Synthesis, Structure, and Spectroscopy of Pseudotetrahedral $Co^{II}N_3(SR)$ Complexes. Active Site Approximations to the Cobalt(II)-Substituted Type 1 Copper Proteins

Jeffery S. Thompson, Theophilus Sorrell, Tobin J. Marks,* and James A. Ibers*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201.

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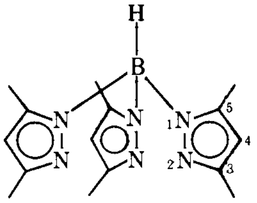
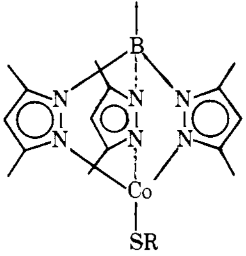
Abstract: Complexes of the stoichiometry $Co^{II}N_3(SR)$ were prepared by the reaction of CoCl(SR) (SR = *O*-ethylcysteinate) with potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $K(HB(3,5\text{-}Me_2pz)_3)$, or by the reaction of $CoBr(HB(3,5\text{-}Me_2pz)_3)$ with NaSR (SR = *p*-nitrobenzenethiolate or pentafluorophenylthiolate). These complexes are synthetic approximations to a proposed active site in the cobalt(II)-substituted blue copper proteins. The complexes were characterized by electronic spectral, NMR, and XPS techniques. The complex pentafluorophenylthiolato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)cobalt(II) was also characterized by single-crystal X-ray diffraction methods. The complex crystallizes in the monoclinic space group $C_{2h}{}^5\text{-}P2_1/n$ with four molecules in a unit cell of dimensions a = 15.46 (1) Å, b = 7.841 (8) Å, c = 22.20 (2) Å, and β = 91.89 (2)° (−162 °C). Least-squares refinement of the 106 variables has led to a value of the conventional R index (on F) of 0.106 for 827 independent reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$. The geometry about the cobalt(II) ion, which is coordinated to three nitrogen atoms and one sulfur atom, is distorted tetrahedral, with N-Co-N angles ranging from 89.3 (7) to 94.1 (7)° and with N-Co-S angles ranging from 107.7 (6) to 138.3 (6)°. The Co-N distances range from 1.97 (2) to 2.01 (2) Å, and the Co-S distance is 2.26 (1) Å.

In the preceding article[1] we discussed the synthesis and properties of certain active site approximations to the type 1 blue copper proteins.[2] We presented our chemical, structural, and spectral results on a series of $Cu^IN_3(SR)$ and $Cu^{II}N_3(SR)$ complexes in which the three-nitrogen donor ligand was the anionic hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $HB(3,5\text{-}Me_2pz)_3{}^-$ (A). Valuable information on the nature of the type 1 binding site(s) has been obtained from electronic spectral,[3] proton nuclear magnetic resonance,[4] CD/MCD,[5a] and magnetic susceptibility[5b] studies of type 1 proteins in which Co(II) has been substituted for Cu(II). Since there are no low molecular weight compounds that approximate the proposed active site configuration of the Co(II)-substituted proteins, and since there is little information connecting the properties of Co(II) and Cu(II) ions in such environments, we have expanded our studies of the type 1 binding site approximations[1,6] by synthesizing and characterizing compounds of the formulation $Co^{II}(HB(3,5\text{-}Me_2pz)_3)(SR)$ (B). We report here the synthesis and spectral properties of three such complexes and the crystal structure of one of them.



A



B

Experimental Section

All chemicals were reagent grade and used as received, unless otherwise noted. The compound potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $KHB(3,5\text{-}Me_2pz)_3$, was prepared according to the literature procedure.[7] The solvents tetrahydrofuran (THF), hexane, and diethyl ether were distilled from sodium-potassium alloy benzophenone ketyl under prepurified nitrogen. All other solvents were stored over molecular sieves (4A) and deaerated prior to use with prepurified nitrogen. Standard Schlenk ware, glovebag, and glovebox techniques were used in the synthesis and manipulation of the complexes described below.

Preparation of *p*-Nitrobenzenethiolato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)cobalt(II), $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6H_4NO_2)$ (2). Dark red $CoBr_2\cdot 6H_2O$ (2.20 g, 0.570 mmol) was dehydrated at approximately 60 °C under high vacuum to yield a green solid. The addition of 25 mL of THF gave an intensely blue solution. To this vigorously stirred blue solution was added over 0.5 h $KHB(3,5\text{-}Me_2pz)_3$ (0.224 g, 0.67 mmol) as a powder. The resulting solution was a slightly lighter shade of blue than the starting solution. To this solution was added potassium *p*-nitrobenzenethiolate (0.130 g, 0.67 mmol) as a red powder, which was obtained by the removal of the solvent from an ethanol solution of potassium *p*-nitrobenzenethiolate prepared as previously described.[1,6a,8] The resulting solution was dark green. Filtration of the solution, reduction of the volume to approximately 10 mL, and slow addition of hexane yielded a green precipitate, which was dried under vacuum. Anal. Calcd for $C_{21}H_{26}BCoN_7O_2S$: C, 49.43; H, 5.15; N, 19.21. Found: C, 48.4; H, 5.12; N, 18.0. Cryoscopic solution molecular weight in benzene is 565 amu (calcd, 510.3 amu). Infrared data in cm^{-1} (Nujol mull): 2510 w, 1570 m, 1545 m, 1330 s, 1260 s, 1205 m, 1190 m, 1090 s, 1070 s, 1030 s, 875 m, 805 s, 745 w, 735 w.

Preparation of Pentafluorophenylthiolato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)cobalt(II), $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6F_5)$ (3). This compound was prepared in a manner analogous to $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6H_4NO_2)$ (**2**). The compound sodium pentafluorophenylthiolate was prepared by the reaction of pentafluorophenylthiol (0.20 g, 0.10 mmol) with sodium methoxide in methanol. The final product is dark blue. Anal. Calcd for $C_{21}H_{22}BCoF_5N_6S$: C, 45.43; H, 3.99; N, 15.14. Found: C, 45.6; H, 4.48; N, 15.1. Cryoscopic solution molecular weight in benzene is 605 amu (calcd, 574 amu). Infrared data in cm^{-1} (Nujol mull): 2510 w, 1410 w, 1260 s, 1170 s, 1090 s, 1010 s, 970 m, 860 m, 800 s, 690 w.

Preparation of *O*-Ethylcysteinato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)cobalt(II), $Co(HB(3,5\text{-}Me_2pz)_3)(SCH_2CH(NH_2)(COOC_2H_5))$ (1). To 10 mL of dry methanol were added sodium metal (0.542 g, 0.022 mol) and then L-cysteine ethyl ester hydrochloride

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Table I. Crystal Data for Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$)

molecular formula	$C_{21}H_{22}BCoF_5N_6S$
mol wt	555.25 amu
a	15.46 (1) Å
b	7.841 (8) Å
c	22.20 (2) Å
β	91.89 (2)°
V	2690 Å^3
Z	4
temp	−162 °C
space group	$C_{2h}^5 - P2_1/n$
crystal dimensions	0.047 × 0.11 × 0.32 mm, V = 0.0017 mm^3
radiation	Mo Kα (λ(Kα_1) = 0.709 30 Å)
takeoff angle	2.5°
scan speed	2° min in 2θ
scan range	0.9° below Kα_1 to 0.9° above Kα_2
receiving aperture	5.6 mm high × 5.8 mm wide, 32 cm from crystal
background counting time	20 s
2θ limits	3.0–42.0°
absorption coefficient	7.6 cm^{-1}
transmission coefficients	0.916–0.966
unique data used ($F_o^2 > 3\sigma F_o^2$)	827

Table II. Positional and Thermal Parameters for the Nongroup Atoms of Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$)

ATOM	X[a]	Y	Z	B11[b] OR B, Å^2
CO	0.23824(29)	0.50271(84)	0.40707(22)	12.2(22)
S	0.11659(55)	0.0364(14)	0.08931(40)	16.3(48)
B	0.0491(22)	0.4565(52)	0.3589(15)	0.10(84)
F1	−0.0558(12)	0.1953(27)	0.05926(86)	2.76(51)
F2	−0.0967(14)	0.3788(31)	−0.03898(90)	3.77(56)
F3	0.0182(13)	0.4436(29)	−0.12271(95)	4.52(60)
F4	0.1847(12)	0.3276(29)	−0.11038(89)	3.46(55)
F5	0.2309(12)	0.1458(26)	−0.01356(78)	1.97(46)
C(41)	0.0904(21)	0.1655(47)	0.0250(15)	1.25(83)
C(42)	0.0027(21)	0.2239(46)	0.0194(14)	0.48(81)
C(43)	−0.0166(28)	0.3157(58)	−0.0295(21)	3.7(11)
C(44)	0.0394(28)	0.3562(61)	−0.0719(20)	4.1(11)
C(45)	0.1278(23)	0.3041(51)	−0.0673(17)	2.12(90)
C(46)	0.1453(25)	0.2044(55)	−0.0208(18)	2.72(97)

B22	B33	B12	B13	B23
27.(10)	10.0(12)	5.2(66)	−0.8(12)	1.8(51)
52.(27)	10.8(26)	3.(11)	0.8(28)	6.3(80)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(B11h^2 + B22k^2 + B33l^2 + 2B12hk + 2B13hl + 2B23kl)]$. The quantities given in the table are the thermal coefficients ×10^4. The bottom two rows are the parameters for Co and S, respectively.

monohydrate (2.02 g, 0.0109 mol) to generate the sodium mercaptide. The purple compound CoCl$_2$·6H$_2$O (3.99 g, 0.0109 mol) was dehydrated at approximately 100 °C under high vacuum for 3 h and was then dissolved in 10 mL of ethanol to yield a dark blue solution. The sodium mercaptide solution was then added dropwise in approximately 0.5 h to this vigorously stirred solution. A green precipitate formed. After the reaction mixture was stirred overnight, the blue supernatant solution was removed by syringe and the green precipitate dried under high vacuum. This green reagent "CoCl(SCH$_2$CH(NH$_2$)(COOC$_2$H$_5$)" was used in subsequent reactions. To KHB(3,5-Me$_2$pz)$_2$ (0.240 g, 0.71 mmol) in 20 mL of stirred THF was added this green cobalt-thiolate compound (0.540 g, 0.71 mmol). The resulting green mixture was stirred for several hours and then suction filtered. Hexane was slowly added by syringe to the reaction vessel. A green precipitate formed. The supernatant was removed by syringe, and the green solid was washed with hexane and dried under high vacuum. Further purification of this compound was frustrated by slow thermal decomposition in solution (see Discussion section), and satisfactory elemental analyses could not be obtained. A typical result is given. Anal. Calcd for C$_{20}$H$_{32}$BCoN$_7$O$_2$S: C, 47.6; H, 6.40; N, 19.4. Found: C, 54.0; H, 7.27; N, 24.4. The compound is not sufficiently soluble in benzene for a solution molecular weight determination. Infrared data in cm^{-1} (Nujol mull): 3450 w, broad, 2510 w, 1740 m, 1605 m, 1580 m, 1550 m, 1260 s, 1280 s, 1070 s, 1050 s, 810 m.

Spectral Studies. Infrared spectra were obtained on Nujol mulls with a Perkin-Elmer 727B infrared spectrophotometer. Samples were prepared in a glovebag under prepurified nitrogen. UV-visible and near-infrared spectra were obtained with a Cary 17D spectrophotometer in a 1-cm cell fitted with Schlenk connections. NMR spectra were obtained with a Perkin-Elmer R20B spectrometer. Each sample was loaded under nitrogen into an NMR tube fitted with a rubber septum. The solvents deuteriobenzene for **2** and **3** or deuterioacetone for **1** were degassed prior to use. A sweep range of 18 kHz was used. XPS spectra were obtained on an AEI ES200A spectrometer with Al Kα X-radiation. Samples were pressed onto indium plates under prepurified nitrogen in a glovebag. Internal carbon was used as a standard. The value of the carbon 1s peak was taken to be 285.4 eV.[9] All XPS spectra were smoothed through the use of an AEI 9-point smoothing routine.

X-ray Study of Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$) (3). Dark blue crystals were grown from a THF–hexane solution at −10 °C. A representative crystal was mounted in a glass capillary under prepurified nitrogen in a glovebox. An examination of the crystal by Weissenberg and precession methods established that it crystallizes with four formula units in a space group C_{2h}^5-$P2_1/n$ of the monoclinic system. A data set was collected on a FACS-I diffractometer at room temperature using Ni-filtered Cu Kα radiation. Although there was nothing obviously wrong with the data set nor with the solution obtained from these data, refinement would not yield a conventional R index below 0.24. The resultant structure displayed distorted tetrahedral geometry about the Co ion and very high thermal motion of the C$_6$F$_5$ group. A data set on another crystal was collected at −162 °C[10] by attaching the crystal to the end of a glass fiber with Apiezon N grease in air and then placing it in a cold nitrogen stream. The lattice constants were determined by a least-squares analysis[11] of the angle settings of 16 hand-centered reflections obtained on a Picker FACS-I diffractometer in the range 11.7° < 2θ < 24.3° using monochromatized Mo Kα_1 radiation (λ = 0.709 30 Å). The refined cell constants, other relevant crystal data, and details of data collection are given in Table I. Intensity data were collected by the standard θ–2θ technique. During the data collection, six standard reflections were collected after every 100 reflections. There was significant decline in intensity (approximately 40%) in five of these standards, and a correction for sample decomposition was necessary.

The intensity data were processed as previously described,[11] with the parameter p chosen as 0.04. Of the 3120 unique data collected 827 independent reflections were found with $F_o^2 > 3\sigma(F_o^2)$ and were used in the subsequent solution and refinement of the structure. The relatively few F_o^2 values above background result from the availability of only very small crystals.

The positions of the Co and S atoms were taken from the solution of the room temperature data set. Full-matrix least-squares calculation and Fourier or difference Fourier methods resulted in the location of all other nonhydrogen atoms. The three 3,5-dimethylpyrazole rings and the pentafluorophenyl (C$_6$F$_5$) moiety were refined as rigid bodies.[1,12] Bond angles and bond distances for the 3,5-dimethylpyrazole model were taken from a previously determined structure.[13] An idealized phenyl group and C–F bonds (C–F = 1.34 Å) were used in the model for the C$_6$F$_5$ moiety. Scattering factors and anomalous dispersion terms for the Co and S atoms were taken from the usual sources.[14] With isotropic thermal parameters for all nonhydrogen atoms, the model refined to values of R and R_w of 0.12 and 0.13. In the final model the Co and S atoms were refined anisotropically, the 3,5-Me$_2$pz rings were treated as rigid groups, but the atoms of the C$_6$F$_5$ ring were refined individually. This final full-matrix least-squares cycle refined to values of R and R_w of 0.106 and 0.117 for the 827 independent reflections and 106 variables and to an error in an observation of unit weight of 2.09 electrons. The final difference map shows a significant amount of electron density in the region of the molecule (0.4–0.8 e/Å^3), as expected with the relatively large R index.

The final positional and thermal parameters for the nongroup atoms, along with their estimated standard deviations, are given in Table II. Table III lists the derived parameters for the atoms belonging

Table III. Derived Parameters for the Rigid Group Atoms of $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6F_5)$

ATOM	X	Y	Z	B, Å^2	ATOM	X	Y	Z	B, Å^2
N(11)	0.15021(10)	0.3721(25)	0.44933(74)	1.25(63)	C(23)	0.10229(90)	0.2983(21)	0.26305(63)	1.31(81)
N(12)	0.07041(12)	0.3778(25)	0.42038(66)	2.79(76)	C(24)	0.33787(92)	0.2648(38)	0.2774(11)	2.81(98)
C(11)	0.13988(89)	0.2770(22)	0.50418(63)	2.14(90)	C(25)	0.0161(10)	0.2722(34)	0.23226(94)	1.41(80)
C(12)	0.05495(97)	0.2254(25)	0.50855(65)	1.32(82)	N(31)	0.3413(10)	0.1950(21)	0.11106(75)	1.71(69)
C(13)	0.01225(90)	0.2860(22)	0.45765(63)	2.55(93)	N(32)	0.4207(11)	0.1434(19)	0.13370(83)	1.67(72)
C(14)	0.2148(11)	0.2470(36)	0.54642(90)	2.67(94)	C(31)	0.33971(91)	0.3785(21)	0.11479(62)	1.27(83)
C(15)	−0.08201(96)	0.2574(36)	0.44520(99)	2.57(93)	C(32)	0.4172(10)	0.4378(19)	0.13936(81)	0.84(82)
N(21)	0.20631(11)	0.3758(25)	0.33090(64)	1.33(66)	C(33)	0.46681(86)	0.2959(22)	0.15100(60)	2.71(10)
N(22)	0.1184(10)	0.3803(25)	0.32025(69)	1.67(68)	C(34)	0.2620(12)	0.4757(30)	0.0937(11)	2.37(78)
C(21)	0.24296(89)	0.2910(23)	0.28009(68)	1.56(85)	C(35)	0.55633(97)	0.3050(34)	0.17804(99)	2.65(97)
C(22)	0.1782(10)	0.2446(26)	0.23905(66)	3.21(10)					

RIGID GROUP PARAMETERS

GROUP	X_C^a	Y_C	Z_C	DELTA^b	EPSILON	ETA
RING1	0.08262(87)	0.3002(17)	0.47170(54)	−0.630(17)	2.288(12)	−2.411(15)
RING2	0.17027(88)	0.3113(17)	0.26231(54)	0.229(17)	−2.079(15)	−2.851(16)
RING3	0.39909(84)	0.3035(19)	0.13086(47)	2.8821(92)	2.979(13)	2.7936(76)

[a] X_C, Y_C, and Z_C are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles δ, ϵ, and η (rad) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **1965** *18*, 511–519.

to the three rigid groups. The root mean square amplitudes of vibration for the Co atom are 0.08 (2), 0.13 (2), and 0.16 (1) Å and for the S atoms are 0.11 (4), 0.14 (2), and 0.17 (2) Å. Table IV is a listing of $10|F_o|$ and $10|F_c|$.[15]

Results and Discussion

The ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate has both the negative charge and steric bulk that are desirable in the synthesis of stable monomeric $Co^{II}N_3(SR)$ complexes. Using a procedure similar to that described for the analogous Cu complexes[1,6a] we were able to prepare the $Co^{II}N_3(SR)$ complex with SR = *O*-ethylcysteinate:

$$CoCl_2 + NaSR \xrightarrow{\text{ethanol}} CoCl(SR) + NaCl \qquad (1a)$$

$$CoCl(SR) + KHB(3,5\text{-}Me_2pz)_3 \xrightarrow{\text{THF}}$$

$$Co(HB(3,5\text{-}Me_2pz)_3)(SR) + KCl \qquad (1b)$$

$$\mathbf{1},\ SR = SCH_2CH(NH_2)(COOC_2H_5)$$

Although most pseudotetrahedral cobalt(II) complexes are blue, complex **1** is green owing to the overlap of a charge transfer band with the visible region of the spectrum (vide infra).

The procedure outlined in eq 1 was attempted unsuccessfully with a variety of aryl mercaptans. The principal products were insoluble polysulfides and the complex $Co^{II}(HB(3,5\text{-}Me_2pz)_3)_2$, previously reported by Trofimenko.[7] Thus, another procedure was used to prepare $Co^{II}N_3(SR)$ complexes with SR = aryl thiolates:

$$CoBr_2 + KHB(3,5\text{-}Me_2pz)_3 \xrightarrow{\text{THF}}$$

$$CoBr(HB(3,5\text{-}Me_2pz)_3) + KBr \qquad (2a)$$

$$CoBr(HB(3,5\text{-}Me_2pz)_3) + NaSR \rightarrow$$

$$Co(HB(3,5\text{-}Me_2pz)_3)(SR) + NaBr \qquad (2b)$$

$$\mathbf{2},\ SR = SC_6H_4NO_2 \quad \mathbf{3},\ SR = SC_6F_5$$

This procedure may be used also for SR = *O*-ethylcysteinate. The complex **2** is green, whereas complex **3** is blue. Solution molecular weights indicate that these complexes are monomeric in benzene.

Solutions of the complexes **1–3** are very sensitive to air and moisture, although crystals of **3** can be handled briefly in air with no apparent decomposition. As with many other transition metal-thiolate complexes,[16,17] complexes **1–3** are not indefinitely stable in solution. Insoluble sulfides are formed, according to the equation

$$2nCo(HB(3,5\text{-}Me_2pz)_3)(SR) \rightleftharpoons [Co(SR)_2]_n + nCo(HB(3,5\text{-}Me_2pz)_3)_2 \qquad (3)$$

The order of decreasing stability in solution for the three thiolate complexes is $\mathbf{3} \sim \mathbf{2} \gg \mathbf{1}$. Thus, the NMR spectra of **1–3** in deuteriobenzene or deuterioacetone always revealed traces of $Co(HB(3,5\text{-}Me_2pz)_3)_2$ (vide infra). While compounds **2** and **3** are sufficiently stable to be isolated and characterized by standard techniques, it proved impossible to obtain compound **1** in an analytically pure state.

Description of the Molecular Structure of $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6F_5)$ (3). The overall crystal structure of the $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6F_5)$ complex is apparent in the stereoscopic drawing of the unit cell (Figure 1). The structure consists of well-separated neutral, monomeric $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6F_5)$ molecules (Figure 2). The ligand $HB(3,5\text{-}Me_2pz)_3^-$ coordinates to the Co ion through the N atoms in the 2 position of each ring. The pentafluorophenylthiolate moiety is coordinated to the Co ion through the S atom. In Figure 2 we see that the methyl groups in the 3 position do provide some steric protection for the Co ion. Presumably in this way dimerization is retarded.

The thermal parameters and estimated standard deviations on the positional and thermal parameters for the three 3,5-dimethylpyrazole rings, the Co ion, and the S atom are reasonable for a low-temperature data set. However, the thermal parameters for the C_6F_5 moiety are large. An inspection of these values (Table II) shows that the thermal parameters increase around the ring (for both C and F atoms) from C(41) to C(44), with the exception of that for C(42). The pattern is that generally expected for disorder or an inadequate thermal description of a wagging motion. We suggest that the same problem prevented successful refinement of the data collected at room temperature. The relatively small number of observations discouraged us from trying a more elaborate refinement of the low-temperature data.

Selected bond distances and angles are presented in Table V.[18] The distances, angles, and numbering scheme for the 3,5-dimethylpyrazole rings have been given previously.[1] The Co–N distances are typical of both Co–N distances in poly(pyrazolyl)borate complexes[19] and Co–N distances in general.[20] The Co–S distance is similar to those reported in the lit-

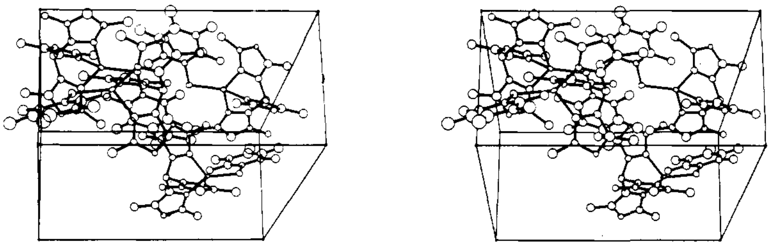

Figure 1. Stereoview of the unit cell of Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$) (3). The *y* axis is almost vertical, and the *x* axis is horizontal and to the right. Vibrational ellipsoids are drawn at the 30% probability level. Thermal parameters of 1.8 Å have been assumed for the B and C(42) atoms here and in Figure 2.

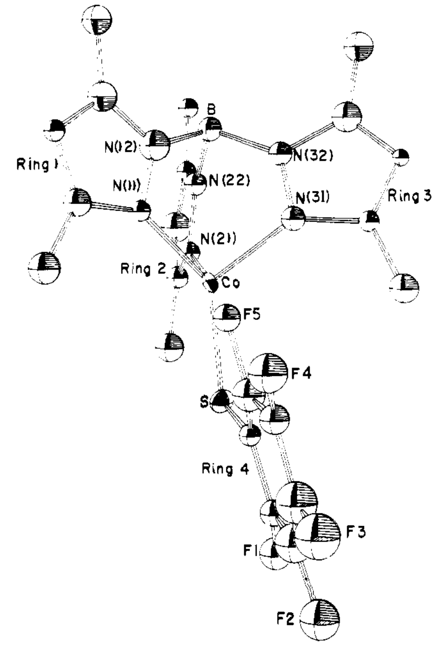

Figure 2. The molecular structure of Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$) (3).

erature (2.25 (1),[21a] 2.272 (2) and 2.316 (4),[21b] 2.342 (4) Å[21c]).

The Co coordination sphere is highly distorted but is clearly pseudotetrahedral rather than planar. The distortion from idealized C_{3v} geometry can be seen more clearly in Figure 3, which shows the Co inner-coordination sphere. The N-Co-N and N-Co-S bond angles range from 89.3 (7) to 138.3 (6)°. Similar distortion of the metal coordination sphere in four-coordinate tris(pyrazolyl)borate complexes has been observed in the Cu(I) complexes Cu(HBpz$_3$)(CO)[22] and K[Cu(HB(3,5-Me$_2$pz)$_3$)(SC$_6$H$_4$NO$_2$)]·2C$_3$H$_6$O.[1] The geometry of the Cu inner-coordination sphere may be described roughly as trigonally distorted tetrahedral, owing in part to the bonding restrictions of the tris(pyrazolyl)borate ligand. The inner-coordination sphere of the cobalt ion is similar to that in the Cu(I) structures because of the tris(pyrazolyl)borate ligand,[1,22] but is somewhat more irregular because of the close approach of an ortho F atom (F(5)) of the SC$_6$F$_5$ group to the Co ion. The Co-F distance of 2.64 (2) Å is not a bonding distance;[23] rather, the F atom is probably forced into that position because of the nature of the bonding of the SC$_6$F$_5$$^-$ group. The S atom is conjugated with the strongly electron-withdrawing C$_6$F$_5$ group (vide infra); in valence bond terms[24] there are significant contributions from resonance structures with an sp^2-hybridized S atom. Therefore, the Co atom must be close to the plane defined by the SC$_6$F$_5$ group; the distance of the Co atom from this plane is 0.40 (5) Å. That the Co and S atoms and C$_6$F$_5$ moiety lie nearly in the same plane causes the ortho F atom (F(5)) to occupy a position close to the Co ion. This close approach may account, at least in part, for the large deviation of the N-Co-S and N-Co-N bond angles from those of C_{3v} symmetry expected for a Co^{II}N$_3$(SR) complex.

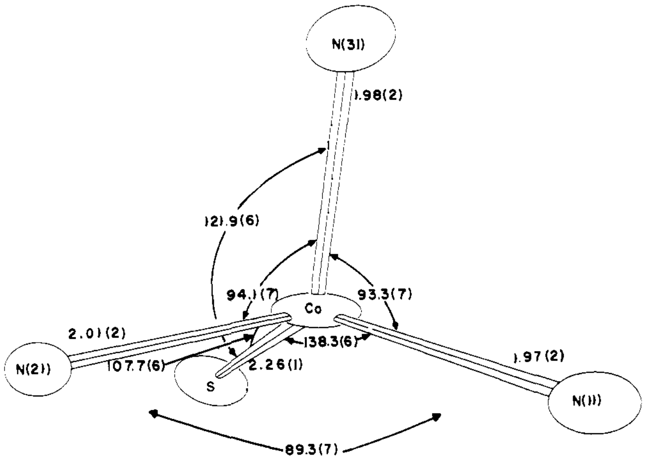

Figure 3. View of coordination geometry about the cobalt ion in Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$).

Table V. Bond Distances (Å) and Bond Angles (deg) for Co(HB(3,5-Me$_2$pz)$_3$)(SC$_6$F$_5$)

Co-N(11)	1.97 (2)	N(11)-Co-N(21)	89.3 (7)
Co-N(21)	2.01 (2)	N(11)-Co-N(31)	93.3 (7)
Co-N(31)	1.98 (2)	N(21)-Co-N(31)	94.1 (7)
Co-S	2.26 (1)	N(11)-Co-S	138.3 (6)
B-N(12)	1.52 (4)	N(12)-B-N(22)	102 (2)
B-N(22)	1.52 (4)	N(12)-B-N(32)	103 (2)
B-N(32)	1.54 (4)	N(22)-B-N(32)	102 (2)
S-C(41)	1.78 (3)	C(41)-S-Co	107 (1)
C(41)-C(42)	1.43 (4)	C(42)-C(41)-S	116 (3)
C(42)-C(43)	1.33 (4)	C(46)-C(41)-S	126 (3)
C(43)-C(44)	1.34 (5)	C(42)-C(41)-C(46)	118 (3)
C(44)-C(45)	1.43 (4)	C(41)-C(42)-C(43)	116 (3)
C(45)-C(46)	1.32 (4)	C(41)-C(42)-F1	124 (3)
C(46)-C(41)	1.38 (4)	C(43)-C(42)-F1	120 (3)
C(42)-F1	1.30 (3)	C(42)-C(43)-C(44)	125 (4)
C(43)-F2	1.34 (4)	C(42)-C(42)-F2	120 (4)
C(44)-F3	1.35 (4)	C(44)-C(43)-F2	115 (5)
C(45)-F4	1.33 (3)	C(43)-C(44)-C(45)	121 (5)
C(46)-F5	1.40 (4)	C(43)-C(44)-F3	124 (4)
		C(45)-C(44)-F3	114 (4)
		C(44)-C(45)-C(46)	113 (4)
		C(44)-C(45)-F4	124 (4)
		C(46)-C(45)-F4	121 (3)
		C(45)-C(46)-C(41)	126 (4)
		C(45)-C(46)-F5	117 (4)
		C(41)-C(46)-F5	116 (4)

Based on spectroscopic and chemical evidence to be described below, we propose that the other Co^{II}N$_3$(SR) complexes **1** and **2** have structures similar to that shown in Figure 2.

Table VI. Visible Spectral Data for $Co(HB(3,5\text{-}Me_2pz)_3)(SR)$ Complexes

SR = $SCH_2CH(NH_2)(COOC_2H_5)$(**1**)[a]	650[b]	(~735[c])
	630	(~800)
	595	(~600)
SR = $SC_6H_4NO_2$ (**2**)	675	(550)
	625	(670)
	586	(246)
SR = SC_6F_5 (**3**)	660	(95)
	605	(350)
	570	(270)

[a] Values for extinction coefficients are only approximate because of thermal decomposition.[29] [b] In nm. [c] In M^{-1} cm^{-1}

Electronic Spectral Studies. The electronic spectral characteristics of pseudotetrahedral cobalt(II) complexes have been thoroughly studied,[5b,25-27] and from these investigations several general statements can be made about the spectral properties of such compounds. Firstly, three d-d electronic transitions are observed for pseudotetrahedral cobalt(II) complexes, the energies of which are relatively invariant.[25,27] The longest wavelength band $\nu_1(^4A_2 \rightarrow {}^4T_2)$ is not usually observed, owing to its low energy (3000-5000 cm^{-1}), which places it in the region of vibrational transitions. The second transition $\nu_2(^4A_2 \rightarrow {}^4T_1(F))$ occurs in the near-infrared region and is often broad. Because of ligand and solvent absorption in this region (overtones of molecular vibrations), the band is frequently not observed in solution spectra. The third transition $\nu_3(^4A_2 \rightarrow {}^4T_1(P))$ occurs in the visible region and often shows considerable structure. The amount of splitting of this band can be qualitatively correlated with the degree of distortion from tetrahedral geometry since it reflects removal of the degeneracy of the $^4T_1(P)$ state.[28] Secondly, the absorption bands for pseudotetrahedral complexes in the visible region are more intense and generally at lower energy than those for octahedral cobalt(II) complexes.[25-27] Thirdly, although the absorption bands for pseudotetrahedral and pentacoordinate cobalt(II) complexes occur at similar energies, the molar absorptivity coefficients for pseudotetrahedral complexes (ϵ_m >250 M^{-1} cm^{-1}) are generally larger than those for five-coordinate complexes (ϵ_m <225 M^{-1} cm^{-1}).[26,27] Lastly, pseudotetrahedral complexes are generally blue, but overlapping charge transfer bands and strong field ligands, which shift the d-d transitions to higher energies, will give rise to colors other than blue; thus, color is not a good indication of geometry.[26c] In summary, the positions, intensities, and degree of splitting of absorption bands in the visible region are structurally diagnostic for cobalt(II) complexes.

The visible spectrum of **2** is shown in Figure 4; the band positions and intensities for **1–3** are listed in Table VI. All spectra were obtained from THF solutions.[29] The only observed d-d transition for each complex was ν_3; ν_1 and ν_2 could not be observed. Therefore, no determination of the strength of the ligand field is possible.[26] The molar absorptivity coefficients for **1–3** are large and unequivocally characteristic of pseudotetrahedral cobalt(II) complexes. The spectrum of each complex in the 500-700-nm region consists of a broad band with two poorly resolved shoulders. We conclude from this splitting of the ν_3 band that the symmetry is lower than tetrahedral in each case. This conclusion is consistent with the results from the crystal structure of **3.** The close similarity of the spectra of the three compounds indicates that **1** and **2** have structures similar to **3.**

The absorption spectrum in the 600-nm region of cobalt(II)-substituted stellacyanin is also presented in Figure 4;[3b] spectra for the other Co(II)-substituted blue copper proteins are virtually identical.[3] Two important conclusions about the nature of the metal binding site can be made through a comparison of the spectra of the substituted proteins with those of **1–3.** Firstly, the intensity and position of the ν_3 absorption band for the substituted protein are characteristic of pseudotetrahedral cobalt(II) complexes in general and are similar to the values observed for **1–3.** This similarity supports the conclusion made by Gray and co-workers[3] that the cobalt(II) ion occupies the same site in the protein as does the copper ion. Without crystallographic data for the cobalt-substituted protein, there is no unequivocal evidence that the two metals occupy the same site. Secondly, the large degree of splitting of the absorption band in the spectrum of the cobalt(II)-substituted protein indicates that the geometry about the cobalt ion is considerably distorted from tetrahedral geometry.[25i] The distortion appears to be greater than that observed for the complexes **1–3** as qualitatively judged by the degree of splitting of the band. A similar conclusion about the metal binding sites in the native systems was reached in our studies of the $Cu^{II}N_3(SR)$ active site approximations,[1,6] based on spectral and EPR data. The crystal structures of the oxidized forms of *Populus nigra* var. *italica* plastocyanin[30a] and *Pseudomonas aeruginosa* azurin[30b] at the present level of refinement show the copper coordination sphere to be distorted tetrahedral.

Further structural information can be obtained for both the compounds **1–3** and the cobalt(II)-substituted proteins through an analysis of the ligand-to-metal charge transfer spectra. Table VII lists the positions of the bands that we have assigned

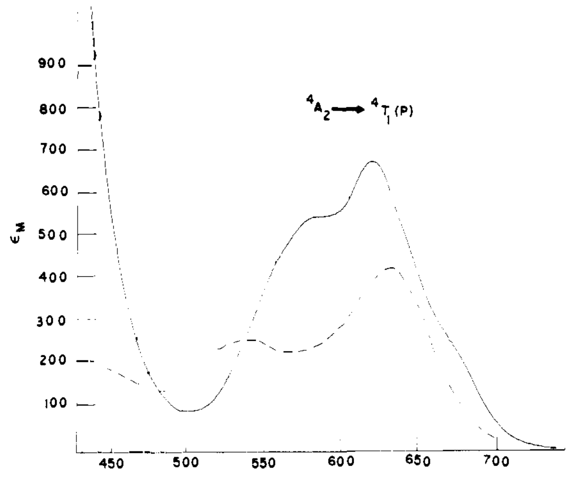

Figure 4. Optical spectra of $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6H_4NO_2)$ (**2**) (—) and cobalt(II)-substituted *Rhus vernicifera* stellacyanin (- - - - -) from ref. 3b.

Table VII. Ligand-to-Metal Charge Transfer Data for $Co(HB(3,5\text{-}Me_2pz)_3)(SR)$ Complexes and Several Cobalt(II)-Substituted Proteins

SR	λ, nm (obsd)	χ_{SR}	λ, nm (calcd)
$SCH_2CH(NH_2)(COOC_2H_5)$	340[a]	2.79	336
$SC_6H_4NO_2$	318	2.87	311
SC_6F_5		2.95	289
Co(II)-Substituted Proteins			
Rhus vernicifera stellacyanin	310[b]	2.85	316
Pseudomonas aeruginosa azurin	330[b]	2.83	322
Phaseolus vulgaris plastocyanin	333[b]	2.86	314

[a] Earlier we reported this band at 388 nm; however, the 340-nm assignment is based on spectra obtained from purer samples. [b] Reference 3b.

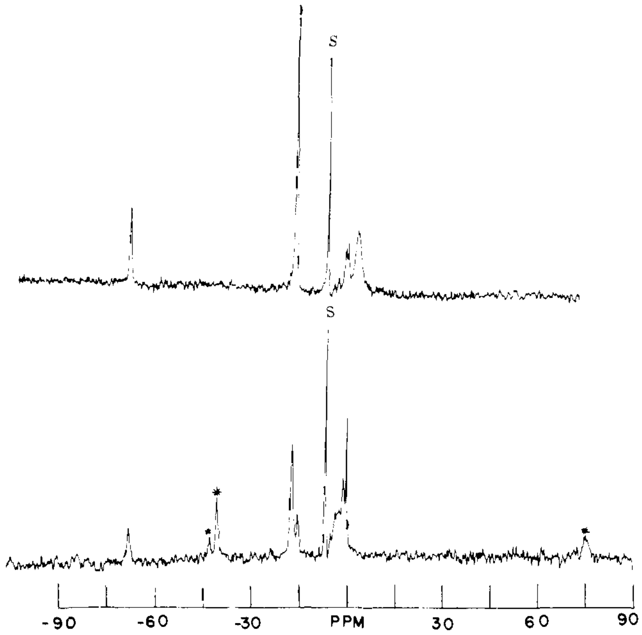

Figure 5. NMR spectra in deuteriobenzene of Co(HB(3,5-$Me_2pz)_3$)-($SC_6H_4NO_2$) (**2**) (bottom) and Co(HB(3,5-$Me_2pz)_3$)(SC_6F_5) (**3**) (top). The resonances for Co(HB(3,5-$Me_2pz)_3)_2$ are marked with an asterisk. The peak for the solvent C_6D_5H is marked with an S. There is some residual diamagnetic material in the 0–7.2-ppm region.

to sulfur-to-cobalt charge transfer, using the following line of reasoning. We have shown previously that the intense blue color of the $Cu^{II}N_3(SR)$ active site approximations and of the blue proteins results from sulfur-to-copper charge transfer.[1,6a] Because there is an approximately linear relationship between the position of a ligand-to-metal charge transfer band and the reduction potential of the metal ion,[31] substitution of a cobalt(II) ion for a copper(II) ion in a given complex should shift the band to higher energy; that is, more energy is required to reduce a Co(II) complex to a Co(I) complex than to reduce the corresponding Cu(II) complex to the Cu(I) complex. Based on estimates of the Co(II)/Co(I) redox couple, the shift in energy with substitution of cobalt(II) ions is predicted to be 13 000–16 000 cm^{-1};[3b] thus, the ligand-to-metal charge transfer bands for **1–3** should and do occur in the near-UV region. It is also characteristic of such bands that their positions shift to lower energy as the reducing power of the ligand system increases. For the $Co^{II}N_3(SR)$ complexes, the band moves to lower energy along the series SC_6F_5 (**3**) > $SC_6H_4NO_2$ (**2**) > $SCH_2CH(NH_2)(COOC_2H_5)$ (**1**), which is also the direction of increasing reducing power of the mercaptide group. Similar results have been obtained from the analysis of the ligand-to-metal charge transfer spectra of the $Cu^{II}N_3(SR)$ complexes.[1,6]

A more accurate prediction of the energies of such bands for $Co^{II}N_3(SR)$ complexes can be made through the use of the optical electronegativity approach of Jørgensen:[32]

$$\nu_{CT}(\mathrm{cm}^{-1}) = 30\,000\,(\chi_{\mathrm{ligand}} - \chi_{\mathrm{metal}}) \qquad (4)$$

The position of a charge-transfer band, ν_{CT}, can be calculated by the substitution of the appropriate empirical optical electronegativity value for the metal atom (χ_{metal}) and of the ligand (χ_{ligand}). We have shown previously[1,6] that the χ_{ligand} values calculated for SR = *O*-ethylcysteinate, *p*-$SC_6H_4NO_2$, and SC_6F_5 (Table VII) are comparable with those of other sulfur-containing ligands, such as diethyl thiophosphate (2.8) and diethyl sulfide (2.9).[32] Substitution of the tabulated value of χ_{Co} for a distorted tetrahedral geometry (1.8)[32] and of χ_{SR}[1,6] into eq 4 yields the calculated positions shown in Table VII. The agreement between calculated and observed band positions is good and is strong evidence for the assignment of ligand-to-metal charge transfer to the bands listed in Table VII for the $Co^{II}N_3(SR)$ complexes. This close agreement between experimental and calculated band positions indicates also that the $Co^{II}N_3(SR)$ complexes and the analogous $Cu^{II}N_3(SR)$ complexes have similar structures, since the position of the charge-transfer band for a $M^{II}N_3(SR)$ complex with a given SR^- ligand is dependent solely on the χ_{metal} value. The positions of these charge-transfer bands are affected by geometry;[32,33] thus, major structural changes with substitution of a cobalt(II) ion for a copper(II) ion are expected to result in a larger difference between the calculated and observed band positions than we find. Thus, the results from the structural and spectral studies of the $Cu^{I}N_3(SR)$, $Cu^{II}N_3(SR)$, and $Co^{II}N_3(SR)$ series of complexes that we have synthesized support the contention that all of the complexes have similar, pseudotetrahedral environments around the central metal.

The comparison of the ligand-to-metal charge transfer spectra of **1–3** with the corresponding spectra of the cobalt(II)-substituted proteins reveals two important features. Firstly, the 13 000–16 000 cm^{-1} shift in energy of the band with the substitution of cobalt(II) for copper(II) ion in the protein systems[3] is comparable with the 11 000–15 000 cm^{-1} shift in energy observed for the substitution of cobalt(II) ion for copper(II) ion in the $M^{II}N_3(SR)$ synthetic analogue complexes. Secondly, the optical electronegativity approach of Jørgensen (eq 4) may be used to calculate the position of the charge transfer band for the cobalt(II)-substituted proteins. Substitution of the tabulated value of χ_{Cu} in a distorted tetrahedral geometry (2.3)[32] and ν_{CT} (cm^{-1}) for the oxidized form of a blue copper protein into eq 4 yields a χ_{ligand} value for that type 1 site; this treatment is analogous to that used previously for $Cu^{II}N_3(SR)$ and $Co^{II}N_3(SR)$ complexes (vide supra). With these χ_{ligand} values and the tabulated value of χ_{Co} in a distorted tetrahedral geometry (1.8),[32] we can calculate the expected positions for the ligand-to-metal charge transfer bands in the electronic spectra of cobalt(II)-substituted proteins; the calculated χ_{ligand} and calculated and observed band positions for several cobalt-substituted blue copper proteins are presented in Table VII. The agreement between the calculated and observed energies for the protein systems is nearly as good as that for the $M^{II}N_3(SR)$ complexes and supports the assignment. This same procedure is generally applicable to the prediction of ligand-to-metal charge transfer band positions in proteins substituted by different metals.

NMR Spectral Studies. The NMR spectroscopy of low molecular weight high-spin cobalt(II) complexes has been thoroughly investigated;[34,35] the cobalt(II) polypyrazolyborate complexes in particular have been extensively studied in order to understand the relative importance and temperature dependences of contact and dipolar contributions to isotropic shifts.[35] In addition, an ^1H NMR study of Co(II)-substituted *Pseudomonas aeruginosa* azurin has been communicated.[4] There are several distinctive characteristics of the ^1H NMR spectra of high-spin cobalt(II) complexes with symmetry lower than cubic. Firstly, large isotropic shifts arising from both contact (hyperfine) and dipolar (magnetic anisotropy) terms are observed.[35] Secondly, owing to the very fast electron spin relaxation time of the cobalt(II) ion, relatively narrow line widths are found at room temperature.[34,35] Thus, cobalt(II) complexes usually exhibit well-resolved ^1H NMR spectra with chemical shift dispersions as high as 100 ppm or more. Generally, the resonances of protons closest to the metal ion suffer the greatest chemical shift displacement and greatest line broadening.

The resonance positions and assignments for the ^1H NMR spectra of compounds **1–3** are summarized in Table VIII; representative spectra are shown in Figure 5. The resonances

Table VIII. NMR Data for $Co(HB(3,5\text{-}Me_2pz)_3)(SR)$ (ppm from Me_4Si)

SR = $SC_6H_4NO_2$ (2)	
methyl H (5 position)	−1.25
methyl H (3 position)	−18.50
pyrazole ring H (4 position)	−61.0
mercaptan *m*-H	−3.5
mercaptan *o*-H	−15.9
SR = SC_6F_5 (3)	
methyl H (5 position)	−1.35
methyl H (3 position)	−16.2
pyrazole ring H (4 position)	−61.5
SR = $SCH_2CH(NH_2)(COOC_2H_5)$ (1)	
methyl H (5 position)	−1.30
methyl H (3 position)	−12.8
pyrazole ring H (4 position)	−65.2

for the boron-bound protons could not be located; they are expected to be very broad and severely shifted. In $Co(HBpz_3)_2$ the observed chemical shift for the boron-bound proton is 115.6 ppm to low field of Me_4Si.[35] The spectrum of **3** (Figure 5) exhibits only three pyrazolylborate resonances and is most easily assigned. All three chemical shifts occur to low field of Me_4Si, and the magnitude of the pyrazolyl 4-H shift is greater than in $Co(RBpz_3)_2$ derivatives (ca. −60 vs. −40 ppm[35]). The close similarity of the $Co(HB(3,5\text{-}Me_2pz)_3)$ ^1H subspectra in **1–3** is excellent evidence for similar molecular and electronic structures. The proton resonances of the mercaptide group in **2** have been assigned on the basis of anticipated distances from the metal ion (Table VIII). The unambiguous assignment of the resonances arising from the *O*-ethylcysteinate ligand in **1** was not possible owing to the complexity of the spectrum. As noted above, the $Co(HB(3,5\text{-}Me_2pz)_3)(SR)$ complexes are, to varying degrees, unstable with respect to disproportionation to yield $Co(HB(3,5\text{-}Me_2pz)_3)_2$ and $(Co(SR)_2)_n$ species (eq 3). Thus, depending on the sample and its age, varying amounts of $Co(HB(3,5\text{-}Me_2pz)_3)_2$ could be detected in the NMR spectra. This complex exhibits resonances at −42.8 (4-H), −40.6 (5-CH_3), and +75.7 ppm (3-CH_3), and it is readily detected in the spectrum of **2** in Figure 5. The proton resonance positions in **1–3** will be a function of both contact and dipolar shifts. Although no attempt has been made to separate and to assess the relative importance of these effects,[36] and although both (especially the dipolar) will be highly sensitive to the spacial distribution of ligands in the coordination sphere,[34,35] it is interesting to compare the data for **1–3** with the results for Co(II)-substituted *Pseudomonas aeruginosa* azurin. In both systems the line widths are comparable and the maximum low-field isotropic shift which is observed (at comparable temperatures) is ca. −60 ppm. The maximum high-field shift in the protein is ca. +30 ppm. Judging from results on $Co(HBpz_3)_2$[35] with respect to $Co(HB(3,5\text{-}Me_2pz)_3)_2$, proton resonances in the pyrazolyl 3 position of $Co(HBpz_3)(SR)$ derivatives would be expected to undergo comparable or greater upfield shifts.

XPS Studies. The XPS (X-ray photoelectron spectroscopy) spectra in the sulfur 2p (S2p) region of several blue copper and cobalt(II)-substituted proteins have been reported.[9,37] Gray and co-workers reported a shift of the S2p peak from the 164-eV region to the 167.5–170-eV region with the incorporation of copper(I), copper(II), or cobalt(II) ions.[9] This shift was interpreted by them as direct evidence of metal-sulfur coordination. Several other groups have studied the XPS spectra of both the blue copper proteins and transition metal-thiolate complexes and have concluded that the 167.5–170-eV peaks were too high in energy to be assigned to thiol S2p transitions; rather, these high-energy bands were attributable to some form of oxidized sulfur,[37a,b] or to charge-transfer satellites.[37c] Transition metal-coordinated thiolate complexes typically show S2p peaks in the 163–164-eV region.[37b,38,39]

Table IX. XPS Data for $Co(HB(3,5\text{-}Me_2pz)_3)(SR)$ Complexes and a Blue Copper Protein

	sulfur 2p binding energy
SR = $SCH_2CH(NH_2)(COOC_2H_5)$ (**1**)	164.1 (±0.2)[a]
SR = $SC_6H_4NO_2$ (**2**)	163.4 (±0.2)[a]
SR = SC_6F_5 (**3**)	165.1 (±0.2)[a]
potato plastocyanin	163.3 (±0.2)[b]

[a] This work. [b] Reference 37a.

The S2p binding energies of the complexes **1–3** and of the blue copper protein plastocyanin are listed in Table IX. The energy observed for **3** is somewhat larger than that previously reported for the S2p ionization.[37,38] However, the complex has a thiolate ligand with a very strong electron-withdrawing group which raises the binding energy. Even with thiolates containing strong electron-withdrawing groups, the S2p binding energy for $Co^{II}N_3(SR)$ complexes falls in or near the range of other transition-metal complexes.[37,38] Indeed, the binding energy for **1**, which has the biologically important cysteine group, is typical of sulfhydryl groups in proteins in general.[39]

Conclusions

In this study we have shown that it is possible to synthesize active site approximations to the blue copper proteins with cobalt(II) ions substituted for copper(II) ions. In one such $Co^{II}N_3(SR)$ complex the Co ion is in a distorted tetrahedral geometry, as determined by diffraction methods. These $Co^{II}N_3(SR)$ complexes give rise to visible spectra that are similar to the spectra of the protein systems. This similarity supports the assignment of a four-coordinate, nonplanar geometry proposed for active sites of the blue copper proteins. In addition, the substitution of cobalt(II) ions for copper(II) ions in $M^{II}N_3(SR)$ complexes effects a shift in the energy of the ligand-to-metal charge transfer bands that is comparable with the difference in the Co(II)/Co(I) and Cu(II)/Cu(I) redox couples. These results are good evidence for the assignment of a ligand-to-metal charge-transfer transition to the band at approximately 600 nm in the spectra of the native systems and for the band in the 310–325-nm region of the spectra of the cobalt(II)-substituted proteins. The XPS studies of the $Co^{II}N_3(SR)$ complexes in the sulfur 2p region indicate that the binding energies for **1–3** are similar to other M–SR complexes. Coordination of a metal ion to a thiolate moiety does not give rise to an anomalously large change in binding energy of the sulfur 2p electrons.

Through the study of $Cu^IN_3(SR)$, $Cu^{II}N_3(SR)$,[1,6] and $Co^{II}N_3(SR)$ complexes we have shown that the unusual spectroscopic properties of the type 1 site are not unique to the protein systems. We have provided an understanding of some of the inorganic aspects of this unusual coordination geometry. The effects of further modifying X in $M^{II}N_2(SR)X$ complexes (X = SR′R″, OR) are under investigation.

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Supplementary Material Available: Table IV, structure amplitude table for $Co(HB(3,5\text{-}Me_2pz)_3)(SC_6H_5)$ (6 pages). Ordering information is given on any current masthead page.

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