Inorg. Chem. **1998,** *37,* 6890−6897

Strong Trans Influence Methoxymethyl Ligand in B_{12} Cobaloxime and Imine/Oxime Model Complexes: Structural, Spectroscopic, and Molecular Mechanics Investigations

Renzo Cini,*,[†] Scott J. Moore,[‡] and Luigi G. Marzilli*,[‡]

Department of Chemical and Biosystem Sciences and Technologies, University of Siena,
Pian dei Mantellini 44, I-53100 Siena, Italy, and Department of Chemistry, Emory University,
Atlanta, Georgia 30322

Received June 15, 1998

The CH_2OCH_3 ligand has a large trans influence comparable to that of bulky alkyl groups but lacks the complication of marked steric effects. However, crystals of model complexes with this ligand have proved difficult to obtain. The crystal structures of the cobaloximes reported here, $Me_3BzmCo(DH)_2CH_2OCH_3\cdot 0.6CH_3OH$ (**1**) and 4-MepyCo(DH)$_2$CH$_2$OCH$_3$ (**2**) [DH = monoanion of dimethylglyoxime, Me_3Bzm = 1,5,6-trimethylbenzimidazole, and 4-Mepy = 4-methylpyridine], triple the number of cobaloxime structures with CH_2OCH_3. Also, these are the first structures in this class of models with an N-donor planar heterocyclic axial donor ligand, L. The planes of the Me_3Bzm and 4-Mepy ligands are almost perpendicular to the respective planes of the four equatorial DH nitrogen donors and bisect the $(O^-)N-Co-N(OH)$ angles. The $Co-N_L$ bond distances average 2.096(2) Å, confirming the strong trans influence of CH_2OCH_3. Geometry optimization via molecular mechanics using MacroModel 5.0 and an AMBER-type force field was applied to both cobaloxime-type and imine/oxime-type B_{12} models. In our initial work with some imine/oxime models, the calculated structures did not compare well to the solid-state structures. Therefore, adjustments to the force field were evaluated. The major adjustment that improved the fit of the computed and experimental structures was an ∼10% reduction of the van der Waals (vdw) parameters for both the N donors and the C(sp^2) atoms linked to the N donors; this adjustment may reflect the electron-withdrawing effect of the metal center. Analysis of $^1H-^{13}C$ coupling constants of Me_3Bzm lends support to the concept that the atoms in the ligands were modified, but only slightly, by the metal center. To reproduce the dependence of geometric features on the trans influence, different force field parameters for L−Co bonds were used for compounds with weak (Cl) and those with strong (CH_2OCH_3) trans influence ligands. These small modifications allowed us to model the structural features of both classes of models well.

Introduction

Because organocobalt compounds are relevant to the chemistry and biochemistry of the vitamin B_{12} coenzymes and because there is a large trans influence of the axial alkyl ligands, an extensive background exists on the solution and solid-state structural properties of B_{12} model compounds.[1−3] With the considerable range in axial bond lengths, ligand dissociation rates, etc., results from studies of organocobalt compounds are potentially useful in improving our fundamental knowledge of factors influencing the properties of metal complexes in general. Organocobalt compounds often serve as test cases for method development. One area of recent interest is molecular mechanics (MM) calculations, a tool of increasing importance for structural investigations of coordination and organometallic chemistry.[4−19] The widely used force fields (empirical potentials) are usually not well refined with respect to the atomic and molecular polarizability and the van der Waals (vdw) dimensions. MM suffers from incomplete information on the stretching, bending, and torsional potentials involving the bonds to the metal.

The relatively large database encompassing the diverse structural features of B_{12} models offers considerable potential for developing force fields. An unfortunate aspect of these compounds is that the best trans influence alkyl ligands tend to be bulky (e.g., *i*-Pr), allowing steric effects to complicate the assessment of the trans influence. The CH_2OCH_3 ligand has a large trans influence comparable to *i*-Pr but lacks this steric

---

* Corresponding author.

[†] University of Siena.

[‡] Emory University.

(1) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1.

(2) Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225.

(3) Polson, S. M.; Cini, R.; Pifferi, C.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 314.

(4) Ling, W.; Welsh, W. J.; Harris, W. R. *Inorg. Chem.* **1994**, *33*, 884.

(5) Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 1548.

(6) Munro, O. Q.; Bradley, J. C.; Hancock, R. D.; Marques, H. M.; Marsicano, F.; Wade, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 7218.

(7) Bernhardt, P. W.; Comba, P. *Inorg. Chem.* **1992**, *31*, 2638.

(8) Sironi, A. *Inorg. Chem.* **1992**, *31*, 2467.

(9) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286.

(10) Perkovic, M. W.; Heeg, M. J.; Endicott, J. F. *Inorg. Chem.* **1991**, *30*, 3140.

(11) Hay, B. P. *Inorg. Chem.* **1991**, *30*, 2876.

(12) Hambley, T. W. *Inorg. Chem.* **1991**, *30*, 937.

(13) Yao, S.; Plastaras, J. P.; Marzilli, L. G. *Inorg. Chem.* **1994**, *33*, 6061.

(14) Zimmer, M. *Chem. Rev.* **1995**, *95*, 2629.

(15) Weisemann, F.; Tiepel, S.; Krebs, B.; Höweler, U. *Inorg. Chem.* **1994**, *33*, 1891.

(16) Comba, P.; Zimmer, M. *Inorg. Chem.* **1994**, *33*, 5368.

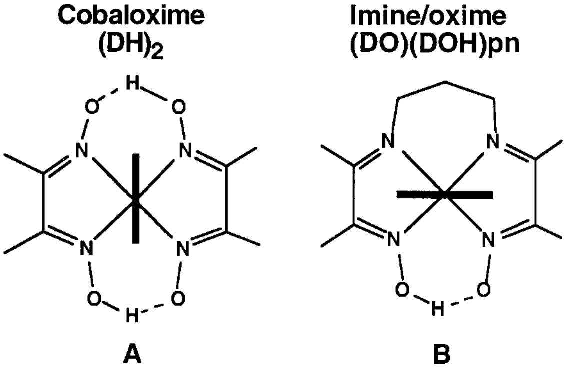
(17) Hancock, R. D.; Reichert, D. E.; Welch, M. J. *Inorg. Chem.* **1996**, *35*, 2165.

(18) Peña-Cabrera, E.; Norrby, P.-O.; Sjögren, M.; Vitagliano, A.; De Felice, V.; Oslob, J.; Ishii, S.; O'Neill, D.; Åkemark, B.; Helquist, P. *J. Am. Chem. Soc.* **1996**, *118*, 4299.

(19) Comba, P.; Hambley, T. W. *Molecular Modeling of Inorganic Compounds*; VCH: Weinheim, 1995; p 197.

10.1021/ic980666i CCC: $15.00

Chart 1



complication.[3,20−22] Although the powerful trans influence and trans effect of CH_2OCH_3 were discovered about a decade ago, most results are from the solution state since crystals of B_{12} model systems with CH_2OCH_3 have proved difficult to obtain. In the cobaloxime class (Chart 1), the only reported structure does not have an N-donor heterocyclic axial ligand and therefore the usefulness of the data is limited.[20] The crystal structures of the cobaloximes reported here, $Me_3BzmCo(DH)_2CH_2OCH_3 \cdot 0.6CH_3OH$ (**1**) and 4-$MepyCo(DH)_2CH_2OCH_3$ (**2**) [DH = monoanion of dimethylglyoxime, Me_3Bzm = 1,5,6-trimethylbenzimidazole, and 4-Mepy = 4-methylpyridine], triple the number of structures available for this important class of models.

An important and dramatic difference between cobaloximes and the next most similar class of models, the imine/oxime class (I/O, Chart 1), is the orientation (different by 90°) of the axial N-donor heterocyclic ligand. We found in the initial phases of this work that the MM simulation with the standard original AMBER force field[23−25] produced two minimized structures of almost equal energy for the I/O ion $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$. The structures differed by the orientation of L around the $Co-N_L$ axis and by the orientation of the propanediyl (pn) bridge. From the experimental results (X-ray in the solid state; NMR in solution), the structures of $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$ and other I/O species[3,26−28] have only the B orientation (Chart 1).

The initial assumption used in such calculations was that the ligand atom parameters were not altered by metal bonding. However, even for H-bonding, it has been reported that the vdw parameters (R^*, radius; ϵ^*, well depth) for a hydrogen with the potential for H-bonding must be smaller than those of aliphatic hydrogens.[29] This decrease is necessary since a significant part of the electron density of the hydrogen atom is shifted toward the heteroatom to which it is covalently linked. It is reasonable that a similar appreciable decrease in the vdw dimensions of some ligand atoms should occur in complexes of transition metals in high oxidation states. In the MM simulations, orientation B was stabilized over orientation A by a reduction of the vdw dimensions of the donor atoms as well as the atoms directly linked to the donor atoms. This computational approach employing modified parameters has been tested by assessing how well the computed structures of other I/O complexes as well as several cobaloximes agree with the experimental structures.

Experimental Section

Materials and Methods. Me_3Bzm was prepared as previously reported.[30] All other reagents were purchased from Aldrich and used without further purification. $H_2OCo(DH)_2CH_2OCH_3$ was prepared from $pyCo(DH)_2CH_2OCH_3$ by treatment with an acidic resin as previously described.[20,31] $Me_3BzmCo(DH)_2(i\text{-}Pr)$ was prepared as previously reported.[21] ^1H NMR data were collected in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) on a GE QE-300 spectrometer and referenced to internal TMS. High-resolution one-bond proton−carbon coupling constants ($^1J_{CH}$) were obtained in $CDCl_3$ at 25 °C using *J*-coupled heteronuclear multiple quantum coherence spectroscopy (JHMQC)[32] on a GE GN-600 Omega spectrometer.

Synthesis. $Me_3BzmCo(DH)_2CH_2OCH_3$ (**1**) was prepared by stirring $H_2OCo(DH)_2CH_2OCH_3$ (0.17 g, 0.48 mmol) with Me_3Bzm (0.080 g, 0.50 mmol) overnight in MeOH (17 mL). The orange precipitate that formed was collected in 50% yield (0.16 g, 0.32 mmol), washed with H_2O and Et_2O, and recrystallized from MeOH/H_2O. ^1H NMR shifts (ppm): 18.64 (s, 2H, br), 7.98 (s, 1H), 7.96 (s, 1H), 7.08 (s, 1H), 4.35 (s, 2H), 3.75 (s, 3H), 3.19 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.09 (s, 12H). Anal. Calcd for $C_{20}H_{31}N_6O_5Co \cdot 0.6\ CH_3OH$: C, 48.17; H, 6.55; N, 16.36. Found: C, 48.12; H, 6.38; N, 16.32.

4-$MepyCo(DH)_2CH_2OCH_3$ (**2**) was prepared by suspending $H_2OCo(DH)_2CH_2OCH_3$ (0.39 g (1.11 mmol) in CH_2Cl_2 (25 mL) containing 0.12 mL (1.23 mmol) of 4-picoline. After stirring overnight, the mixture was filtered and the solvent evaporated to give 0.47 g of crude 4-$MepyCo(DH)_2CH_2OCH_3$. The product was recrystallized as orange prisms from MeOH/H_2O. ^1H NMR shifts (ppm): 18.36 (s, 2H, br), 8.46 (d, 2H), 7.12 (d, 2H), 4.34 (s, 2H), 3.16 (s, 3H), 2.33 (s, 3H), 2.11 (s, 12H). Anal. Calcd for $C_{16}H_{26}N_5O_5Co$: C, 44.96; H, 6.14; N, 16.39. Found: C, 44.73; H, 6.05; N, 16.25.

X-ray Crystallographic Data. A red crystal of **1** and a red-orange crystal of **2** were each mounted on a glass fiber and used for data collection on a Siemens P4 diffractometer. Cell parameters were calculated from the least-squares refinement of the angles of 30 (**1**) and 25 (**2**) randomly selected reflections ($10 < 2\theta < 30°$ (**1**) and $10 < 2\theta < 35°$ (**2**)). Three standard reflections, measured every 2 h, had no significant decrease in intensity. Data were corrected for Lorentz−polarization effects and for absorption through the ψ scan technique, assuming the crystal had an ellipsoidal shape. Detailed crystallographic data are presented in Table 1.

Solution and Refinement of the Structures. The structures were solved through the Patterson and Fourier synthesis techniques and refined via full-matrix least-squares cycles. The scattering factors for neutral atoms were from SHELX 86[33] and SHELX 93.[34] All calculations were carried out on PC-Pentium Okidata computers using the SHELX 86,[33] SHELX 93,[34] and PARST 95[35] packages. The Co, N, C, and O

---

(20) Marzilli, L. G.; Bayo, F.; Summers, M. F.; Thomas, L. B.; Zangrando, E.; Bresciani-Pahor, N.; Mari, M.; Randaccio, L. *J. Am. Chem. Soc.* **1987**, *109*, 6045.

(21) Charland, J.-P.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1993**, *32*, 4256.

(22) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

(23) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S., Jr.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765.

(24) Weiner, S.; Kollman, P. A.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.

(25) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M., Jr.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

(26) Gerli, A.; Marzilli, L. G. *Inorg. Chem.* **1992**, *31*, 1152.

(27) Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908.

(28) Marzilli, L. G.; Gerli, A.; Calafat, A. M. *Inorg. Chem.* **1992**, *31*, 4617.

(29) Hagler, A.; Euler, E.; Lifson, S. *J. Am. Chem. Soc.* **1974**, *96*, 5319.

(30) Simonov, A. M.; Pozharskii, A. E.; Marianovskii, V. M. *Indian J. Chem.* **1967**, *5*, 81.

(31) Toscano, P. J.; Chiang, C. C.; Kistenmacher, T. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 1513.

(32) Moore, S. J.; Iwamoto, M.; Marzilli, L. G. *Inorg. Chem.* **1998**, *37*, 1169.

(33) Sheldrick, G. M. *SHELX 86: Program for Crystal Structure Determination*; University of Göttingen: Germany, 1986.

(34) Sheldrick, G. M. *SHELXL 93: Program for Refinement of Crystal Structures*; University of Göttingen: 1993.

(35) Nardelli, M. *PARST 95: A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis*; University of Parma: Italy, 1995.

Table 1. Selected Crystal Data and Structure Refinement[a] for $Me_3BzmCo(DH)_2CH_2OCH_3 \cdot 0.6CH_3OH$ (**1**) and for 4-$MepyCo(DH)_2CH_2OCH_3$ (**2**)

	1	**2**
empirical formula	$C_{20.6}H_{33.4}CoN_6O_{5.6}$	$C_{16}H_{26}CoN_5O_5$
fw	513.66	427.35
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
unit cell dimens		
a, Å	8.1150(10)	8.398(1)
b, Å	15.8670(10)	29.235(3)
c, Å	19.266(2)	8.858(1)
β, deg	94.240(10)	115.62(1)
V, Å^3	2473.9(4)	1961.0(4)
ρ_{calc}, g cm^{-3}	1.379	1.448
absorption coeff, mm^{-1}	0.738	0.912
$F(000)$	1076	896
cryst dimens, mm	0.40 × 0.30 × 0.40	0.30 × 0.40 × 0.15
θ range, deg	$5.14 < 2\theta < 50.00$	$5.38 < 2\theta < 50.00$
no. of indep reflns	4333 [R(int) = 0.0263]	3421 [R(int) = 0.0141]
final R1, wR2[b] [$I > 2\sigma(I)$]	0.0393, 0.1215	0.0434, 0.1153
(all data)	0.0496, 0.1311	0.0555, 0.1324
largest diff. peak and hole	0.663 and −0.232 e Å^{-3}	0.610 and −0.470 e Å^{-3}

[a] Details in common: 293 ± 2 K; $Z = 4$. [b] Weighting scheme as in ref 3.

atoms were refined anisotropically, whereas the H atoms were treated isotropically. The hydrogen atom of the oxime bridges (**1**, **2**) and those of the 4-Mepy ring (**2**) were located from the Fourier difference map. All the other H-atoms in **1** were set in calculated positions and allowed to ride on the atoms to which they are linked. The remaining H atoms of **2** were located in fixed positions via the HFIX option of SHELX 93. In **2** the thermal parameters of the H atoms were constrained to 1.2 times the values of the thermal parameters of the atoms to which they are bound.

A Fourier difference synthesis at the isotropic refinement stage showed two new peaks near the carbon ligand from the methoxymethyl group in **1**; this was interpreted as statistical disorder of the methoxymethyl group. The peaks were assigned the scattering factors of oxygen and carbon and labeled as O(5B) and C(10B), respectively. As refined, the site occupation factors of the atoms relevant to the two orientations of the methoxymethyl ligand were restricted to sum up to 1. The final refinement gave occupancies of 0.457(9) and 0.543(9) for the A and B orientations, respectively.

Statistical disorder was also found for the methyl groups of the Me_3-Bzm ligand. Because residual electron density was found around the carbon atoms when just one set of three atoms was considered, a second set was allowed to refine through the AFIX 123 instruction of SHELX 93.[34] The site occupation factors of the two sets of H atoms were refined to 0.80(2) and 0.20(2), respectively. Since the thermal parameters of the methanol C(M) and O(M) atoms in **1** were relatively high at the end of the refinement procedure, the site occupation factor of both atoms was fixed at 0.6, in agreement with the analytical data. Selected geometrical parameters for the structures are reported in Tables 2 and 3.

Table 2. Selected Bond Lengths (Å) for $Me_3BzmCo(DH)_2CH_2OCH_3 \cdot 0.6CH_3OH$ (**1**) and 4-$MepyCo(DH)_2CH_2OCH_3$ (**2**)

	1	**2**
Co−N(1)	1.882(2)	1.888(3)
Co−N(2)	1.882(2)	1.880(2)
Co−N(3)	1.888(2)	1.880(3)
Co−N(4)	1.886(2)	1.885(3)
Co−N(5)	2.093(2)	2.099(2)
Co−C(9)	2.033(3)	2.029(3)
O(1)−N(1)	1.359(3)	1.351(4)
O(2)−N(2)	1.335(3)	1.346(3)
O(3)−N(3)	1.368(3)	1.344(4)
O(4)−N(4)	1.336(3)	1.351(4)
O(5)−C(9)		1.336(5)
O(5)−C(10)		1.437(5)
O(5A)−C(9)	1.321(6)	
O(5A)−C(10A)	1.43(2)	
O(5B)−C(9)	1.292(7)	
O(5B)−C(10B)	1.36(2)	
N(1)−C(2)	1.290(4)	1.294(4)
N(2)−C(3)	1.305(4)	1.301(4)
N(3)−C(6)	1.294(4)	1.301(5)
N(4)−C(7)	1.296(4)	1.297(5)
N(5)−C(11)	1.401(3)	1.339(4)
N(5)−C(15)		1.343(4)
N(5)−C(20)	1.319(4)	
N(6)−C(18)	1.381(4)	
N(6)−C(19)	1.458(4)	
N(6)−C(20)	1.352(4)	
C(2)−C(3)	1.457(5)	1.458(5)
C(6)−C(7)	1.465(4)	1.460(6)

Table 3. Selected Bond Angles (deg) for $Me_3BzmCo(DH)_2CH_2OCH_3 \cdot 0.6CH_3OH$ (**1**) and 4-$MepyCo(DH)_2CH_2OCH_3$ (**2**)

	1	**2**
N(1)−Co−N(2)	81.56(11)	81.06(11)
N(1)−Co−N(3)	176.75(10)	178.04(11)
N(1)−Co−N(4)	97.69(11)	99.08(13)
N(1)−Co−N(5)	90.28(10)	91.85(10)
N(2)−Co−N(3)	99.63(11)	98.33(12)
N(2)−Co−N(4)	176.82(10)	177.60(11)
N(2)−Co−N(5)	93.84(10)	91.49(10)
N(3)−Co−N(4)	80.96(10)	81.44(13)
N(3)−Co−N(5)	92.66(9)	90.03(10)
N(4)−Co−N(5)	89.25(9)	90.91(10)
N(1)−Co−C(9)	90.87(13)	84.65(13)
N(2)−Co−C(9)	85.29(14)	89.85(14)
N(3)−Co−C(9)	86.22(13)	93.49(14)
N(4)−Co−C(9)	91.63(14)	87.78(14)
N(5) −Co− C(9)	178.45(13)	176.02(12)
Co−N(1)−O(1)	123.4(2)	123.0(2)
Co−N(1)−C(2)	117.1(2)	117.0(2)
Co−N(2)−O(2)	122.2(2)	123.0(2)
Co−N(2)−C(3)	115.8(2)	117.1(2)
Co−N(3)−O(3)	122.9(2)	123.1(2)
Co−N(3)−C(6)	117.3(2)	116.8(3)
Co−N(4)−O(4)	122.7(2)	122.3(2)
Co−N(4)−C(7)	116.9(2)	116.7(3)
Co−N(5)−C(11)	132.9(2)	121.4(2)
Co−N(5)−C(15)		121.9(2)
Co−N(5)−C(20)	122.0(2)	
Co−C(9)−O(5)		119.5(3)
Co−C(9)−O(5A)	120.6(3)	
Co−C(9)−O(5B)	123.0(4)	
C(9)−O(5)−C(10)		113.4(3)
C(9)−O(5A)−C(10A)	119.1(7)	
C(9)−O(5B)−C(10B)	118.2(8)	

Molecular Mechanics. The strain energies of the complexes have been computed as the sum $E_{Tot} = E_b + E_\theta + E_\phi + E_{nb} + (E_{hb}) + (E_\epsilon)$, where E_b, E_θ, E_ϕ, E_{nb}, E_{hb}, and E_ϵ are the bond length deformation, the valence angle deformation, the torsional angle deformation, the nonbonding interaction, the hydrogen-bond interaction, and the electrostatic contributions, respectively. The E_{hb} and E_ϵ contributions have been included only when specified. The algorithm and force field ("final quality") employed were those of AMBER[23−25] contained in MacroModel[36] version 5.0 (MMOD) implemented on a Silicon Graphics Indigo workstation. Modification of the force field was necessary in order to account for the interactions between the metal center and the ligand atoms. The force field parameters for the stretching and bending vibrations were obtained through a "trial and error" method, which achieved the best agreement between calculated and observed structures.

---

(36) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

Starting values were obtained by applying Badger's rule,[37,38] using the parameters from the Herschbach and Laurie[39] (stretching) and Halgren's (bending) equations.[40,41] The initial values for the parameters of the latter equations were based on those found for some sulfoxide compounds of ruthenium.[42]

The new force field parameters are reported in Table 4. The total strain energy, E_{Tot} (Table 5), was minimized through the Polak−Ribiere conjugate gradient minimization method until the root-mean-square value (rms) of the first derivative vector was <0.0025 kcal/mol Å. The starting structures were those found for the solid state via single-crystal X-ray diffraction[3,26,27,43] for $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$, $[pyCo((DO)(DOH)pn)Cl]^+$, $[pyCo((DO)(DOH)pn)CH_3]^+$, $[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$, $pyCo(DH)_2Cl$, $Me_3BzmCo(DH)_2CH_2OCH_3$, and $4\text{-}MepyCo(DH)_2CH_2OCH_3$. The $C(sp^2)-H$ and $C(sp^3)-H$ bond distances for this MM investigation were all set to 1.101 and 1.113 Å, respectively, as found in the original AMBER.[23−25]

The E_ϵ contribution was included in simulations of $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$. Differences between the energy values of the minima computed with and without the electrostatic contribution were <0.2 kcal/mol. Therefore, all the calculations were carried out in the absence of the E_ϵ term and solvation effects. Atomic charges were evaluated by using GAUSSIAN-92/DFT.[44] Energetics, charges, and population analyses reported have been calculated using the hybrid density functional theory B3LYP method[45,46] with the LANL2DZ basis set.[44,47] The geometrical parameters were those found in the solid-state structure as determined by X-ray diffraction. No geometry optimization was applied. Solvent (chloroform) effects were treated via the GB/SA model[48] of MMOD for all the molecules, at the first stage of the calculations.

Results

Structural Results. The ORTEP representations[49] for $Me_3BzmCo(DH)_2CH_2OCH_3$ (**1**) and $4\text{-}MepyCo(DH)_2CH_2OCH_3$ (**2**) are presented in Figures 1 and 2, respectively. The cobalt atom is at the center of a distorted octahedron in both cases.

(a) Equatorial Ligand. The two DH moieties are nearly planar in both structures with a dihedral angle (α) between the planes of 2.79(7) and 3.88(9)° for the Me_3Bzm and 4-Mepy complexes, respectively. The metal atom deviates slightly (0.0502(4) and 0.0353(4) Å, respectively) from the plane of the equatorial nitrogen donors, toward N(5). The hydroxyl group of the methanol molecule in the crystal structure of **1** is linked to the O(2) atom (O(M)(0.5 + x, 0.5 − y, −0.5 + z)···O(2), 2.83(8) Å; O(M)−H···O(2), 115(5)°).

(b) Me_3Bzm and 4-Mepy Ligands. The atoms of the axial N-donor ligand in both complexes are strictly coplanar, the largest deviation being 0.029(4) Å for C(14) in **2**. The orientation of the L plane with respect to the equatorial plane can be described by the torsion angle "ϕ" defined in the systems with L = Me_3Bzm as the torsion angle B2−N(5)−Co−N*, where N* is the midpoint between N(1) and N(4). The "ϕ" values for **1** and **2** are 3.9(2) and 4.8(3)°, respectively; these values are very close to that found for $Me_3BzmCo(DH)_2(CH(CN)CH_2CN)$.[50]

Table 4. Selected Force Field Parameters (Atom and Bond Symbols as in MMOD[36] and AMBER[23−25])

stretching[a]	r_o (Å)	k_r (kcal/(mol Å^2))
Co−N2	1.90	150
Co−N2 *trans* to Cl	2.00	120
Co−N2 *trans* to CH_2OCH_3	2.10	110
Co−N2 *trans* to CH_2Cl	2.10	110
Co−C3	2.00	127
Co−Cl	2.20	105
Cl−C3	1.77	240
O3−C3	1.47	350
N2−OM/O3	1.34	350
N2=C2	1.30	450
N2−C2	1.40	350
C3−C3	1.53	310
N2−C3	1.45	355
C2−C3	1.50	335
C2*C2 conjugate systems	1.39	469
C2=C2	1.34	480
H−C3	1.11	331
H−C2	1.10	340
H−O3	0.96	553
O3−Lp (lone pair)	0.70	400

bending[a]	θ_o	k_θ (kcal/(mol rad^2))
Co−N2−OM/O3	120	35
Co−N2*C2	120	40
Co−N2−C3	120	30
Co−C3−Cl	109.5	50
Lp−O3−00	112	40
00*Co*00 *trans*	180	10
00*Co*00 *cis*	90	30

torsional parameters[c] (kcal/mol)	V_1	V_2	V_3
Co−N2=C2−C2	0	5.3	0
Co−N2=C2−C3	0	5.3	0
Co−N2=C2−H1	0	5.3	0
Co−N2−O3−H2	0	1.0	0
Co−N3−C3−C3	0	0	0.8
Co−N3−C3*C2	0	0.6	0.4
Co−N3−C3−H1	0	0	0.4
Lp-O3−00−00	0	0	0.07

van der Waals parameters[d]	R^*	ϵ^*
C2	1.85	0.12
C2[e] (linked to N donors)	1.70	0.11
C3	1.80	0.06
C3[e] (linked to Co)	1.65	0.05
N2	1.75	0.16
N2[e] (linked to Co)	1.55	0.12
Co	2.35	0.35

[a] Substructure (coordination sphere and I/O or cobaloxime system). Co(−C3)(−N2)[b]−N2=C2−C2=N2(−1)−C3−C3−C3−N2(−1)=C2−C2=N2(−1)−O3−H2 Co(−C3)(−N2)[b](−N2(−OM)=C2−C2=N2(−1)−O3−H2)−N2(−OM)=C2−C2=N2(−1)−O3−H2. [b] Nitrogen donor from the axial L ligand. [c] All the potentials around the metal−donor bonds were taken equal to zero. [d] In general, the values were those of MMOD for all the atoms. Here we report the new values used in this work as well as the values from MMOD or the values used for all the other atoms of the same type. [e] New values.

(c) Axial Fragment and Me_3Bzm or 4-Mepy Coordination. The Co−N(5) and Co−C(9) distances are 2.093(2) and 2.033-

---

(37) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128.
(38) Badger, R. M. *J. Chem. Phys.* **1935**, *3*, 710.
(39) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458.
(40) Halgren, A. *J. Mol. Struct.* **1988**, *163*, 431.
(41) Halgren, A. *J. Am. Chem. Soc.* **1990**, *112*, 4710.
(42) Geremia, S.; Calligaris, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1541.
(43) Geremia, S.; Dreos, R.; Randaccio, L.; Tauzher, G.; Antolini, L. *Inorg. Chim. Acta* **1994**, *216*, 125.
(44) Frish, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Reploge, E. S.; Gomperts, R.; Andres, L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Beker, J.; Stewart, J.-J. P.; Pople, J. A. *Gaussian:* Gaussian, Inc.: Pittsburgh, PA, 1992.
(45) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.
(46) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
(47) Cini, R.; Musaev, D. G.; Marzilli, L. G.; Morokuma, K. *J. Mol. Struct.* **1997**, *392*, 55.
(48) Still, W. C.; Tempczyk, A.; Hawley, R. C.; Hendrickson, T. *J. Am. Chem. Soc.* **1990**, *112*, 6127.
(49) Zsolnai, L. *XPMA and ZORTEP: Programs for Representaion of Molecular Structures*; University of Heidelberg, 1994.
(50) Charland, J.-P.; Attia, W. M.; Randaccio, L.; Marzilli, L. G. *Organometallics* **1990**, *9*, 1367.

Table 5. Total Strain Energy (kcal/mol) for Selected Optimized Structures

molecule	structure type A[a]	B[a]
$[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$	50.49	50.29
$[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$	24.22	18.44
$[pyCo((DO)(DOH)pn)CH_3]^+$	19.51	18.61
$[pyCo((DO)(DOH)pn)Cl]^+$	21.27	19.51
$Me_3BzmCo(DH)_2CH_2OCH_3$	43.53	46.01
$4\text{-}MepyCo(DH)_2CH_2OCH_3$	13.57	15.21
$pyCo(DH)_2Cl$	11.97	14.19

[a] For I/O models, all A and B structures are *anti*-CH_2 and *syn*-CH_2, respectively.

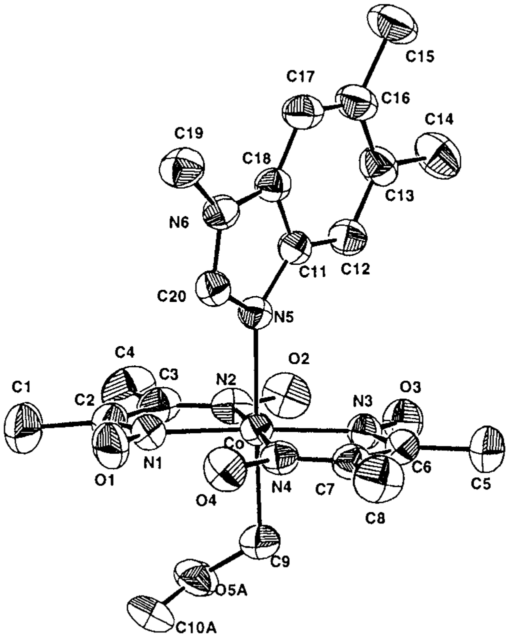


Figure 1. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-hydrogen atoms of **1**.

(3) Å for **1**, and 2.099(2) and 2.029(3) Å for **2**. The Co−C bond is significantly shorter for **1** and **2**, than for the R = *i*-Pr analogue. In contrast, the Co−N values are similar to those in the corresponding R = *i*-Pr complexes.[21,22] NMR coupling constants obtained from the JHMQC spectra of Me_3Bzm cobaloximes have been shown to correlate well with Co−N(5) distances and are unrelated to Co−C bond distances.[32] The $^1J_{CH}$ values for the *i*-Pr and CH_2OCH_3 complexes in solution (Table 6) are similar, especially for B2, B7, and B12, Chart 2; thus, the $^1J_{CH}$ values and the crystallographic results agree well.

The angles Co−N(5)−C(20) and Co−N(5)−C(11) for $Me_3BzmCo(DH)_2CH_2OCH_3$ are 122.0(2) and 132.9(2)°, respectively. The angle C(20)−N(5)−C(11) is 105.1(2)°. Values previously reported for these angles in other complexes are in the ranges 120.8(4)−122.7(2), 132.2(3)−134.4(3), and 104.7(2)−105.3(3)°.[21] The dihedral angles (γ) of the Me_3Bzm and the 4-Mepy planes with the plane of the equatorial nitrogen atoms are 87.77(6) and 87.2(1)°, respectively, showing that the metal atom lies almost in the plane of the axial ligand (deviation = 0.0457(4) and 0.0780(5) Å, respectively).

The CH_2OCH_3 moiety in $Me_3BzmCo(DH)_2CH_2OCH_3$ (**1**) is affected by statistical disorder, with CH_2−O(5A) almost eclipsed on Co−N(1) and CH_2−O(5B) nearly eclipsed on Co−N(4) [torsion angles O(5A)−C(9)−Co−N* and O(5B)−C(9)−Co−N* are 61.0(4) and −29.0(5)°, respectively]. The torsion angle O(5)−C(9)−Co−N* is 134.6(3)° for $4\text{-}MepyCo(DH)_2CH_2OCH_3$ (**2**), such that C(9)−O(5) and Co−N(3) are eclipsed. The two CH_2−O bond distances for **1** average 1.306(6) Å, whereas the O−CH_3 bond lengths average 1.40(2) Å. The CH_2−O and O−CH_3 lengths are 1.336(5) and 1.437(5) Å, respectively, for **2**. The CH_2−O bond distance is much shorter than that of a single C(sp^3)−O bond (average, 1.418(16) Å[51]); this suggests that some shift of the oxygen lone pairs into the C−O bond occurs. A similar effect was found for some imino ether complexes of platinum(II).[52]

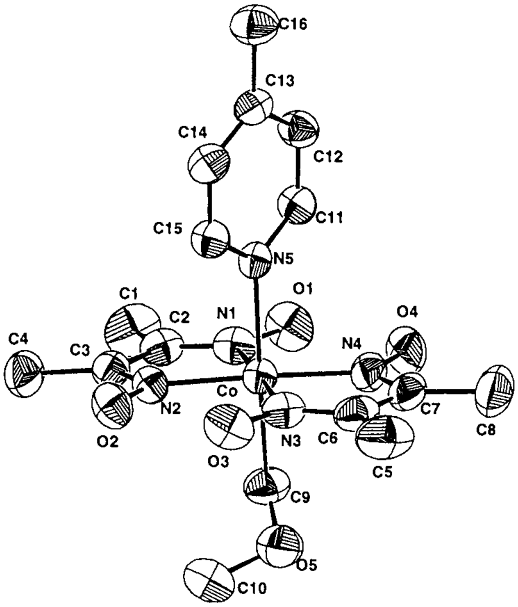


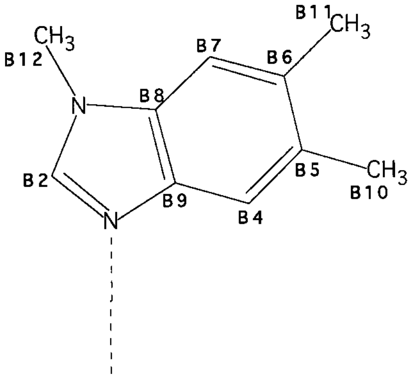
Figure 2. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-hydrogen atoms of **2**.

Table 6. $^1J_{CH}$ (Hz) for $Me_3BzmCo(DH)_2R$ Complexes

position	Me_3Bzm[a]	CH_2OCH_3	*i*-Pr	CH_3[a]	Cl[a]	Me_3BzmH^+ [a]
B2	204.3	207.8	207.9	208.2	209.9	218.6
B4	159.6	163.5	163.3	163.3	164.8	166.5
B7	158.5	159.0	159.0	159.2	160.4	163.2
B10	126.0	126.1	126.1	126.2	126.6	overlap
B11	126.1	125.8	125.7	126.0	126.5	overlap
B12	139.6	140.1	140.1	140.4	141.2	143.4

[a] Previously reported values, ref 32.

Chart 2



Molecular Mechanics. The total strain energies obtained for various geometries are discussed below. The optimized geometries of seven compounds computed with the force field

---

(51) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1.

(52) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130.

parameters reported in Table 4 are in good overall agreement with the solid-state structures determined by X-ray diffraction (Supporting Information). In fact, except for a few metric parameters for the often disordered methoxymethyl group, the computed and experimental bond lengths and angles differ by <0.06 Å and 5°, respectively. The quality of these fits and the force field parameters relevant to the bond stretching, bending, and torsion interactions generally agree well with those in MM studies previously reported for other metal complexes.[4−19,53] Inclusion of the electrostatic term did not play an important role in predicting the conformation of the energy-minimized structures. In contrast, the nonbonding parameters were crucial in accounting for the stability of the B conformation with respect to the A conformation (Chart 1) as discussed below.

With the caveat that the conformation and metric parameters for the methoxymethyl group are not well defined in solution or solid states, we note, as an aside, two observations concerning this group and arising from the MM analysis of **1** and **2**. [The experimental bond distance for $O-CH_3$ (1.359(11) Å) found in the solid state for $[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$ is not comparable to the other found structures and computed structures containing the CH_2OCH_3 group because of the relatively high thermal parameter of the methyl carbon atom ($U = 0.1538$ Å^2) due to thermal or statistical disorder (Figure 2).[3] Thus, it is not too surprising that the largest discrepancies between computed and experimental values were found for the $H_2C-O(CH_3)$ distance (0.16 Å) of the alkyl ligand, and the $H_2C-O-CH_3$ and $Co-C-O$ bond angles (7.7 and 7.3°, respectively).] First, in order for MM geometry optimization to reproduce nicely the orientation of CH_2OCH_3 in the solid state, the two lone pairs of the oxygen atom must be included in the calculation. Without the lone pairs, the minimum energy structure has the CH_2-O bond exactly bisecting the (O)N−Co−N(O) angles, and the $O-CH_3$ bond points away from the equatorial plane. Second, the geometry of the $CH_2-O(CH_3)$ moiety is reproduced poorly by using the classical force field parameters for sp^3-hybridized carbon and oxygen atoms, suggesting the hypothesis that the CH_2-O linkage possesses some double-bond character.

Discussion

Our structural results confirm that the cobaloximes with pyridine and benzimidazole ligands have the A-type conformation, regardless of the strength of the trans influence of the ligand opposite to the N-donor heterocyclic ligand. Consequently, these cobaloxime complexes are not so useful as the I/O complexes studied here for evaluating the values of the force field parameters. We therefore begin this discussion with the I/O computational findings. Recall that for the I/O complexes the experimental geometry found in the solid state is invariably B-type. We further note that the propanediyl (pn) bridge is flexible and that the middle CH_2 group can be either syn or anti to the L ligand with respect to the equatorial plane. These conformations will be specified as *syn*-CH_2 and *anti*-CH_2, respectively.

Our initial computations employed the vdw parameters for C, H, and N in the original AMBER force field. The total strain energy for the B-type optimized structure of $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$ is 55.07 kcal/mol. In this case, the starting geometry for the minimization was that of the solid-state structure, *syn*-CH_2-B-type. When the starting geometry was *anti*-CH_2, the absolute minimum was represented by an *anti*-CH_2-A-type structure with a total strain energy of 52.42 kcal/mol. Simulations on other I/O derivatives carried out on the basis of the vdw parameters of original AMBER or MM2 force fields always produced results similar to those reported above for $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$: the *anti*-$CH_2$-A-type structure was more stable than any B-type structure.

These observations prompted us to consider the appropriateness of using the original nonbonded AMBER parameters for the donors and eventually for the atoms directly bound to the donors. We reasoned that some drift of electron density toward the metal center due to σ and possibly π donation can change the vdw dimensions (R*) and the well depth (ϵ*) of some ligand atoms. This concept led us to investigate modifying these force field parameters, which, in fact, are usually the most problematic in MM analysis. Both the function involved (namely Exp-6 (MM3, MM2),[54−56] Lennard-Jones 6-9 (VFF),[57,58] 6-12 (VFF, AMBER,[23−25] CHARMM[59])) and the R* and ϵ* parameters[6,60−62] are often a matter of discussion and debate. The AMBER minimizing option of MMOD works through the 6-12 function and uses the parameters reported in the literature.[23−25] As evidenced by Hagler et al.[29] and by Kollman et al.[23] the R* value (1.00 Å) for potentially H-bonding hydrogens (N−H, O−H, S−H) is significantly smaller (∼0.3 Å, 27%) than the aliphatic H atoms (1.37 Å), owing to the shift of their electron density to the heteroatom to which they are attached. A significant reduction was also applied to the values of ϵ* (0.038 kcal/mol, aliphatic; 0.020 kcal/mol, H(N,O,S)).

When the vdw parameters (R* and ϵ*) of the C and N ligating atoms and the C atoms linked to these donor atoms were decreased by ∼10% from the values normally used for the free ligands in the original AMBER (Table 4), E_{Tot} of the B form for I/O models decreased with respect to that of the A form. This amount of reduction in ϵ* has been employed elsewhere.[17] For example, calculations with the reduced vdw parameters gave total strain energies of 50.49 and 50.29 kcal/mol for *anti*-CH_2-A-type and *syn*-CH_2-B-type structures of $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$, respectively (Table 5). Since the A form has never been observed experimentally for I/O models, reductions of the values of R* even greater than ∼10% might be reasonable.

The relative stability of A- and B-type structures was not greatly influenced by reducing the R* value for the metal atom below 2.35 Å. When the value was significantly increased, the geometry of the full molecule was not reproduced well. Thus the value R*(Co) appears to be appropriate. Furthermore, values reported in the literature for Co and other metal complexes compare well with those used in this work.[13]

The force field developed with $[Me_3BzmCo((DO)(DOH)pn)CH_2Cl]^+$ was successfully applied to $[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$, and the analysis showed interesting features. The X-ray structure of $[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$ is the *syn*-CH_2-B-type, with the CH_2-O vector projection almost bisecting the N−Co−N angle of the pn bridge. Optimization does not change significantly this structure, which converges to 18.44

---

(53) Hansen, L.; Cini, R.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1992**, *31*, 2801.

(54) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 1, 8551.

(55) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *89*, 8127.

(56) Bukert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982; p 339.

(57) Dauber-Osguthrope, P.; Roberts, V. A.; Osguthrope, D. J.; Wolff, J.; Genest, M.; Hagler, A. T. *Proteins* **1988**, *4*, 31.

(58) Lifson, S.; Hagler, A. T.; Dauber, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 5111.

(59) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187.

kcal/mol. Another optimized *syn*-CH_2-B-type structure (18.14 kcal/mol) has the CH_2-O vector almost bisecting the (O)N−Co−N(O) angle, the $O-CH_3$ vector pointing away from the equatorial system, and the pn bridge syn to py. Finally, optimizing an *anti*-CH_2-A-type structure and a *syn*-CH_2-B-type structure with a similar CH_2OCH_3 conformation [CH_2-O eclipsed with Co−N(O−) and with $O-CH_3$ almost parallel with the equatorial donors plane] leads to a total strain energy of 24.22 and 21.32 kcal/mol, respectively. The *anti*-CH_2-A-type and *syn*-CH_2-B-type structures have minima at 24.22 and 21.32 kcal/mol, respectively. Thus, the B-type structures are preferred for $[pyCo((DO)(DOH)pn)CH_2OCH_3]^+$ also.

Solid $[pyCo((DO)(DOH)pn)Cl]^+$ and $[pyCo((DO)(DOH)pn)CH_3]^+$ both have an *anti*-CH_2-B-type structure.[26,27] On optimization, the structures maintain this conformation and converge to 21.27 and 19.98 kcal/mol, respectively. Although the corresponding *anti*-CH_2-A-type forms converge to lower energies, the *syn*-CH_2-B-type structures were again most favored (Table 5). Thus, the order *anti*-CH_2-B-type > *anti*-CH_2-A-type > *syn*-CH_2-B-type appears to be quite independent of the trans influence.

The structures of **1** and **2** optimized such that the common A-type conformation of L in cobaloximes was maintained (Table 5), thus showing that our force field makes the correct predictions. Furthermore, the root-mean-square of the all-atom superimposition of the X-ray and computed structures is smaller than 0.015 Å. Finally, the structure of $pyCo(DH)_2Cl$ converged to 11.97 and 14.19 kcal/mol for the A- and B-type structures, respectively (Table 5).

The equatorial bond lengths of the coordination sphere of cobaloximes do not differ appreciably.[1,2] As a consequence, differences in the electronic nature and bulkiness of R and L do not influence the $Co-N_{eq}$ bond lengths (comparisons of bond angles also show a close similarity). For example, the experimental $Co-N_{eq}$ ranges are 1.888(3)−1.906(3) Å, for $pyCo(DH)_2Cl$; 1.880(2)−1.888(3) Å, for $4\text{-}MepyCo(DH)_2CH_2OCH_3$; and 1.882(2)−1.888(2) Å, for $Me_3BzmCo(DH)_2CH_2OCH_3$. The computed $Co-N_{eq}$ ranges were 1.913−1.935, 1.920−1.924, and 1.917−1.922 Å for the three compounds, respectively. The computed values were slightly larger (average 0.03 Å) than the experimental values. When the same analysis was carried out for the I/O structures, the average difference between computed and experimental values was even smaller (0.02 Å), an improvement we attribute to the larger experimental distances for Co−N(pn) (average, 1.914 Å) than for Co−N(O) (average 1.886 Å). Our force field uses the same values for the Co−N(sp^2) bonds with no distinction between N(O) and N(pn). The equilibrium bond distance (r_o) of 1.90 Å (Table 4) found by using the procedure reported above therefore seems acceptable as a compromise for N(O) and N(pn)-sp^2 hybridized donors. For simulating cobaloximes only, better agreement was obtained when a smaller value for r_o (e.g., 1.886 Å) was applied.

For the high energy B-type computed structures of the cobaloxime molecules, the butterfly distortion of the equatorial planes is, as expected, larger than that for the A-type (computed and experimental) structures; this bending results primarily from the repulsions of the H(L) atoms and the atoms of the equatorial moieties. Dihedral angles, α, and displacement from the plane of the four N_{eq} for the computed B-type molecules follow: 19.6°, 0.065 Å for $Me_3BzmCo(DH)_2CH_2OCH_3$; 14.5°, 0.039 Å for $4\text{-}MepyCo(DH)_2CH_2OCH_3$; and 20.9°, 0.108 Å for $pyCo(DH)_2Cl$. These values indicate that the bending would be greatest for weak trans influence ligands and suggest that Me_3Bzm has a greater steric size than py-type ligands. However, this B-type computed structure of $Me_3BzmCo(DH)_2CH_2OCH_3$ has Co−N(5)−C(20) and Co−N(5)−C(11) bond angles of 121.3 and 132.3°, respectively, in excellent agreement with the values computed for the more stable A-type structure (122.1 and 131.0°). These values are similar to those found for the X-ray A-type structure (122.0 and 132.9°, respectively). One might have expected that a lopsided ligand like Me_3Bzm would display a larger dissymmetry in the $Co-N_L-C(N)$ and $Co-N_L-C(C)$ angles for the B- than the A-type structures for cobaloximes. For example, the increased steric interaction between H12 (i.e., B4H, Chart 2) and the equatorial plane atoms might be released by an opening of the $Co-N_L-C(C)$ angle. This opening does not occur and it seems likely that the dissymmetry in these angles in the A-type cobaloximes already reflects a balance of steric size between the small and large parts of the lopsided Me_3Bzm ligand. In support of this concept, the $Co-N_L-C(N)$ and $Co-N_L-C(C)$ bond angles reported for I/O (B-type) X-ray structures are ca.. 122 and 133°.[3,63]

The $^1J_{CH}$ values for Me_3Bzm bound in a series of cobaloximes increase as the trans R group becomes less electron-donating, a result indicating slightly more s character contributed to the hybrid orbitals involved in the CH bond. This rehybridization is consistent with increased electron donation from Me_3Bzm to the Co. More specifically, the $^1J_{CH}$ changes may be interpreted in terms of an increase in the electronegativity of the C substituent (i.e., N bound to Co) favoring bonding with C hybrid orbitals with more p character.[64] The percentage of s character (ρ) in the C hybrid orbitals in CH bonds has been examined for other systems in terms of $^1J_{CH}$ values according to the equation $^1J_{CH}$ (Hz) $= 500\rho$.[65] For the position showing the strongest response to the trans influence of R (i.e., B2, Chart 2), we observed an increase in ρ from 40.86% for the free ligand to an average of 41.69% for the complexed ligand to 43.72% for the protonated ligand. Such changes in hybridization of the ring carbons should also be reflected as a small decrease in the vdw parameters. Reductions in R^* and ϵ^* for the B2 carbon atom in particular were found necessary in this study for the MM reproduction of experimental structures. However, although we are using very conservative reduction in parameters (the minimum needed to get the I/O B-type conformation lower in energy than the *anti*-CH_2-A-type conformation), the relatively modest changes in $^1J_{CH}$ suggest that this conservative approach is justified. Furthermore, we must not forget that MM methods are still simply tools and one should not expect to fine-tune parameters from one complex to the next. Indeed, the variation in the $^1J_{CH}$ values for complexed ligand is small, consistent with the standard assumption that this fine-tuning is not needed.

However, the use of the simplest MM model makes simulating trans influences in coordination and organometallic compounds a difficult, if not impossible, task. To account for the different trans influence of various ligands, different force field parameters for the $Co-N_L$ bond were used for Cl, 2.00 (r_o, Å), 120 (k_r, kcal/mol), and for the R ligands, 2.10 (r_o, Å), 110 (k_r, kcal/mol) (Table 4). With this modification, the computed and X-ray $Co-N_L$ bond distances agreed within 0.06 Å.

---

(60) Drew, M. G. B.; Hollis, S.; Yates, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1892.

(61) Halgren, T. A. *J. Am. Chem. Soc.* **1992**, *114*, 7827.

(62) Sun, H.; Mumby, S. J.; Maple, J. R.; Hagler, A. T. *J. Am. Chem. Soc.* **1994**, *116*, 2978.

(63) Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 2170.

(64) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(65) Drago, R. S. In *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992.

In conclusion, MM analysis of I/O B_{12} model compounds has led to the discovery of the importance of modifying the vdw parameters of the ligand atoms close to the metal. By applying a ∼10% reduction of the parameters, we found that the calculations can model the experimentally observed B-type structure favored for I/O models. This discovery would not have been made if the MM calculations had been restricted to cobaloximes, for which the preferred conformation is clearly of the A-type. When implemented in MM analysis, this concept allowed us to reproduce cobaloxime structures nicely. Although we have increased substantially the number of structures with the methoxymethyl ligand, the diversity of the conformations and the disorder problem preclude a thorough analysis of bonding and the development of force field parameters to treat this ligand. Consequently, the poorest fit in our MM analysis involves this group. Nevertheless, even this poor fit could not be made without including the lone pairs on the ether oxygen atoms. The apparent insensitivity of the dissymmetry of the Co−N−C bond angles to the A- or B-type structure seems to be accommodated well by the force field. The computations further predict that there would be substantial butterfly bending in the cobaloximes if the planar L N-donor heterocyclic ligands were able to adopt the B-type conformation and that this bending would increase as the trans influence of the other axial ligand decreased. There is no direct experimental test for this prediction. However, the prediction seems reasonable since, for I/O models, butterfly bending does seem to reflect the trans influence, and butterfly bending is small in an I/O model in which a lariat maintains the axial N-donor ligand in the A-type conformation.[66]

Acknowledgment. R.C. thanks Consiglio Nazionale delle Ricerche (CNR, Roma) and Università di Siena for financial support; Centro di Calcolo at Università di Siena for (CUCES) for the use of the Silicon Graphics Indigo, and Mr. Francesco Berrettini, Centro Analisi e Determinazioni Strutturali (CIADS) at Università di Siena, for X-ray data collection. We thank Suzette M. Polson for the synthesis of the $Me_3BzmCo(DH)_2CH_2$-OCH_3. This work was supported by NIH Grant GM 29225 (to L.G.M.). Instrument purchases were funded by the NIH and the NSF.

Supporting Information Available: Tables of complete bond lengths and angles for X-ray and computed structures, hydrogen atom coordinates, and anisotropic thermal parameters (28 pages).

IC980666I

---

(66) Gerli, A.; Sabat, M.; Marzilli, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 6711.