysis of **2**, whereas the reverse process (**3** $\rightarrow$ **2**) is readily detectable in the case of **3** and occurs about 60% as fast as the rearrangement of **3** to **9** and **8**.

These observations are compatible with a change in mechanism for the major portion of the carbon rearrangement, from a largely concerted one in the case of *exo*-methyl reactant **2** to a diradical pathway in *endo* compound **3**. The principal observable reactions of the diradical intermediate, formed by C-7–C-1 cleavage of **3**, are recyclization with retention of configuration at the migration terminus to give *cis-exo* product **9** and recyclization after rotation about C-6–C-7 to give epimerization product **2**.[10,11]

The ratio $k_{inv}(exo)/k_{inv}(endo)$ is given by the product of two ratios: (i) the overall[7] pyrolysis rate ratio (0.8) and (ii) the ratio of the fractions of total product obtained with inversion (91:1.4). The minimum value of $k_{inv}(exo)/k_{inv}(endo)$ is 54.

The present results indicate that the configuration-inverting transition state from *endo*-methyl reactant **3** is sterically too strained to permit the electronically "allowed" concerted process to occur. They also clearly define as CW the sense of the configuration-inverting motion in the rearrangement of *exo*-methyl reactant **2**. Although we would greet proposed alternatives with interest, we presently consider "orbital symmetry" control of the geometry of the transition state an attractive explanation of these findings.

(10) The relative rates of rearrangement of **2** and **3** do not permit **2** to be a significant intermediate in the formation of **9** from **3** at low conversion.

(11) Conceivably, **2** may originate in cleavage of the C-6–C-7 bond of **3** and not the C-7–C-1 bond, but it seems unlikely that α-acetoxy activation would be superior to allylic activation.[12]

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Utilization of Steric Compression to Assign the Absolute Configuration and Ring Conformation of Some Transition Metal Complexes

Sir:

In recent years in the field of transition metal stereochemistry considerable research has been undertaken to determine the absolute configuration and ring conformation of transition metal complexes. The assignments are generally made by analysis of the ORD or CD spectra of the complex[1] or by X-ray determination of its structure.[2] Recently, however, nuclear magnetic resonance (nmr) has been utilized to determine the absolute configuration of the cobalt(III) complexes with the ligand ethylenediamine-N,N′-di-L-α-propionic acid (LL-EDDP) in terms of the magnetic anisotropy of the C–N bond.[3] Nuclear magnetic resonance has also confirmed the absolute configuration of the cobalt(III) complexes containing *l*-propylenediamine and ethylenediamine-N,N′-diacetic acid (EDDA),[4] and trends in the chemical shifts of the methyl signals of certain propylenediamine complexes of cobalt(III) and platinum(IV) have been related to the absolute configuration of these complexes.[5] These assignments made use of the different electronic environments of certain protons in the two diastereomers.

In coordination compounds containing organic ligands, there are several ways in which the electronic environment about a proton can be influenced by intramolecular interactions. These include anisotropy effects from bonds within the molecules,[6] involvement of the metal d-electron system on the ligand substituents,[7] and van der Waals interaction or steric compressions.[8] Utilizing the last-mentioned effect of steric compression we have examined the absolute configurations and ring conformations of some cobalt(III) complexes.

This effect, which has been observed in certain organic molecules,[9] is produced when a hydrogen atom is forced into proximity of some other atom in the molecule. The proton involved in the compression is found to resonate at a lower field than when the compression is absent. For the complexes under study the distance between the two nuclei involved in the compression is 2–3 Å which results in a shift of 0.1–0.3 ppm. A shift of similar magnitude was observed by Terrill and Reilley[10] in connection with the *trans*-1,2-cyclohexanediamine-N,N′-tetraacetatocobalt(III) cation and was assumed to be in part due to steric compression.

We have prepared a series of bis(amino acid) complexes of cobalt(III) containing optically active amino acids and find that it is possible to assign the absolute configuration of these complexes using nmr steric compression. The compounds synthesized were *trans*-(O)-$[Co(en)(AA)_2]^+$ and *trans*-(O)-$[Co(en)(AA)(gly)]^+$ (Table I) which were prepared from the reaction of the optically active amino acid (AA) with either $[Co(en)(AA)(H_2O)Cl]^+$ or $[Co(en)gly(H_2O)Cl]^+$[11] and separated from the various *cis* isomers by ion-exchange chromatography. The compounds were characterized by their elemental analyses and visible absorption spectra which exhibited bands at 360 and 533 mμ with a shoulder at 450 mμ characteristic of *trans*-CoO_2N_4 complexes. The diastereomers were separated on a cation-exchange resin and distinguished by the sign of the dominant component of the CD spectrum in the first spin-allowed d–d transition region.

The relative arrangement of the α protons in the two diastereomers is seen in Figure 1. In these compounds one would expect that the amino acid ring would not be planar but slightly puckered, placing the substituent on the amino acid in a equatorial position and forcing the α proton into a position adjacent to the amino pro-

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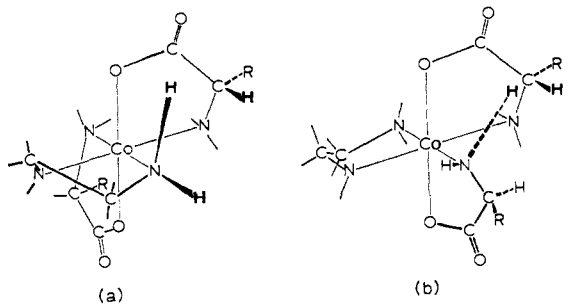

Figure 1. The diastereomers of bis(L-amino acid)ethylenediaminecobalt(III): (a) $\Lambda(C_3)$; (b) $\Delta(C_3)$. The atoms in bold type are those involved in compressions. The bond lengths to these atoms have been exaggerated to emphasize the interactions involved in compression.

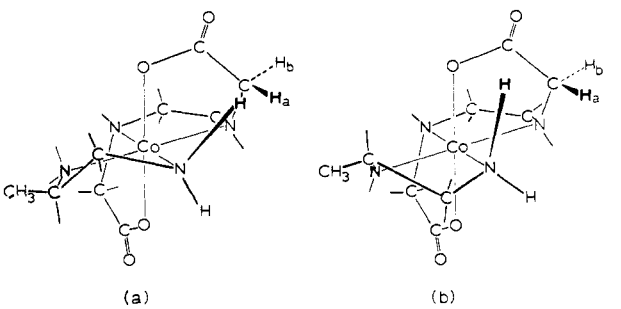

Figure 2. (a) $\Lambda(C_3)$*trans*-(O)-[Co(*l*-pn)(EDDA)]$^+$. (b) $\Lambda(C_3)$ *trans*-(O)-[Co(*d*-pn)(EDDA)]$^+$.

ton on the other amino acid or diamine.[12] The presence of steric compression is seen by studying the nmr signals of the α proton or in some cases the substituent group of the amino acid. In considering the bis(L-alanato) complex, the $\Lambda(C_3)$ isomer places the α proton between two amine protons of the diamine at some distance from them while in the $\Delta(C_3)$ isomer this proton is near one of the amine protons of the amino acid. The latter isomer should then exhibit a steric compression relative to the former. Similar reasoning can be applied to the methyl group on the L-alanine, although, because of its near-equatorial position, the shifts will not be as great. The steric compression would be greater for the methyl group in the $\Lambda(C_3)$ isomer as the methyl group is most coincident with the amine proton. The data in Table I show that the bis(L-alanato) isomer which exhibits the lower field signal for the α proton (at 3.81 ppm) also has the higher field methyl signal (at 1.53 ppm) and can be assigned the $\Delta(C_3)$ absolute configuration. The other bis(amino acid) complexes are assigned absolute configurations in like fashion. These assignments are consistent with the work of Mason[1] who assigns the $\Delta(C_3)$ absolute configuration to that isomer which has a negative CD band for the $A \rightarrow E$ transition in the first spin-allowed d–d transition region.

Table I. Nuclear Magnetic Resonance Data of Some Cobalt(II) Amino Acid Complexes

Complex[a]	Nmr of complex with: −CD[b,c]	+CD	Ref
trans-(O)-[Co(en)(L-ala)$_2$]$^+$	3.81[d]	3.61	*h*
	1.53[e]	1.55	
trans-(O)-[Co(en)(gly)(L-thr)]$^+$	3.75[d]	3.63	*h*
trans-(O)-[Co(en)(gly)(L-ser)]$^+$	4.03[d]	3.85	*h*
[Co(en)$_2$(L-ala)]$^{2+}$	4.15[d]	3.98	*h*
	1.48[e,f]	1.5	
[Co(en)$_2$(L-val)]$^{2+}$	3.78[d]	3.57	12
	0.93[e]	1.02	
	1.13[e]	1.15	
[Co(L,L-dimethyltrien)(L-ala)]$^{2+}$	4.0[d,f,g]	3.7	13

[a] L-ala = L-alanine, L-thr = L-threonine, L-ser = L-serine, gly = glycine, L-val = L-valine, en = ethylenediamine, L,L-dimethyltrien = L,L-2,9-dimethyltriethylenetetramine. [b] All complexes assigned $\Delta(C_3)$ absolute configuration. [c] Shifts in ppm from DSS. [d] α-Proton signal of amino acid. [e] Methyl signal. [f] Estimated from published spectra. [g] CD and nmr from compound which is enantiomeric with complex having negative CD. [h] This work.

A survey of the literature reveals several cobalt(III) complexes whose absolute configurations could have been assigned on the basis of steric compression. Buckingham, Durham, and Sargeson[13] studied the bis(ethylenediamine)cobalt(III) complexes with L-alanine and with L-valine (Table I). The stereochemistry of the α protons and methyl groups in the diastereomers is the same as for the bis(amino acid) compounds. These authors relate the absolute configuration of these complexes to increased separation of the methyl signals in the $\Delta(C_3)$ [Co(en)$_2$(L-val)]$^{2+}$ cation, whereas it is seen that the shift in the α-proton signal due to compression is a much more sensitive signal to consider.

Similarly, Asperger and Liu[14] have studied the L-*cis*-cobalt(III) complexes of L,L-2,9-dimethyltriethylenetetramine with D- and L-alanine (Table I). Owing to the stereoselective nature of the substituted trien, the α-*cis* complexes occur only in the $\Delta(C_3)$ absolute configuration. The L,L-dimethyl(trien) complex with L-alanine exhibits a steric effect similar to the $\Lambda(C_3)$ [Co(en)$_2$(L-ala)]$^{2+}$ cation, while the complex with D-alanine can be compared with the $\Delta(C_3)$ [Co(en)$_2$(L-ala)]$^{2+}$ compound.

The complexes of EDDA or LL-EDDP (Table II) with propylenediamine have steric considerations analogous to *trans*-(O)-[Co(en)(L-ala)$_2$]$^{2+}$. Figure 2 indicates the arrangement of the EDDA in the $\Lambda(C_3)$ absolute configuration. For LL-EDDP the methyl group occupies position H_b while in DD-EDDP it occupies position H_a. The diamine in Figure 2a is *l*-pn while in Figure 2b it is *d*-pn giving the ring backbones the k and k′ conformation, respectively.[15,16] When the diamine is in the k′

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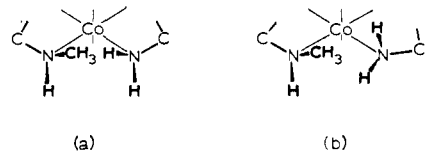

(a) (b)

Figure 3. Regions of the *trans,trans*-$[Co(Meen)_2X_2]^+$ isomers exhibiting steric compression: (a) *meso* isomer; (b) *d,l* isomer.

conformation, the steric compression is most pronounced and the signal of the H_a proton appears at a lower field than that in the other diastereomer. If the methyl group occupies position H_a, as in the DD-EDDP compound, the position of the methyl group signal in the complex with the k′ conformation is at a lower field than the other diastereomer.

Table II. Nmr Data for *trans*-(O)-[Co(en)(EDDA)]$^+$-Type Complexes[a,b]

Complex	H_a	H_b	CH_3[f]	Ref
[Co(en)(EDDA)]$^+$	4.19	3.37		4
[Co(*l*-pn)(EDDA)]$^+$ [c]	4.26	3.36		4
	4.23			
[Co(*d*-pn)(EDDA)]$^+$ [d,e]	4.16	3.34		4
[Co(en)(LL-EDDP)]$^+$	3.99		1.45	3
[Co(*l*-pn)(LL-EDDP)]$^+$ [c]	4.15		1.45	3
	4.08			
[Co(*d*-pn)(LL-EDDP)]$^+$ [d,e]	3.93		1.47	3
[Co(en)(DD-EDDP)]$^+$		3.53	1.55	3
[Co(*l*-pn)(DD-EDDP)]$^+$ [c]		3.54	1.61	3
[Co(*d*-pn)(DD-EDDP)]$^+$ [d,e]		3.51	1.53	

[a] Complexes with $\Lambda(C_3)$ absolute configuration. [b] Shifts in ppm from DSS. [c] k′ diamine conformation. [d] k diamine conformation. [e] Signal from enantiomeric compound. [f] Methyl signal from EDDP.

The technique is also useful for a series of *trans*-bis(diamine)cobalt(III) complexes. Buckingham, Marzilli, and Sargeson[17] have prepared the *meso*- and *d,l*-*trans,trans*-$[Co(N\text{-}Meen)_2X_2]^+$ compounds where X is NO_2^-, Cl^- or $^1/_2NO_2^-$, $^1/_2Cl^-$. Corey and Bailar[15] have discussed the different interactions between the possible conformations for the diamine rings. They concluded that the most stable situation exists when both rings have the same conformation (kk or k′k′) as found in the *d,l* isomers (Figure 3b). The *meso* isomer (Figure 3a) has one ring as k and one as k′, which should be less stable than the racemate because of the interaction in the *meso* isomer between the methyl group attached to one nitrogen atom and the proton on the neighboring nitrogen. The nmr data of these compounds show that this methyl group is involved in a compression when compared with the racemate (Table III).

Table III. Nmr Spectra of *trans,trans*-$[Co(N\text{-}Meen)_2X_2]^+$ [a,b]

X_2	*meso*[c]	*d,l*[c]
NO_2^-	2.34	2.23
$^1/_2NO_2^-$, $^1/_2Cl^-$	2.4	2.29
	2.57	2.46
Cl^-	2.4	2.37

[a] Shift in ppm from DSS. [b] N-Meen = N-methylethylenediamine. [c] Methyl group signal.

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Transient Bromine Atom Charge-Transfer Complexes Observed by Pulse Radiolysis[1]

Sir:

Pulse radiolysis[2] has been used to study transient charge-transfer complexes in organic reactions. It is known from kinetic spectroscopy data[3-6] that iodine and chlorine atoms can form complexes with various electron donors. Only little is known about bromine atom complexes.[7] Bromobenzene as well as various liquid systems with aliphatic and aromatic bromine compounds were studied at room temperature. In all

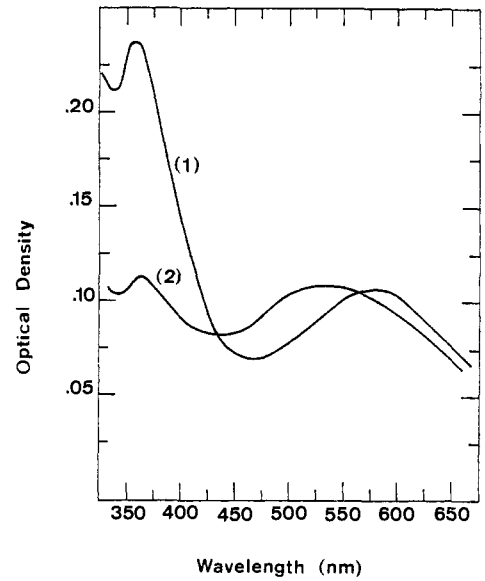

Figure 1. Transient absorption spectra at the end of an electron pulse: (1) in pure deaerated bromobenzene; (2) in oxygen-saturated bromobenzene.

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