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The Crystal and Molecular Structure of 1,9-Diamino-4-methyl-3,7-diazanonane-3,7-diacetato(2–)cobalt(III) Nitrate Monohydrate—a Complex Exhibiting Large ^{13}C NMR Steric Shifts

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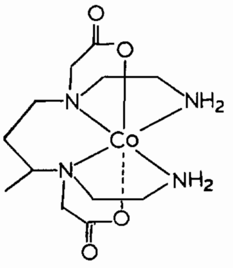
Past studies have shown major ^{13}C NMR chemical shift differences between methylene carbon atoms proximal (in a γ position) and distal to a ligand methyl substituent in [Co(mddda)]$^+$ (mddda = 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate-(2–), $NH_2CH_2CH_2N(CH_2COO^-)CH_2CH_2CH(CH_3)N(CH_2COO^-)CH_2CH_2NH_2$). Since the chemical shift differences have been attributed to γ steric shifts associated with the methyl group on the hexadentate ligand, an X-ray crystal structure determination has been carried out on [Co(mddda)]$NO_3 \cdot H_2O$ to examine the steric features. The compound crystallizes in the space group $P2_1/c$ with $a = 9.756(2)$ Å, $b = 14.912(4)$ Å, $c = 11.783(2)$ Å, $\beta = 95.70(2)°$, and $Z = 4$. Intensities were collected on an automated diffractometer and the structure was refined to a conventional R factor of 0.058. The crystal contains a racemic mixture of ΔΛΔ(R) and ΛΔΛ(S) enantiomeric cationic complexes, where the R and S labels designate the absolute configurations of the chiral methyl-substituted carbon atom of the ligands. These diastereomers are those required to maintain an equatorial methyl group on the central six-membered chelate ring, whose conformations are λ skew-boat for the ΔΛΔ isomer and δ skew-boat for the ΛΔΛ isomer. The respective conformations of the two skewed five-membered chelate rings are δδ and λλ. Though most corresponding bond lengths and bond angles in the two portions of the molecule are nearly the same, those differences which are observed indicate nonbonded interactions between the methyl substituent and adjacent methylene groups. Consideration of these interactions and geometrical variations indicates that bond angle distortion may play an important role in the γ shifts oberserved.

Introduction

The hexadentate ligand 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate(2–) (mddda) coordinates with cobalt(III) to give a cationic complex, [Co(mddda)]$^+$ (*1*) containing a central six-membered chelate ring, two in-plane (meridional) ethylenediamine chelate rings, and two out-of-plane (axial) glycinate chelate rings [1]. Owing to the presence of a methyl substituent on the six-membered backbone ring, the two portions of the ligand proximal and distal to the methyl group are nonequivalent. Of particular interest are the large ^{13}C NMR chemical shift differences between corresponding methylene groups attached to the tertiary nitrogen atoms in the nonequivalent halves of the ligand. Shift differences of 4.31 ppm for the glycinate methylene carbon atoms and of 2.26 ppm for the ethylenediamine carbon atoms adjacent to the tertiary nitrogens have been found [1]. Since in both cases the ^{13}C NMR resonance of the methylene carbon atom γ to the methyl substituent is upfield from that found for the corresponding methylene group in the other half of the ligand, it has been proposed [1] that the ^{13}C NMR chemical shift nonequivalences arise from upfield γ steric shift effects [2].



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In order to examine the steric environments of the methylene groups distal and proximal to the methyl substituent in [Co(mddda)]$^+$, a crystal structure determination has been carried out on this complex as the monohydrated nitrate salt. This is the first structure determination reported for an mddda complex.

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Experimental

The compound [Co(mddda)]I was prepared as described previously [1]. Initial X-ray studies indicated a disorder problem with crystals of this salt and therefore the nitrate salt, [Co(mddda)]$NO_3 \cdot H_2O$, was prepared by ion exchange. A crystal was selected from needles deposited from 50% aqueous ethanol and mounted on a glass fiber. X-ray data were collected on a Syntex *P3/F* diffractometer system. Preliminary work showed the space group to be monoclinic, $P2_1/c$. The lattice parameters were obtained from a least-squares fit to 25 automatically centered settings [3]. The crystallographic and data collection parameters are summarized in Table I.

Following an empirical absorption correction, the data were phased using the cobalt atom, which was located from a Patterson map, and the resulting difference map permitted the location of the other nonhydrogen atoms. Isotropic and anisotropic refinements before inclusion of the hydrogen atoms converged at R(F) = 0.102 and R(F) = 0.074, respectively. The ligand hydrogen atoms were fixed in idealized positions and the water molecule hydrogen atoms were fixed in positions located from a difference map. Hydrogen atom isotropic thermal parameters were fixed at 1.2 times the last U_{eq} value of the atom to which each hydrogen atom was attached. Neutral atom scattering factors were used for all atoms and anomalous dispersion corrections were applied to non-hydrogen atoms. The final difference map showed the three largest peaks (1.2 to 0.8 $e^-/Å^3$) to be within 1.01 Å from the cobalt atom. All remaining difference peaks were 0.5 $e^-/Å^3$ or less. Atomic coordinates and isotropic or equivalent thermal parameters are given in Table II. Since steric variations within the molecule are of some importance in the interpretation of the NMR spectra, hydrogen atom parameters, though fixed, are also given in this table. Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

TABLE I. Crystal and Data Collection Parameters for [Co(mddda)]$NO_3 \cdot H_2O$.

Formula	$CoC_{12}N_5O_8H_{26}$
Formula weight	427.4
F_{000}	896
a, Å	9.756(2)
b, Å	14.912(4)
c, Å	11.783(2)
β, deg	95.70(2)
V, $Å^3$	1705.7(6)
Z	4
ρ(calcd), g/cm^{-3}	1.66
Reflections measd	±*h*, +*k*, −*l*
Space group	$P2_1/c$
Crystal dimens, mm	0.09 × 0.17 × 0.55
Radiation	Mo Kα (λ = 0.71069 Å)
Data collection temperature, °C	18
Absorption coefficient, cm^{-1}	11.0
Scan range, deg	1.2 below $2\theta(K\alpha_1)$ to 1.2 above $2\theta(K\alpha_2)$
Background time	0.5 × scan time
2θ limits, deg	1.0–55.0
Standards	2 every 94 reflections
Reflections collected	4703
Unique reflections	4334
Unique data used	2367 with $I > 5\sigma(I)$
Variables refined	235
w^{-1}	$\sigma^2(F_o) + (gF_o)^2$, g = 0.033
$R(F) = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.058
$R_w(F) = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.057

Discussion

Description of the Crystal Structure

The crystal contains a racemic mixture of ΔΛΔ and ΛΔΛ [4] cationic complexes, NO_3^- anions, and water molecules held together by a complex system of ionic interactions and hydrogen bonds. The asymmetric cation, shown in a stereoscopic view in Fig. 1, sits at a general crystallographic position, as it must in the absence of disorder. In agreement with other studies [1], the two glycinate oxygen atoms are *trans* to each other.

Around the meridian of the complex are a skewed five-membered ethylenediamine chelate ring, a central six-membered 1,3-diaminobutane chelate ring with a skew-boat conformation, and a second skewed five-membered ring. In the order given above, the absolute configurations [4] of the enantiotopic chelate ring conformations are δλδ in the ΔΛΔ isomer and λδλ in the ΛΔΛ isomer. Molecular models indicate a strong preference for this observed conformational stereoselectivity. Indeed, for the structurally related complexes (+)-[Co(penten)]$^{3+}$ (penten = N,N,N′,N′-tetrakis(2′-aminoethyl)-1,2-ethanediamine) [5] and $(-)_{589}$-[Co(*R*-mepenten)]$^{3+}$ (mepenten = N,N,N′,N′-tetrakis-(2′-aminoethyl)-1,2-propanediamine) [6] only ΔΛΔ, δλδ or ΛΔΛ, λδλ conformers are found. (In these two complexes, the axial groups are aminoethyl rather than acetate and the central chelate ring is five-membered rather than six-membered.) Moreover, the central six-membered chelate ring in the ΛΔΛ complex $(-)_{546}$-[Co(1,3-pdta)]$^-$ (pdta = 1,3-diaminopropane-N,N,N′,N′-tetraacetate) is δ skew-boat [7]. A comparison of dihedral angles indicates little difference between the central ring conformation of [Co(mddda)]$^+$ and the conformations of other skew-boat six-membered diamine chelate rings (Table III). As found for $(-)_{546}$-[Co(1,3-pdta)]$^-$ [7], but not for six-membered chelate rings formed by simple diamines, the C–C–C bond angle in the

TABLE II. Atomic Positions and Thermal Parameters for $[Co(mddda)]NO_3 \cdot H_2O$.[a]

Atom	x/a	y/b	z/c	U_{eq} or U_{iso}
Co	0.18107(7)	0.05703(5)	0.21914(6)	0.0202(2)
N(1)	−0.0167(4)	0.0724(3)	0.2195(4)	0.027(1)
H(1A)	−0.0421	0.0622	0.2951	0.030
H(1B)	−0.0635	0.0301	0.1679	0.030
C(2)	−0.0569(6)	0.1641(4)	0.1832(5)	0.038(2)
H(2A)	−0.0796	0.1657	0.1020	0.046
H(2B)	−0.1351	0.1830	0.2205	0.046
C(3)	0.0643(6)	0.2249(4)	0.2165(5)	0.035(2)
H(3A)	0.0784	0.2303	0.2980	0.040
H(3B)	0.0477	0.2832	0.1833	0.040
N(4)	0.1886(4)	0.1835(3)	0.1723(4)	0.027(1)
C(5)	0.3148(6)	0.2320(4)	0.2207(5)	0.37(2)
H(5A)	0.3060	0.2939	0.1988	0.045
H(5B)	0.3211	0.2274	0.3023	0.045
C(6)	0.4473(6)	0.1956(4)	0.1804(5)	0.042(2)
H(6A)	0.4605	0.2257	0.1103	0.050
H(6B)	0.5207	0.2113	0.2373	0.050
C(7)	0.4589(6)	0.0946(5)	0.1584(5)	0.039(2)
H(7)	0.4123	0.0816	0.0846	0.045
N(8)	0.3861(4)	0.0393(3)	0.2406(4)	0.029
C(9)	0.4016(6)	−0.0595(4)	0.2193(5)	0.039
H(9A)	0.4933	−0.0783	0.2459	0.044
H(9B)	0.3842	−0.0717	0.1392	0.044
C(10)	0.2991(6)	−0.1092(4)	0.2831(5)	0.040
H(10A)	0.3227	−0.1030	0.3638	0.046
H(10B)	0.2985	−0.1716	0.2630	0.046
N(11)	0.1627(5)	−0.0695(3)	0.2504(4)	0.030(1)
H(11A)	0.1208	−0.0990	0.1833	0.033
H(11B)	0.1058	−0.0771	0.3116	0.033
C(12)	0.1744(6)	0.1884(4)	0.0443(4)	0.032(2)
H(12A)	0.0966	0.2253	0.0194	0.038
H(12B)	0.2565	0.2145	0.0197	0.038
C(13)	0.1538(5)	0.0966(4)	−0.0081(4)	0.027(2)
O(14)	0.1614(3)	0.0288(2)	0.0615(3)	0.025(1)
O(15)	0.1355(4)	0.0886(3)	−0.1124(3)	0.037(1)
C(16)	0.4346(5)	0.0603(4)	0.3624(4)	0.033(2)
H(16A)	0.4845	0.0096	0.3955	0.040
H(16B)	0.4944	0.1115	0.3645	0.040
C(17)	0.3162(5)	0.0804(4)	0.4310(4)	0.027(2)
O(18)	0.1954(4)	0.0836(2)	0.3762(3)	0.028(1)
O(19)	0.3369(4)	0.0948(3)	0.5344(3)	0.041(1)
C(20)	0.6100(6)	0.0684(6)	0.1565(6)	0.058(3)
H(20A)	0.6165	0.0051	0.1430	0.070
H(20B)	0.6597	0.0829	0.2286	0.070
H(20C)	0.6488	0.1007	0.0969	0.070
N(21)	0.2369(8)	0.7163(4)	0.0642(4)	0.057(2)
O(22)	0.3509(7)	0.7425(4)	0.0545(5)	0.085(3)
O(23)	0.1442(6)	0.7687(4)	0.0840(5)	0.080(2)
O(24)	0.2122(8)	0.6333(5)	0.0602(6)	0.104(3)
O(25)	−0.0494(5)	−0.0688(4)	0.4095	0.068(2)
H(25A)	0.0025	−0.0965	0.4752	0.082
H(25B)	−0.1456	−0.0642	0.4173	0.082

[a] Values of the fixed coordinates and thermal parameters (U_{iso}) are given for the hydrogen atoms, which follow the atoms to which they are attached. $U_{eq} = \langle U^2 \rangle$ values are given for the nonhydrogen atoms.

central chelate ring of $[Co(mddda)]^+$ (C(5)–C(6)–C(7), 118.9(5)°) is much larger than that expected for a tetrahedral carbon atom.

In the mddda ligand, the absolute configuration of the methine carbon to which the methyl substituent is attached may be either *R* or *S* [9]. In the present

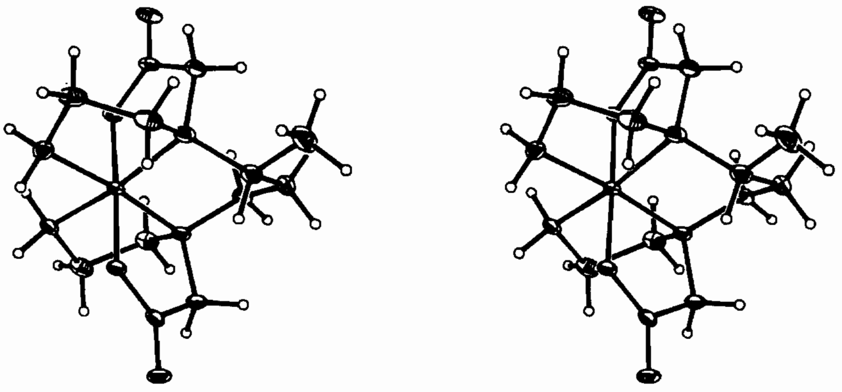
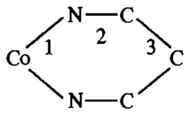


Fig. 1. Stereoscopic view of the $[Co(mddda)]^+$ complex cation shown as the ΔΛΔ(*R*) enantiomer. The thermal elipsoids are plotted at the 25% probability level.

TABLE III. Dihedral Angles in Six-Membered Diamine Rings.



Compound	Dihedral Angles, (°)			Ref.
	1	2	3	
$[Co(mddda)]NO_3 \cdot H_2O$				a
distal to CH_3	−28.5(4)	64.3(5)	−34.2(7)	
proximal to CH_3	−32.8(4)	66.6(5)	−35.3(7)	
$[Co(tn)_3][Ni(CN)_5] \cdot 2H_2O^b$	26.6	−61.2	32.9	8
$(-)_{546}$-$[Co(1,3\text{-pdta})] \cdot 2H_2O$	28.5	−61.2	33.6	7

[a] This work. [b] Average for skew-boat ring only.

structure a racemic mixture of ligand is present. In the $[Co(mddda)]^+$ complex, a methyl group attached to an *R* configuration carbon will be axial if the central chelate ring is δ and equatorial if the central chelate ring is λ. The opposite is true for an *S* configuration. Furthermore, molecular models indicate a severe nonbonded interaction between an axial methyl group and the adjacent carboxylate group. Thus a preference for an *R* ligand in the ΔΛΔ isomer and an *S* ligand in the ΛΔΛ isomer is indicated and only these diastereomers are found in the structure of $[Co(mddda)]NO_3 \cdot H_2O$. A closely related stereoselective effect has been observed for $(-)_{589}$-[Co(*R*-mepenten)]$^{3+}$ [6, 10, 11].

Interatomic distances and angles (given in Table IV with the atom designations presented in Fig. 2) are remarkably similar for corresponding sets of atoms proximal and distal to the methyl substituent with the notable exceptions of some parameters involving the tertiary nitrogen atoms. The Co–N(8) distance of 2.008 Å is 0.040 Å larger than the Co–N(4) distance and is also significantly larger than cobalt–tertiary nitrogen atom distances in closely related complexes of edta (ethylenediaminetetraacetate) or edta-like ligands [5–7, 10], though it is not significantly different from cobalt–primary amine distances in complexes containing simple bidentate diamine ligands forming six-membered rings [11]. Furthermore, each C–N(8)–C bond angle is larger than the corresponding C–N(4)–C bond angle. Such a difference indicates more s-electron character in the C–N(8) bonds than in the C–N(4) bonds and thus more p character in the N(8) lone pair. This expected difference in hybridization is in agreement with the observed Co–N bond length difference though no cause/effect relationship is claimed.

The difference between the Co–N(4) and Co–N(8) bond lengths found in the crystal structure of $[Co(mddda)]^+$ is considerably greater than that expected for variations in crystal packing forces. Furthermore, it seems unlikely that it is due to an electronic effect since methyl group substitution at

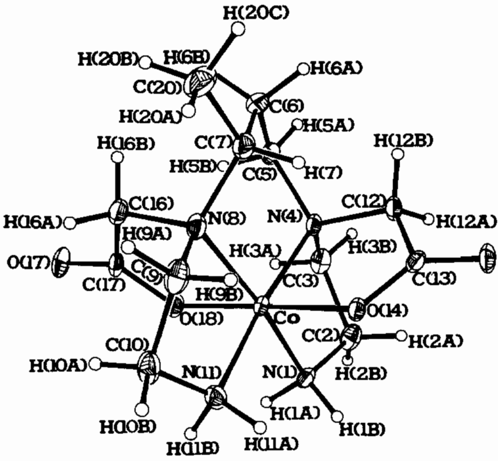


Fig. 2. Atom designations for [Co(mddda)]$^+$.

α-carbon atoms in simple bidentate diamine ligands apparently causes no change in Co–N bond length—at least in the direction observed here [11–13]. (There is a small difference between the two Co–tertiary amine distances reported for the related complex, $(-)_{589}$-[Co(*R*-mepenten)]$^{3+}$ [6]; however, owing to the large standard deviations in this structure, no conclusions can be drawn.) Thus the observed difference between the Co–tertiary amine distances involving nitrogen atoms proximal and distal to the methyl substituent are likely due to nonbonded repulsions between the methyl group and methylene groups, C(9) and C(16), attached to the adjacent nitrogen atom, N(8). Such interactions would tend to open up the C–N(8)–C angles, as observed. They would also be expected to increase the N(8)–C(9)–C(10) bond angle relative to the N(4)–C(3)–C(2) angle and the N(8)–C(16)–C(17) angle relative to the N(4)–C(12)–C(13) angle. These latter effects are also observed though they are small and may not be significant.

TABLE IV. Selected Interatomic Distances (Å) and Angles (°) for [Co(mdda)]$NO_3 \cdot H_2O$.^{a}

Distances			
Co–N(1)	1.944(4)	N(4)–C(5)	1.492(7)
Co–N(11)	1.934(4)	N(8)–C(7)	1.503(8)
Co–N(4)	1.968(4)	C(2)–C(3)	1.511(8)
Co–N(8)	2.008(4)	C(9)–C(10)	1.504(9)
Co–O(14)	1.895(3)	C(12)–C(13)	1.507(7)
Co–O(18)	1.884(3)	C(16)–C(17)	1.504(8)
N(1)–C(2)	1.474(7)	C(5)–C(6)	1.520(9)
N(11)–C(10)	1.473(7)	C(6)–C(7)	1.535(9)
N(4)–C(3)	1.500(7)	C(13)–O(15)	1.230(6)
N(8)–C(9)	1.505(7)	C(17)–O(19)	1.233(6)
N(4)–C(12)	1.503(6)	C(13)–O(14)	1.298(6)
N(8)–C(16)	1.499(6)	C(17)–O(18)	1.288(6)
C(7)–C(20)	1.527(8)		
Angles			
N(1)–Co–N(4)	87.2(2)	C(2)–N(1)–Co	110.2(3)
N(11)–Co–N(8)	87.6(2)	C(10)–N(11)–Co	110.1(3)
N(4)–Co–O(14)	86.6(2)	C(3)–N(4)–Co	104.1(3)
N(8)–Co–O(18)	85.9(2)	C(9)–N(8)–Co	102.9(3)
N(1)–C(2)–C(3)	107.6(4)	C(12)–N(4)–Co	109.0(3)
N(11)–C(10)–C(9)	107.5(4)	C(16)–N(8)–Co	108.0(3)
N(4)–C(3)–C(2)	107.5(4)	C(5)–N(4)–Co	114.2(3)
N(8)–C(9)–C(10)	108.5(5)	C(7)–N(8)–Co	112.1(3)
N(4)–C(12)–C(13)	111.2(4)	C(13)–O(14)–Co	116.1(3)
N(8)–C(16)–C(17)	111.7(4)	C(17)–O(18)–Co	117.4(3)
C(3)–N(4)–C(12)	109.4(4)	C(12)–C(13)–O(15)	119.8(5)
C(9)–N(8)–C(16)	109.6(4)	C(16)–C(17)–O(19)	120.4(5)
C(3)–N(4)–C(5)	109.4(4)	C(12)–C(13)–O(14)	116.8(4)
C(9)–N(8)–C(7)	111.6(4)	C(16)–C(17)–O(18)	116.8(4)
C(12)–N(4)–C(5)	110.5(4)	C(5)–C(6)–C(7)	118.9(5)
C(16)–N(8)–C(7)	112.2(4)	C(6)–C(7)–C(20)	110.0(5)
		N(8)–C(7)–C(20)	112.8(5)
N(4)–C(5)–C(6)	113.7(5)	N(4)–Co–O(18)	94.2(2)
N(8)–C(7)–C(6)	112.4(5)	N(8)–Co–O(14)	95.6(2)
		N(1)–Co–N(11)	90.2(2)

^{a}Where parameters are grouped in pairs, the first value involves ligand atoms distal to the methyl substituent and the second value involves chemically similar atoms proximal to the methyl substituent.

Origin of the ^{13}*C Upfield 'Steric' Shift*

Two simple theories have been proposed to acount for the upfield ^{13}C shift resulting from alkyl substituents. Grant and Cheney have proposed a valence bond model based on the polarization of electrons due to steric interactions [14] between hydrogen atoms. Using methyl-substituted cyclohexanes and benzenes as model systems and factor analysis, they estimate the 'steric' shift by the following equation:

$$\delta = +1680 \operatorname{Cos} \theta \exp(-2.671 r)$$

where θ is the H···H–C angle and r the H···H distance. Summing over all H···H interactions between the methyl group and methylne groups of the chelate rings adjacent to this substituent, we calculate shift differences opposite those observed (δC(16) − δC(12): observed, 4.31 ppm; calculated, −0.54 ppm. δC(9) − δC(3): observed, 2.26 ppm; calculated, −0.99 ppm). Here idealized hydrogen atom coordinates have been used to calculate the geometrical parameters, and the methyl group is assumed to be staggered. The shortest contacts are H(20A)···H(9A) at 2.18 Å (C(9)–H(9A)···H(20A) angle, 101.5°) and H(20B)···H(16B) at 2.42 Å (C(16)–H(16B)···

H(20B) angle, 106.6°). Because these nonbonded angles are greater than 90°, downfield shifts, rather than the observed upfield shifts, are predicted. Thus, although structural analysis is in accord with a γ steric interaction, the sterically induced polarization theory of Grant and Cheney does not account for the observed shifts.

A different model proposed by Gorenstein argues for a generalized 'gauche' NMR effect [15]. It is proposed that the γ effect originates from a bond angle distortion dependent upon nonbonded interactions. Evidence that bond angle distortion significantly affects ^{13}C chemical shift has been found in another complex system [16]. Though in the [Co(mddda)]-$NO_3 \cdot H_2O$ structure the differences between bond angles in the two portions of the molecule are rather small, they are in the correct direction proposed [15] to lead to upfield shifts for C(9) and C(16). All C–X–C and C–X–N bond angles for X = N(8), C(9), or C(16) are larger than the corresponding angle for X = N(4), C(3), or C(12).

Conclusions

The observed structure variations in $[Co(mddda)]^+$ are consistent with nonbonded 1–4 repulsive interactions between the methyl substituent and adjacent methylene groups. This observation is in accord with a γ steric shift explanation [1] of the ^{13}C NMR chemical shift differences between methylene groups proximal and distal to the methyl substituent. Our analysis indicates that sterically induced bond angle distortion [15] may play a more important role than sterically induced charge polarization [14] in the shift differences observed.

Acknowledgements

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