The First X-ray Structural Evidence Demonstrating Thiolate Coordination in an Organocobalt B_{12} Model Complex: Implications for Methionine Synthase

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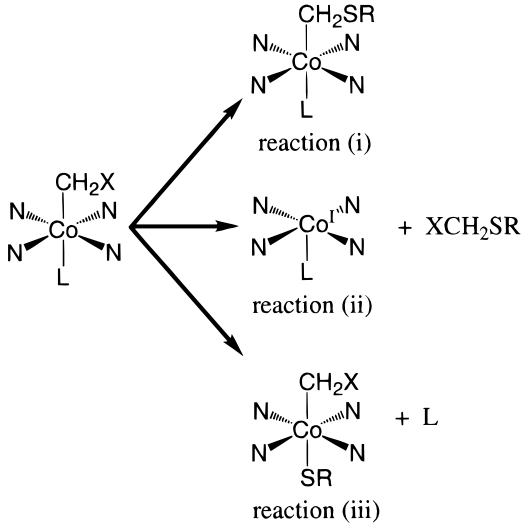
Enzyme-bound methyl-B_{12} transfers its methyl group to homocysteine during methionine synthesis. However, treatment of several types of organocobalt B_{12} models with arene- and alkanethiolates under ambient conditions leads only to thiolate ligation. The structure of $[AsPh_4][EtSCo(DH)_2CH_3]$ (DH = monoanion of dimethylglyoxime), the first characterization by X-ray crystallography of an organocobalt complex containing a unidentate coordinated thiolate, demonstrates unambiguously the S-ligation of ethanethiolate to Co, *trans* to the CH_3 ligand. This compound contains a very long Co−S bond (2.342(2) Å). However, the length of the Co−C bond (2.005(7) Å) is typical; this result strongly supports reported FT-Raman spectroscopic data indicating that the thiolate-type ligand does not have a strong *trans* influence and does not significantly weaken the Co−C bond in the ground state. Since a strong *trans* influence alkyl ligand weakens the *trans* Co−C bond, we examined the effect of EtS^- on Co((DO)(DOH)pn)$(CH_3)_2$ [(DO)(DOH)pn = N^2,$N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime) is an imine/oxime quadridentate ligand]. Even for this compound, no attack on the Co−C bond was observed, although independently synthesized EtSCo((DO)(DOH)pn)CH_3 was stable. Furthermore, thiolate did not cleave the Co−C bond of an organocobalt complex with a highly distorted Co−C group. Several new spectroscopic and ligand-exchange reactions were observed in this study. Ligand-responsive NMR shift trends in these other new complexes also indicate that thiolate ligands have a weak *trans* influence.

Introduction

Methionine synthase (MS) is a methylcobalamin (MeCbl, MeB_{12})-dependent enzyme that catalyzes the reaction that converts homocysteine to methionine.[1] One proposed mechanism for this alkylation reaction involves demethylation of MeCbl by homocysteine attack at the C of the $Co^{III}CH_3$ group of MeCbl to form a Co^{I}Cbl intermediate.[2] Thus, elucidating the interaction of thiolates with Co(III) complexes is of considerable importance for understanding the MeCbl function. One potential mode for activating the Co(III)−C bond for demethylation is to replace the ligand *trans* to the alkyl group with a better donor.[3−5] However, a FT-Raman study of the influence of the *trans* ligand on the Co−C stretching frequency suggests that significant Co−C bond weakening will occur only if the *trans* ligand is a very strong donor, *e.g.* an alkyl ligand.[4] Reactions of model systems have been used to address various aspects of thiolate B_{12} chemistry, including three types of reactions of thiolates with organocobalt compounds (Scheme 1): (i) attack at the organometallic carbon to form a thioether; (ii) reaction (i) followed by cleavage of the Co−C bond; or (iii) coordination at the Co *trans* to the alkyl group (thiolate ligation). The reports of reactions of thiolates with organocobalt complexes have been controversial. The reported result that thiol-promoted Co−C bond cleavage (reaction ii) of organocobaloximes ($LCo(DH)_2R$, Chart 1) occurred under neutral to acidic conditions[6,7] could not be reproduced.[8−10] Treatment of

Scheme 1. Possible Reactions of Thiolates with Organocobalt Compounds



MeCbl with the thiolate form of β-mercaptoethanol resulted in methylation of the thiolate and Co−C bond cleavage (reaction ii).[11] Another reaction involving methylation of a thiolate by an organocobalt compound (reaction ii) was reported recently[12] for the five-coordinate model CH_3Co^{III}Pc (Pc = phthalocyanine). The thiolate ligation reaction pathway (reaction iii) has been invoked in several instances for MeCbl and organocobalt B_{12}

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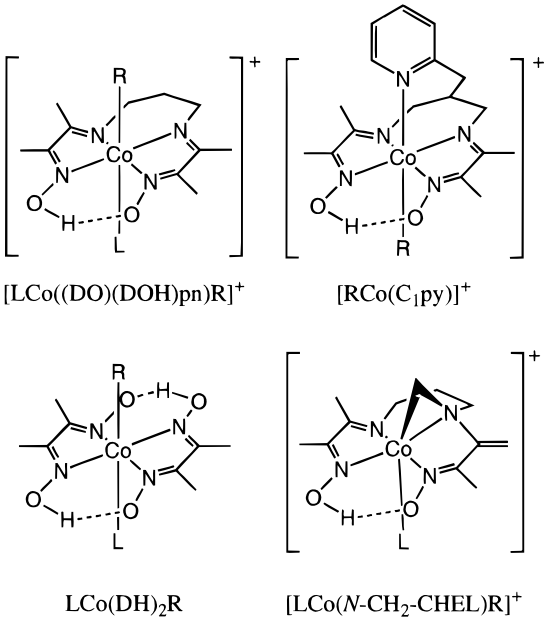
Chart 1



models, although no characterized isolated complexes of this type have been reported. The first reports of thiolato organocobaloximes[9] and imine/oxime-type organocobalt(III) complexes[13] {[LCo((DO)(DOH)pn)R]X, Chart 1} used UV−vis measurements as evidence of thiolate ligation.[9,13] Later, ^{1}H NMR evidence for a thiolato organocobaloxime was presented, but the isolated complex could not be adequately characterized.[14] It was suggested that CH_3 transfer from $CH_3Co^{III}Pc$ was inhibited by the formation of the inactive thiolato complex $CH_3Co^{III}Pc(SPh)$;[12] however, this complex was not isolated. In contrast, it was suggested that thiolate ligation did not occur in MeCbl (thus replacing the 5,6-Me_2Bzm) since no change was observed in the ^{13}C NMR spectrum of a sample of MeCbl treated with the thiolate form of dithiothreitol.[11]

The mechanisms of several reactions involving Co species and sulfur compounds are not fully understood, but these could involve Co species with coordinated sulfur ligands. For example, $H_2OCo(DH)_2CH_3$ was used as a catalyst to cleave disulfides in basic solution.[14] In another system, $CoCl_2$ in the presence of organohalides appeared to mimic MeCbl-dependent enzymes and produced thioethers from thiols.[15]

We report evaluations of the interactions of thiolates with a number of inorganic and organocobalt B_{12} model systems and compare the resulting complexes to each other. FT-Raman data[12] suggest that thiolate ligands are not sufficiently strong donors to weaken the Co−C bond in the ground state. This result is consistent with the suggestion that thiolate ligation could hinder attack at the Co-C bond, but there are no reported X-ray data to confirm the conclusion of the Raman study. We present the first X-ray evidence for an organocobalt B_{12} model containing a thiolate ligand and discuss the use of ^{1}H NMR spectroscopy to detect thiolate ligation. Finally, we examine the ligand-responsive NMR shift trends in order to assess the electronic *trans* influence of thiolate ligands.

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Experimental Section

Materials and Methods. (Abbreviations: *N*-MeImd = *N*-methylimidazole; py = pyridine.) The following were prepared as previously reported: $[Co(DH)_2py]_2$,[16,17] $pyCo(DH)_2Cl$,[18] $H_2OCo(DH)_2CH_3$,[18] Co((DO)(DOH)pn)Cl_2,[19,20] [pyCo((DO)(DOH)pn)Cl]PF_6,[21] [H_2OCo((DO)(DOH)pn)CH_3]ClO_4,[18] [Me_3PCo((DO)(DOH)pn)CH_3]PF_6,[4] [BrCo(C_1py)]ClO_4,[22] [CH_3Co(C_1py)]ClO_4.[22] [*N*-MeImdCo((DO)(DOH)pn)Cl]PF_6 was prepared similarly to the procedure for the ClO_4 salt.[23] $Me_2PhPCo(DH)_2CH_3$ was prepared from *t*-BupyCo$(DH)_2CH_3$[24] by a simple ligand-exchange reaction. *Caution! Perchlorate salts may be explosive and should be handled in small quantities with appropriate precautions.*[25] 3,5-Dimethylthiophenol (3,5-Me_2PhSH), 2,6-dimethylthiophenol = (2,6-Me_2PhSH), sodium *p*-toluenesulfinate dihydrate (Na[4-MePhSO_2]·$2H_2O$), *p*-thiocresol (4-MePhSH), potassium isopropylxanthate (K[*i*-$C_3H_7OCS_2$]), and sodium ethanethiolate (NaSEt, technical grade) were obtained from Aldrich, $AgNO_3$ was obtained from Apache Chemicals, and [NEt_4]OH (25% w/w solution in MeOH) was obtained from Sigma. Analytical results (Atlantic Microlabs, Atlanta, GA) and selected NMR data (GE QE300; referenced vs TMS) are listed in the Supporting Information.

[$AsPh_4$][EtSCo$(DH)_2CH_3$]·H_2O. In the drybox, a methanolic solution of NaSEt (0.07 g in 1−2 mL) was added to a solution of $H_2OCo(DH)_2CH_3$ (0.20 g, 0.62 mmol) in MeOH (7 mL), and the red solution was stirred for 30 min. A solution of [$AsPh_4$]Cl (0.28 g, 0.62 mmol in 1 mL of H_2O) was added to the reaction mixture outside the drybox, and the solution was quickly placed on a rotary evaporator to minimize exposure to air. After most of the MeOH was removed, the bright orange solid that precipitated was quickly isolated by vacuum filtration, washed with H_2O, and dried under vacuum for 5 h before being reintroduced into the drybox. Yield: 0.35 g (75%).

[NEt_4][3,5-Me_2PhS] (Based on a Known Procedure[26]). In the drybox, 3,5-Me_2PhSH (4.50 g, 32.6 mmol) was added to anhydrous MeOH (50 mL) in a three-necked flask. [NEt_4]OH (27 mL of 25% w/w solution in MeOH, 36 mmol) was then added. The covered flask was removed from the drybox, and the mixture was heated under nitrogen at reflux for 2.5 h. After the flask had cooled, MeOH was removed under reduced pressure, and the flask was then reintroduced into the drybox. The white solid was collected and recrystallized from CH_3CN/Et_2O at −35 °C. Yield: 6.05 g (69%). [NEt_4][4-MePhS] and [NEt_4][2,6-Me_2PhS] were prepared similarly.

[$AsPh_4$][3,5-Me_2PhSCo$(DH)_2CH_3$]·$1.5H_2O$. In the drybox, methanolic solutions of [NEt_4][3,5-Me_2PhS] (0.14 g, 0.51 mmol in 1 mL) and $H_2OCo(DH)_2CH_3$ (0.20 g, 0.62 mmol in 7 mL) were mixed, and the red solution was stirred for 30 min. Outside the drybox, the solution was diluted with water (20 mL) and treated with [$AsPh_4$]Cl (0.28 g, 0.62 mmol in 1 mL of H_2O). The solution was placed in a rotary evaporator quickly to minimize exposure to air. After most of the MeOH was removed, the bright orange solid that precipitated was isolated quickly by vacuum filtration, washed with H_2O, and dried under vacuum. Yield: 0.08 g (16%).

EtSCo((DO)(DOH)pn)CH_3·$0.5H_2O$. In the drybox, a solution of NaSEt (0.06 g in 1 mL of MeOH) was added to a methanolic solution of [H_2OCo((DO)(DOH)pn)CH_3]ClO_4 (0.20 g, 0.46 mmol in 8 mL). After 15 min of stirring, degassed H_2O was added to the solution. A dark red solid formed as the MeOH was removed by rotary evaporation. The solid was isolated by filtration, washed with a small amount of H_2O, and vacuum-dried for several hours. Yield: 0.09 g (51%).

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3,5-Me_2PhSCo((DO)(DOH)pn)CH_3. In the drybox, a solution of $[H_2OCo((DO)(DOH)pn)CH_3]ClO_4$ (0.20 g, 0.46 mmol) in MeOH (15 mL) was treated with $[NEt_4][3,5\text{-}Me_2PhS]$ (0.14 g, 0.51 mmol) in MeOH (1 mL). After 30 min of stirring, the solution was exposed to air, and H_2O (5 mL) was added. The volume of the red solution was reduced (to <5 mL), and precipitation began. After the mixture was chilled for 2 h (−35 °C), the dark pink solid that formed was isolated, washed quickly with H_2O, and vacuum-dried. Residual salts were removed by washing with cold H_2O. Recrystallization was accomplished from MeOH/H_2O. The compound is reasonably stable to air oxidation. Yield: 82%.

[Me_2PhPCo((DO)(DOH)pn)CH_3]PF_6·0.5H_2O. In the drybox, a suspension of $[H_2OCo((DO)(DOH)pn)CH_3]PF_6$ (0.25 g, 0.52 mmol) in CH_2Cl_2 (35 mL) was treated with PMe_2Ph (0.109 mL, 0.77 mmol) to give a bright orange solution, which became clear yellow after being stirred overnight. Solvent was removed under reduced pressure until the volume was ∼5 mL. The yellow, air-stable solid that precipitated was collected and washed with ether. Yield: 0.23 g (74%).

py$Co(DH)_2$(3,5-Me_2PhS). Method 1 (Based on a Known Procedure[6]). A solution of 3,5-Me_2PhSH (0.30 g, 1.9 mmol in 2 mL of MeOH) was added to a suspension of $[Co(DH)_2py]_2$ (0.64 g, 1.25 mmol) in MeOH (15 mL) in the drybox. After 1.5 h of stirring the solution, a dark green solid precipitated. The solid was isolated, washed with Et_2O, and vacuum-dried. Yield: 0.76 g (79%). 4-MePhSCo$(DH)_2$py (80%) and 2,6-Me_2PhSCo$(DH)_2$py (53%) were prepared similarly.

Method 2. In the drybox, a solution of $[NEt_4][3,5\text{-}Me_2PhS]$ (0.18 g, 0.68 mmol in 1 mL of MeOH) was added to a suspension of pyCo$(DH)_2Cl$ (0.25 g, 0.62 mmol) in MeOH (20 mL). The solution darkened within seconds and was stirred overnight. The green powder that formed was collected, washed with Et_2O, and dried under vacuum. Yield: 0.20 g (64%). 4-MePhSCo$(DH)_2$py was prepared similarly in 39% yield.

[*N*-MeImdCo((DO)(DOH)pn)(3,5-Me_2PhS)]PF_6. In the drybox, a solution of $[NEt_4][3,5\text{-}Me_2PhS]$ (0.13 g, 0.47 mmol in 1 mL of MeOH) was added to a suspension of [*N*-MeImdCo((DO)(DOH)pn)Cl]PF_6 (0.25 g, 0.45 mmol) MeOH (20 mL). The solution darkened within seconds. After the solution was stirred overnight, it was chilled to −35 °C until a green solid formed (in a few days). The solid was collected by vacuum filtration, washed with Et_2O, and dried under vacuum. Yield: 0.19 g (64%). Recrystallization was accomplished from MeOH/ Et_2O. [*N*-MeImdCo((DO)(DOH)pn)(4-MePhS)]PF_6 was prepared similarly.

[*N*-MeImdCo((DO)(DOH)pn)(4-$MePhSO_2$)]PF_6. A suspension of [*N*-MeImdCo((DO)(DOH)pn)Cl]PF_6 (0.25 g, 0.45 mmol) in MeOH (25 mL) was treated with Na[4-$MePhSO_2$]·$2H_2O$ (0.11 g, 0.50 mmol). The pink suspension turned to a red solution, and an orange solid precipitated after 10 min. After 1 h, the solid was collected, washed with H_2O, and dried under vacuum. Yield: 0.19 g (62%).

[*i*-$C_3H_7OCS_2$Co(C_1py)]ClO_4. A solution of $[BrCo(C_1py)]ClO_4$ (0.5 g, 0.88 mmol) in a 1:1 MeOH:H_2O mixture (50 mL) was treated with $AgNO_3$ (0.15 g, 0.88 mmol). The solution was stirred overnight and then filtered to remove AgBr. K[*i*-$C_3H_7OCS_2$] (0.16 g, 0.90 mmol) was added to the filtrate. The brown solid that precipitated immediately was isolated and then recrystallized from MeOH. Yield: 0.16 g (37%).

[4-$MePhSO_2$Co(C_1py)]ClO_4. A solution of $[BrCo(C_1py)]ClO_4$ (0.5 g, 0.88 mmol) in a 1:1 MeOH:H_2O (50 mL) mixture was treated with $AgNO_3$ (0.15 g, 0.88 mmol). The solution was stirred overnight and then filtered to remove AgBr. Na[4-$MePhSO_2$]·$2H_2O$, (0.19 g, 0.90 mmol) was added to the filtrate. MeOH was removed by rotary evaporation, and the aqueous solution was extracted with $CHCl_3$. The combined organic extracts were dried with $MgSO_4$, and the solvent was removed by rotary evaporation. Adding MeOH to the residue produced a suspension, from which a golden yellow solid was isolated by filtration and washed with Et_2O. Yield: 0.10 g (18%).

[4-MePhSCo(C_1py)]ClO_4. In the drybox, a solution of $[NEt_4]$[4-MePhS] (0.04 g, 0.16 mmol, in 1 mL of MeOH) was added to a suspension of $[BrCo(C_1py)]ClO_4$ (0.10 g, 0.16 mmol) in MeOH (20 mL). The color changed immediately to dark green. After 2 h of stirring, the solution was chilled to −35 °C. The green needles that formed were isolated after 1 day, washed with MeOH and Et_2O, and vacuum-dried. Yield: 0.04 g (40%).

[3,5-Me_2PhSCo(C_1py)]ClO_4. In the drybox, a solution of $[NEt_4][3,5\text{-}Me_2PhS]$ (0.04 g, 0.15 mmol in 1 mL of MeOH) was added to a suspension of $[BrCo(C_1py)]ClO_4$ (0.085 g, 0.15 mmol) in MeOH (18 mL). An immediate color change to dark green was observed. The solution was stirred for 30 min, and the green precipitate that formed was isolated, washed with Et_2O, and vacuum-dried. Yield: 0.03 g (30%).

Co((DO)(DOH)pn)(*i*-$C_3H_7OCS_2$)$_2$. To a solution of Co((DO)(DOH)pn)Cl_2 (0.53 g, 1.45 mmol) in a 5:3 MeOH:H_2O solution (40 mL) was added $AgNO_3$ (0.49 g, 2.9 mmol). After the mixture was stirred for 30 min, AgCl was removed by filtration, and the filtrate was diluted with MeOH to a volume of 200 mL. A solution of K[*i*-$C_3H_7OCS_2$] (0.50 g, 2.9 mmol in 10 mL of H_2O) was then added. The fine brown powder that precipitated was collected on a filter and washed with H_2O and Et_2O. Yield: 0.52 g (63%).

Co((DO)(DOH)pn)(4-$MePhSO_2$)$_2$. A solution of Co((DO)(DOH)pn)Cl_2 (1.00 g, 2.7 mmol) in a 5:4 MeOH:H_2O mixture (90 mL) was treated with $AgNO_3$ (0.92 g, 5.4 mmol). The solution, stirred for 30 min, was filtered to remove AgCl. The filtrate was diluted with MeOH to a volume of 200 mL, and a solution of Na[4-$MePhSO_2$]·$2H_2O$ (1.16 g, 5.4 mmol, in 10 mL of H_2O) was added. The solution was allowed to evaporate slowly in the hood. The large red crystals that formed were collected after 1 day and washed with H_2O and Et_2O. Yield: 0.70 g (42%).

X-ray Crystallography. An orange-red crystal of $[AsPh_4]$-$[EtSCo(DH)_2CH_3]$ (0.26 × 0.44 × 0.45 mm) recrystallized from MeOH/ Et_2O was used for data collection. Intensity data were collected at −100 °C on a Siemens P4 instrument using an LT2 low-temperature device. The crystal system and high-angle cell constants were determined by automatic reflection selection, indexing, and least-squares refinement (XSCANS Version 2.0). Three check reflections were measured every 97 reflections; there was no significant deviation in intensity. Intensity data were corrected for Lorentz and monochromator polarization and absorption (semiempirical method based on azimuthal scans). The structure of $[AsPh_4][EtSCo(DH)_2CH_3]$ was solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures on F^2 using SHELXL-93. The H atoms were generated at calculated positions (d(O−H) = 0.85 Å; d(C−H) = 0.96 Å). All H atoms were constrained using a riding model with isotropic thermal parameters fixed at 20% greater than that of the bonded atom. Crystal data and refinement parameters are presented in Table 1, and selected bond lengths and bond angles appear in Table 2.

Table 1. Crystallographic Data for $[AsPh_4][EtSCo(DH)_2CH_3]$

empirical formula	$C_{38}H_{54}AsCoN_4O_7S$
fw	844.76
space group	$P2_12_12_1$
a (Å)	9.091(2)
b (Å)	17.098(6)
c (Å)	26.505(2)
V (Å^3)	4120(2)
Z	4
d(calc)	1.36 mg m^{-3}
abs coeff	1.31 mm^{-1}
radiation	Mo Kα (λ = 0.710 73 Å)
temperature (K)	173
min/max transm	0.267/0.355
abs structure param	0.00(2)
refinement method	full-matrix least-squares on F^2
final R indices [$I > 2\sigma(I)$]	R = 4.34%; R_w = 9.96%
R indices (all data)	R = 5.51%; R_w = 11.34%

Results and Discussion

X-ray Crystallography. The structure of $[AsPh_4]$-$[EtSCo(DH)_2CH_3]$ (Figure 1) reveals coordination of ethanethiolate, *trans* to the CH_3 group. This is the first report of an organocobalt complex containing a unidentate coordinated thiolate characterized by X-ray crystallography. $[HgI_2]$-$[pyCo(DH)_2SCH_3]$ is the only other unidentate (alkanethiolato)-cobalt(III) complex characterized by X-ray crystallography.[27]

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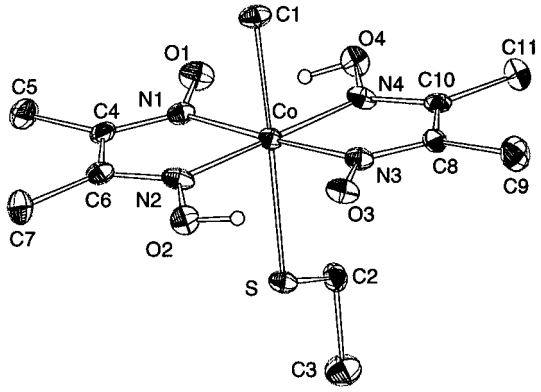

Figure 1. Perspective drawing of $[AsPh_4][EtSCo(DH)_2CH_3]$ with 50% probability for the thermal ellipsoids.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[AsPh_4][EtSCo(DH)_2CH_3]$

Bond Lengths (Å)			
Co−N(4)	1.852(6)	Co−N(3)	1.886(7)
Co−N(2)	1.853(6)	Co−C(1)	2.005(7)
Co−N(1)	1.876(6)	Co−S	2.342(2)
Bond Angles (deg)			
N(4)−Co−N(2)	179.8(3)	N(1)−Co−S	92.3(2)
N(4)−Co−N(1)	98.5(3)	N(3)−Co−S	90.2(2)
N(2)−Co−N(1)	81.4(3)	C(1)−Co−S	177.9(2)
N(4)−Co−N(3)	81.5(3)	C(4)−N(1)−Co	117.0(5)
N(2)−Co−N(3)	98.6(3)	O(1)−N(1)−Co	121.8(5)
N(1)−Co−N(3)	177.4(3)	C(6)−N(2)−Co	117.2(5)
N(4)−Co−C(1)	88.1(3)	O(2)−N(2)−Co	125.1(5)
N(2)−Co−C(1)	91.7(3)	C(8)−N(3)−Co	116.3(5)
N(1)−Co−C(1)	87.2(3)	O(3)−N(3)−Co	121.7(5)
N(3)−Co−C(1)	90.3(3)	C(10)−N(4)−Co	116.8(5)
N(4)−Co−S	94.0(2)	O(4)−N(4)−Co	124.9(5)
N(2)−Co−S	86.2(2)	C(2)−S−Co	107.6(3)

The three other reported cases of organocobalt compounds containing a Co−S bond were not B_{12} models. In these, the coordinated carbon was part of a chelate, with *cis* Co−C and Co−S bonds (Table 3).[27−34] Only one contained a thiolate, in a three-membered Co−C−S ring.[30] The other two contained a Co−S thioether bond.[28,29]

The 2.005(7) Å Co−C bond for $[AsPh_4][EtSCo(DH)_2CH_3]$ falls within the normal distance range for cobaloximes of the type $LCo(DH)_2CH_3$.[35] Examples of typical Co−C bond lengths: 1.990(5) (L = H_2O), 1.998(5) (L = py), 2.009(7) (L = *N*-MeImd), 2.011(3) Å (L = PMe_3).[35] We recently found by FT-Raman spectroscopy that the Co−CH_3 stretching frequency (ν_{Co-CH_3}), a parameter related to Co−C bond strength, was only slightly dependent on the nature of the *trans* ligand, L.[4] For the primary series studied, $[LCo((DO)(DOH)pn)CH_3]^{0/+}$ (Chart 1), the frequency decreased from 505 to 455 cm^{-1}, with stronger electron-donating character of the *trans* L in the following order: Cl^-, *N*-MeImd, py, 3,5-Me_2PhS^-, PMe_3, CD_3^-.[4] However, ν_{Co-CH_3} values for most of the compounds were clustered near 500 cm^{-1}, with the lowest value by far found for CD_3^-, which is known to have a very large *trans* influence. Thus, the similar Co−C bond length for $[AsPh_4][EtSCo(DH)_2CH_3]$ compared to those of other cobaloximes is consistent with the Raman data.

Table 3. X-ray Crystal Structural Data (Bond Distances in Å) for Organocobalt and Cobalt Thiolato and Thioether Complexes

	Co−C	Co−S	Co−N (*trans* to S)	ref
Organometallic Complexes				
$[AsPh_4][EtSCo(DH)_2CH_3]$	2.005(7)	2.342(2)		
$[Co(aeaps)_2]S_2O_6$[a−c]	2.026(3)	2.2482(9)	2.011(3)	28
Co(Me3L′)[a−c]	1.969(5)	2.203(2)		29
CoCS(Cp*)(CO)[a,b,d]	2.039(10)	2.216(4)		30
Coordination Complexes				
$[HgI_2][CH_3SCo(DH)_2py]$		2.286	1.989(5)	27
$[Co(L\text{-}Cys)(dien)]_3(ClO_4)_3$[b]		2.266(3)	2.013(8)	31
$[Na\subset222][Co(SC_6HF_4)_2(TPP)]$		2.346(3)		32
		2.330(3)		
$[Co(SPh)_2(phen)_2]ClO_4$		2.305(4)	1.97(1)	33
		2.289(4)	1.97(1)	
$[Ph_4P][Co(SPh\text{-}i\text{-}Pr_3)_4]$		2.206(3)		34
		2.211(3)		
		2.206(3)		
		2.204(3)		

[a] Carbon is chelated. [b] Sulfur is chelated. [c] Thioether coordination. [d] Co−C−S three-membered ring. Abbriations: aeaps = 2-aminoethyl 3-aminopropyl sulfide; Me3L′ = a dithiapropyl-substituted triazene 1-oxide; $salenC_2(SEt)$ = *N*,*N*′-disalicylidene-2-methyl-4-(ethylthio)-1,2-butanediamine; Cp* = pentamethylcyclopentadiene; L-CysH = L-cysteine; dien = diethylenetriamine; phen = 1,10-phenanthroline; *i*-Pr_3PhSH = 2,4,6-triisopropylbenzenethiol; SC_6HF_4 = 2,3,5,6-tetrafluorobenzenethiol; TPP = *meso*-tetraphenylporphyrin; Na⊂222 = 222 cryptated sodium.

The Co−S bond of $[AsPh_4][EtSCo(DH)_2CH_3]$ is significantly longer than those in known examples of (alkanethiolato)-organocobalt complexes (Table 3). However, most of the latter have chelated sulfur, and relatively short bond lengths can be attributed to the chelate effect. The Co−S bond of the unidentate thiolate ligand in the related inorganic cobalt complex $[HgI_2][pyCo(DH)_2SCH_3]$[27] is lengthened by the interaction of S with Hg. However, the Co−S bond in $[AsPh_4][EtSCo(DH)_2CH_3]$ is longer, further evidence of the large *trans* influence of CH_3. There are other examples of long Co−S bonds (Table 3), but these involve ArS complexes and these aryl ligands appear to be weaker donors.

Interaction of Organocobalt Complexes with Thiolates. We now discuss our investigations into the interactions of various B_{12} models with two kinds of thiolate ligands: arenethiolates and the more reactive alkanethiolates. These experiments often led to the isolation of inorganic and organocobalt thiolato complexes. ^1H NMR spectroscopy has proved useful in indicating coordination of thiolates, in identifying oxidized S-containing organic products and in assessing the potential formation of thioethers. A downfield shift of the CH_2 signal from free EtS^- (Table 4) indicates oxidation to the disulfide. A signal at ∼2.1 ppm (s, 3H, SCH_3) is expected for thioethers. We also prepared complexes containing other sulfur ligands in order to assess the effects of S-ligation on spectra.

(a) Cobaloximes. Formation of the organocobaloxime thiolato complex $[CH_3SCo(DH)_2CH_3]^-$ in 1:1 CD_3OD:D_2O solution was suggested[14] on the basis of the upfield shift of the ^1H NMR signal for CH_3S^- relative to the signal for free CH_3S^-. Loss of CH_3SH under reduced pressure from the isolated compound $[AsPh_4][CH_3SCo(DH)_2CH_3]$ prevented its characterization by elemental analysis.[14] We successfully prepared $[AsPh_4][EtSCo(DH)_2CH_3]$ by reaction of $H_2OCo(DH)_2CH_3$ with NaSEt (reaction iii), and we were able to characterize the

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Table 4. ^{1}H NMR Shifts (ppm) of Sulfur Species and of Cobaloximes in CD_3OD

	S-ligand signals	oxime CH_3	axial CH_3
EtS^-	2.50, 1.26		
EtSSEt	2.68, 1.29		
$H_2OCo(DH)_2CH_3$		2.23	0.67
$[AsPh_4][EtSCo(DH)_2CH_3]$	1.89, 1.06	2.15	0.61
$[AsPh_4][3,5\text{-}Me_2PhSCo(DH)_2CH_3]$	6.68, 6.62	1.88	0.66
$[4\text{-}MePhSO_2Co(DH)_2CH_3]^-$ [a]	7.29, 7.16	1.96	0.80
$[i\text{-}PrOCS_2Co(DH)_2CH_3]^-$ [a]	5.62	2.17	0.76

[a] Prepared *in situ.*

compound by elemental analysis and X-ray crystallography (see above). The EtS ^{1}H NMR signals for $[AsPh_4][EtSCo(DH)_2CH_3]$ in CD_3OD solution are upfield of the signals for EtS^- (by 0.6 (CH_2) and 0.2 (CH_3) ppm, Table 4). Addition of NaSEt (0.5 equiv) to the solution of $[AsPh_4][EtSCo(DH)_2CH_3]$ CD_3OD did not change the spectrum of the complex, and the EtS^- signals were in the normal position; therefore, EtS does not appear to undergo fast exchange.

The methyl group of MeB_{12} was reported to transfer to dithiothreitol, reaction ii ($t_{1/2} = 1.5$ h at 43 °C).[11] In contrast, the MeB_{12} model CH_3CoPc transferred a CH_3 group to benzenethiolate at ambient temperature with $t_{1/2} = 0.4$ s.[12] Wishing to test for modes of reactivity of thiolates with organocobaloximes other than S-ligation, we selected a cobaloxime with a strongly coordinating axial ligand *trans* to the methyl group to block the ligand-exchange reaction with EtS^- (reaction iii). Treatment of a CD_3OD solution of $Me_2PhPCo(DH)_2CH_3$ with EtS^- (5 equiv) resulted in only <10% displacement of Me_2PhP to form $[EtSCo(DH)_2CH_3]^-$ after 5 days, with no NMR evidence of any other reactions. Thus, alkylation of the thiolate (reaction ii) was not favored under the reaction conditions. We also treated a cobaloxime having a good leaving group on the organometallic carbon, *N*-MeImdCo$(DH)_2CH_2Br$, with NaSEt (2.5 equiv). The ^{1}H NMR of the CD_3OD solution indicated that, even after 4 days, only extensive *N*-MeImd replacement to form $[EtSCo(DH)_2CH_2Br]^-$ occurred (upfield EtS signals observed at 1.89 (q, SCH_2) and 1.05 ppm (t, CH_3)); there was no evidence for the formation of $[EtSCo(DH)_2CH_2SEt]^-$ (reaction i).

We prepared organocobalt complexes using other S-donor ligands. An arenethiolato complex, $[AsPh_4][3,5\text{-}Me_2PhSCo(DH)_2CH_3]$, was prepared similarly to the EtS^- analog. In addition, we prepared complexes containing innocent S-donor ligands *in situ*, $[i\text{-}C_3H_7OCS_2Co(DH)_2CH_3]^-$ and $[4\text{-}MePhSO_2Co(DH)_2CH_3]^-$. The different S-donors did not significantly affect the position of the ^{1}H NMR Co−CH_3 signal compared to other axial ligands (Table 4), although an upfield shift of the oxime CH_3 signal was observed for the S-donor ligands containing an aromatic ring ($3,5\text{-}Me_2PhS^-$ and $4\text{-}MePhSO_2^-$).

(b) Imine/Oximes. We obtained the neutral organocobalt imine/oxime compound EtSCo((DO)(DOH)pn)CH_3 by anaerobic treatment of a MeOH solution of $[H_2OCo((DO)(DOH)pn)CH_3]PF_6$ with NaSEt (reaction iii). Air-stable $3,5\text{-}Me_2PhSCo((DO)(DOH)pn)CH_3$ was prepared similarly using $[NEt_4][3,5\text{-}Me_2PhS]$. The ^{1}H NMR spectrum of EtSCo((DO)(DOH)pn)CH_3 in CD_3OD exhibited thiolato ligand signals significantly upfield of the free thiolate values, as expected.

In order to test for an alternative reaction of thiolates with imine/oxime organocobalt complexes, we examined by ^{1}H NMR complexes with a strongly coordinating axial ligand *trans* to the methyl to block the ligand-exchange reaction (iii). While treatment of $Me_2PhPCo(DH)_2CH_3$ with NaSEt resulted in ~10% L displacement after 5 days, treatment of $[Me_3PCo((DO)(DOH)pn)CH_3]ClO_4$ in CD_3OD with NaSEt (1 equiv) resulted in the slow formation of ~25% EtSCo((DO)(DOH)pn)CH_3 after 2 days (reaction iii). After 4 days, no further reaction was evident. With time, the imine CH_3 ^{1}H NMR signal disappeared. We attribute this phenomenon, observed in several other cases, to the known D-exchange of this type of methyl group.[36,37] We treated a CD_3OD solution of Co((DO)(DOH)pn)$(CH_3)_2$ with 1 equiv of NaSEt. As mentioned above, only the alkyl ligand has a sufficiently strong *trans* influence to significantly weaken the Co−C bond, as indicated both by FT-Raman spectroscopy and by X-ray structural data.[4,38] In addition to the D-exchange of the imine CH_3 protons, EtSCo((DO)(DOH)pn)CH_3 formed as a minor product after 1 day (total 20% after 2 days). However, it is unlikely that EtS^- caused the displacement of the CH_3 group, since Co((DO)(DOH)pn)$(CH_3)_2$ is known to decompose in protic solvents to give methane and $[(solvent)Co((DO)(DOH)pn)CH_3]^+$.[39] In a control experiment with no NaSEt present, we observed ~15% decomposition to $[MeOHCo((DO)(DOH)pn)CH_3]^+$. In contrast, in CD_3CN we observed no reaction for Co((DO)(DOH)pn)$(CH_3)_2$ treated with up to 6 equiv of NaSEt, except for partial D-exchange of the imine CH_3 protons.

(c) Lariat-Type Imine/Oximes. The lariat-type complexes ($[RCo(C_1py)]X$, Chart 1)[21] are a new class of imine/oxime-type B_{12} models that contain a pyridyl group covalently attached to the equatorial ligand. We studied the formation of organocobalt thiolato imine/oxime lariat-type complexes by ^{1}H NMR spectroscopy. The ^{1}H NMR shift of the pyridyl α-H can be used to indicate whether the pendant pyridyl was bound to Co. A shift of the coordinated pyridyl α-H signal well upfield of 8.55 ppm is due largely to the influence of Co anisotropy.[40]

A CD_3OD solution of $[CH_3Co(C_1py)]ClO_4$ was treated with 1.1 equiv of NaSEt, and the pyridyl α-H signal shifted from 8.38 ppm in $[CH_3Co(C_1py)]ClO_4$ to 8.52 ppm, a shift consistent with the thiolato ligand replacing pyridyl (reaction iii, Table 5). The $-CH_2S$ quartet appeared at 1.65 ppm, a shift similar to that for EtSCo((DO)(DOH)pn)CH_3 (Supporting Information). The equatorial imine CH_3 protons underwent D-exchange after a brief exposure to NaSEt in CD_3OD. After 2 days, signals for a second, closely related species arose (Table 5), consistent with two slightly different organocobalt thiolato species. Furthermore, after 2 weeks, the two new Co−CH_3 signals became equal in intensity, a result also consistent with methyl transfer. Using additional thiolate initially (2 equiv) did not alter the course of the reaction. Most likely, the second species is a geometric isomer that formed as a result of Co(II)-catalyzed methyl transfer.[41] Realkylation of the Co(II) compound could occur on the opposite side of the equatorial ligand, on the side of the pendant pyridyl moiety (Scheme 2). Such a situation would arise whenever a strong unidentate ligand replaced the pendant pyridyl. Thus, we studied the effect of the treatment of $[CH_3Co(C_1py)]ClO_4$ with 1 equiv of PMe_2Ph in CD_3OD. After only 1 h, the resulting ^{1}H NMR spectrum contained two slightly different $[CH_3Co(C_1py)PMe_2Ph]ClO_4$ species, *viz.*, two CH_3 doublets at 0.98 (3 Hz) and 1.03 ppm (4 Hz), due to ^{1}H−^{31}P coupling (comparable values for $[PhMe_2PCo((DO)(DOH))CH_3]PF_6$ were 1.01 ppm (4 Hz)). In addition, other data were

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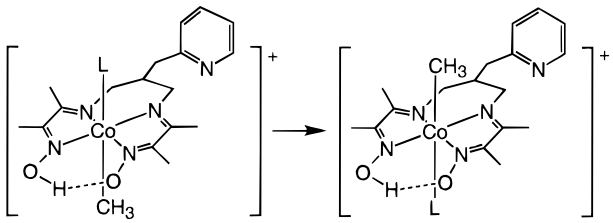
Table 5. ^{1}H NMR Shifts (ppm) of $[CH_3Co(C_1py)]ClO_4$ in CD_3OD Treated with NaSEt

NaSEt	α	β	γ	axial CH_3	N−CH_2	imine CH_3	oxime CH_3	EtS (CH_2S)	EtS (CH_3)
none	8.38	7.22 7.39	7.73	0.84	4.26, 3.93	2.32	2.21		
1 equiv[a]	8.52	7.32 7.45	7.83	0.58	3.93, 3.46	*b*	2.22[d]	1.65	1.04
1 equiv, with time[c]	8.52 sh	7.32 sh 7.45 sh	7.83 sh	0.51	4.00, 3.32	*b*	2.20[d]	1.76 2.68[e]	 1.29[e]

[a] Complete reaction. [b] Signal disappeared (D-exchange). [c] Signals of a second new species formed from 1 equiv of solution with time. After 2 weeks, the signals of the two species were similar in intensity. [d] Signals diminished significantly in intensity with time. [e] EtSSEt. sh = shoulder.

Scheme 2



consistent with Scheme 2; *viz.*, the two α-H signals had downfield signals at 8.51 and 8.66 ppm.

(d) Distorted Model. We studied the reaction of NaSEt with the organocobalt complex [*N*-MeImdCo(*N*-CH_2-CHEL)]ClO_4 (Chart 1)[37] by ^{1}H NMR. This compound contains a distorted coordination environment, and there is a relatively open avenue for attack on the carbon attached to Co. However, addition of 2.4 equiv of NaSEt to a CD_3OD solution of [*N*-MeImdCo(*N*-CH_2-CHEL)]ClO_4 resulted only in thiolate displacement of *N*-MeImd (reaction iii). The signals for the free *N*-MeImd integrated for 1 equiv (relative to the olefin and axial methylene protons). Prolonged exposure of [*N*-MeImdCo(*N*-CH_2-CHEL)]-ClO_4 to NaSEt led to decomposition, with formation of ethyl disulfide identified on the basis of its ^{1}H NMR signals.

Inorganic (Thiolato)cobalt(III) Complexes. (a) Cobaloximes. We further explored thiolate chemistry relevant to cobalt by preparing a number of inorganic B_{12} model complexes. We prepared cobaloximes containing unidentate N-donors *trans* to an arenethiolate ligand by the reported redox method (eq 1).[6] Alkanethiolates can also be incorporated into a cobaloxime containing an N-donor axial ligand by treatment of cobal(II)-oxime ("$Co^{II}(DH)_2$" generated *in situ* in basic solution) in the presence of py with dimethyl disulfide (eq 2).[6]

$$[Co(DH)_2py]_2 + 2PhSH \rightarrow 2pyCo(DH)_2(PhS) + H_2 \quad (1)$$

$$"Co^{II}(DH)_2" + py + 0.5CH_3SSCH_3 \rightarrow pyCo(DH)_2SCH_3 \quad (2)$$

We wished to test whether compounds of the type pyCo-$(DH)_2$SR (R = alkyl, aryl) could also be prepared from a Co(III) precursor. We found that addition of tetraalkylammonium salts of arenethiolates to solutions of cobaloximes such as pyCo$(DH)_2$Cl led to selective substitution of the halide (eq 3). However, treatment of a suspension of pyCo$(DH)_2$Cl in

$$pyCo(DH)_2Cl + [NEt_4][ArS] \rightarrow pyCo(DH)_2(ArS) + [NEt_4]Cl \quad (3)$$

CD_3OD with 1 equiv of NaSEt did not proceed as in eq 3. Instead, the ^{1}H NMR spectrum of the resulting brown-red solution contained signals for two different S-containing compounds. The integration of the dominant thiolate signals (δ 1.74 (q, 4H, SCH_2), 1.00 (t, 6H, CH_3)) relative to the single oxime CH_3 signal (δ 2.26 (s, 12H)) suggested that the bis(thiolato) complex $[Co(DH)_2(SEt)_2]^-$ formed. The 0.8 ppm upfield shift of the SCH_2 signal compared that of to free NaSEt supports this conclusion. The minor S-containing product (signals at 2.69 (q) and 1.29 (t) ppm) accounts for <5% of the S-containing signals initially, increasing to 20% overnight. The downfield shift of these signals compared to those of NaSEt suggests that EtSSEt formed (Table 4). Thus, alkane- and arenethiolates reacted differently with Co(III) complexes, and the above redox method (eq 2) is the only successful procedure reported for the preparation of an alkanethiolato inorganic cobaloxime complex.

An EP value (an electronic parameter) for the ArS ligand was determined in order to assess its electronic *trans* influence quantitatively. The EP value is derived from the ^{13}C shift for the γ-C for complexes of the type pyCo$(DH)_2$R(or X),[42] ranging from −1.56 for X = Cl (weak *trans* influence) to +0.24 for CH_2OCH_3 (strong *trans* influence). We expected the EP value to be close to the EP value of −0.75 that we calculated for *t*-BupyCo$(DH)_2$S(*t*-Bu).[35,43] We assigned ^{13}C NMR signals of pyCo$(DH)_2$(3,5-Me_2PhS) at 138.12 ppm and of pyCo$(DH)_2$(4-MePhS) at 138.14 ppm to the py γ-C and used 138.13 ppm to calculate an EP value of −0.65. This result means that the ArS^- ligand has a moderate electronic *trans* influence, similar to that of the alkyl donors $-CH_2CF_3$ and $-CH_2CN$.

(b) Imine/Oximes. Although Co(II) imine/oxime complexes are known,[44,45] these have not been used to prepare thiolate derivatives (*cf.* eqs 1 and 2). We found routes for the synthesis of thiolato imine/oxime-type complexes starting with Co(III) compounds (eq 4). We treated a MeOH solution of [*N*-

$$[LCo((DO)(DOH)pn)Cl]PF_6 + RS^- \rightarrow [LCo((DO)(DOH)pn)SR]PF_6 + Cl^- \quad (4)$$

MeImdCo((DO)(DOH)pn)Cl]PF_6 with $[NEt_4][ArS]$ to produce complexes of the type [*N*-MeImdCo((DO)(DOH)pn)(ArS)]PF_6 (ArS = 4-MePhS, 3,5-Me_2PhS). Our attempts using this method to prepare arenethiolate complexes containing N-donors weaker than *N*-MeImd or alkanethiolate complexes with any N-donor failed. For example, even the bulky arenethiolate $[NEt_4][2,6-Me_2PhS]$ (1 equiv) displaced py from [pyCo((DO)(DOH)pn)-Cl]PF_6, as suggested by the lack of py signals in the ^{1}H NMR spectrum of the isolated product. In addition, we treated a suspension of [*N*-MeImdCo((DO)(DOH)pn)Cl]PF_6 in CD_3OD with the alkanethiolate NaSEt (1 equiv). Integration of the dominant thiolate signals (δ 1.59 (q, 4H), 1.00 (t, 6H)) suggested that the bis(thiolato) complex Co((DO)(DOH)pn)$(SEt)_2$ had

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Table 6. ^{1}H NMR Shifts (ppm) of Lariat-Type Complexes $[RCo(C_1py)]ClO_4$ (or PF_6) in $CDCl_3$

	α	*β*	*γ*	axial CH_3	N−CH_2	imine CH_3	oxime CH_3
$[ClCo(C_1py)]ClO_4$[a]	7.80	7.25 7.33	7.75	...	4.42, 4.20	2.59	2.44
$[4\text{-}MePhSO_2Co(C1py)]ClO_4$	7.88	7.05 7.21	7.63	...	4.58, 4.28	2.46	2.08
$[4\text{-}MePhSCo(C_1py)]ClO_4$	8.09	7.06 7.38	7.62	...	4.40, 4.24	2.25	2.12
$[CH_3Co(C_1py)]ClO_4$	8.31	7.14 7.40	7.65	0.79	4.36, 3.93	2.37	2.23

[a] Reference 40.

formed (unchanged starting material was still suspended). Thus, the reaction (eq 4) was successful only for L = *N*-MeImd and $RS^- = ArS^-$ and failed for all N-donors when $RS^- = EtS^-$.

(c) Lariat-Type Imine/Oximes. We prepared without complication the inorganic thiolato lariat-type complexes $[ArSCo(C_1py)]ClO_4$ (ArS = 4-MePhS, 3,5-Me_2PhS) by treating $[BrCo(C_1py)]ClO_4$ with the appropriate $[NEt_4][ArS]$ reagent (1 equiv). The ^{1}H NMR shift of the α-H signal in a $CDCl_3$ solution of $[4\text{-}MePhSCo(C_1py)]ClO_4$ was 8.09 ppm, or 0.46 ppm upfield of the free py α-H C_1py signal (Table 6). Therefore, the pendant pyridyl is bound to Co in a $CDCl_3$ solution of $[4\text{-}MePhSCo(C_1py)]ClO_4$. The formation and successful isolation of $[ArSCo(C_1py)]ClO_4$ contrast with our results for the quadridentate imine/oximes (complete replacement of py). Treatment of $[BrCo(C_1py)]ClO_4$ with the more reactive thiolate NaSEt (1 equiv) resulted in the formation of brown needles. At least two species were present in the ^{1}H NMR spectrum (in $CDCl_3$) of the product, and many signals were broad. In addition, there are signals at 2.70 (q) and 1.32 (t) ppm, which match those of EtSSEt in this solvent (Supporting Information). Thus, although conditions may exist which allow a product to be formed and isolated, alkanethiolates cause synthetic problems even for lariat-type complexes.

As mentioned above, the shifts of ^{1}H NMR signals, particularly for protons close to Co, are influenced by Co anisotropy.[40,46] The effect is to shift the signals of the equatorial ligand protons in the direction opposite to those of the axial ligand protons. The axial L ligand signals are most useful since these are not affected by the anisotropy of the R or X axial ligand, whereas the equatorial ligand signals are so influenced. The shift trends tend to parallel the *trans* influence. For example, the $[ClCo(C_1py)]ClO_4$ α-H signal is well upfield of that for $[CH_3Co(C_1py)]ClO_4$ (in $CDCl_3$). The equatorial methyl signals have the opposite relationship (Table 6). The shift of the α-H signal for $[4\text{-}MePhSCo(C_1py)]ClO_4$ is between those of the Cl and CH_3 analogs, consistent with a moderate *trans* influence. The α-H signal for an analog containing an oxidized S-donor, $[4\text{-}MePhSO_2Co(C_1py)]ClO_4$, is closer to that of the Cl analog. The signals of three of the four equatorial CH_3 groups for these two S-donor complexes were upfield of the corresponding signals for both the Cl and CH_3 complex (Table 6). We attribute this upfield shift to the proximity of the anisotropic aromatic rings to the equatorial ligand. In contrast, the ^{1}H shift of the imine CH_3 of the 4-$MePhSO_2$ complex is significantly *downfield* from both the 4-MePhS and the CH_3 complexes (Table 6). This imine CH_3 shift for the $[N\text{-}MeImdCo((DO)(DOH)pn)4\text{-}MePhSO_2]PF_6$ complex is also relatively downfield. These shifts suggest the anisotropic effect of the aromatic ring is nearly absent. There is a reasonable explanation for this result. The negative oxygens of the 4-$MePhSO_2$ ligand are repelled by the oxime oxygens. As a consequence, the ring would be preferentially oriented away from the oxime region and toward the imine region.

Conclusions

The alkanethiolate ligand is comparable to alkylphosphines in its affinity for axial coordination to B_{12} models. It is a much stronger ligand than biologically relevant N-heterocycles such as benzimidazole and imidazole. The principal reaction following addition of thiolates to organocobalt complexes is S-ligation, not Co−C bond cleavage. This finding holds also for both the dialkyl complex $Co((DO)(DOH)pn)(CH_3)_2$, with strong *trans* ligands, and for a complex with a highly distorted alkyl group sterically exposed to attack by the thiolate.

The influence of the thiolate ligand on the length of the *trans* Co−C bond has been shown to be small in this first crystallographic determination of the structure of this type of compound. NMR shift trends are also consistent with the new structural results and the previously reported FT- Raman data and indicate that thiolates have a moderate *trans* influence. It is thus likely that thiolates will not significantly influence the Co−CH_3 bond in methylcobalamin. Therefore, thiolate ligation by homocysteine is unlikely to be an important step in the enzymatic processes involving methionine synthase. In fact, the protein may act to prevent thiolate ligation since the results presented here and elsewhwere in the studies with CH_3-$Co^{III}Pc$[12] suggest that such ligation may impede attack at the Co−C bond.

The structure of $[AsPh_4][EtSCo(DH)_2CH_3]$ revealed that the Co(III)−S bond *trans* to the Co−C bond is unusually long compared to other Co(III)−S containing alkanethiolate complexes. However, relevant structural information is limited to this compound, and additional data are needed to confirm this result.

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Supporting Information Available: A packing diagram and tables of crystallographic data, bond lengths, bond angles, atomic coordinates, and displacement coefficients for $[AsPh_4][EtSCo(DH)_2CH_3]$, along with tables of elemental analyses and ^{1}H NMR data (14 pages). Ordering information is given on any current masthead page.

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