The space-group symmetry of $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$ is $P4_2bc$ (C_{4v}^8).[1] Important in the hypothesis by Banks et al.[1] is the structural feature that Mn^{2+} and Fe^{3+} ions occupy three distinct crystallographic sites. As seen in Figure 1, ions located on M(1) and M(2) sites are perfectly ordered. Ions located on M(3) sites are not ordered within the a-b plane, but for the ideal composition $x = 0.50$, they are most likely ordered (alternate Fe^{3+}-Mn^{2+}) along the c axis. All of these conditions minimize the number of Fe^{3+}-Fe^{3+} near neighbors as predicted by Pauling's fourth rule.[10] Along this same line of thought, one would expect the Fe^{3+}-Fe^{3+} near neighbors to be minimized over the entire composition range. This is easily seen to be the case if composition changes in Fe^{3+} and Mn^{2+} occur only on M(3) sites. This of course would mean the $K_xMn_xFe_{1-x}Fe_3$ phase belongs to space group $P4_2bc$ at all compositions. Then, the fractions of nearest neighbors which are Fe^{3+}-Fe^{3+} at the compositions studied are 0.200, 0.133, 0.067, 0.033, and 0.00 for $x = 0.40$, 0.45, 0.50, 0.55, and 0.60, respectively.

The calculated values for the molar Curie constants given in Table II are the same for all compositions since Mn^{2+} and Fe^{3+} both have $S = {}^5/_2$. The experimental values of C_M and Θ become surprisingly large at $x = 0.45$ and 0.40. From Figure 3, it is seen that these constants are approximated from χ^{-1} values between 200 and 300 K and are, therefore, not very accurate. It is obvious that better values of C_M and Θ could be obtained if measurements of χ were extended to higher temperatures. However, if the values of χ^{-1} between 200 and 300 K are asymptotic to a line extrapolated from higher temperatures, then the values of C_M and Θ would be still greater. There is little doubt, nevertheless, that the large values of C_M and Θ at $x = 0.45$ and 0.40 are related to the number of Fe^{3+}-Fe^{3+} nearest neighbors, or perhaps Fe^{3+} clusters.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation (Grants DMR 79-00313, DMR 76-83360, and DMR 74-11970) for finanical support, including the purchase of major equipment, and The University of Mississippi for cost sharing. The work done at the Polytechnic Institute of New York was partially supported by Army Grant No. DAAG 29-75-G-0096. They also thank the NASA Langley Research Center for the loan of an electromagnet and power supply. Appreciation is expressed to The University of Mississippi Computer Center for providing data reduction time.

Registry No. FeF_3, 7783-50-8; $KMnF_3$, 13827-01-5.

(10) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322

Cobalt(III) Complexes of Stereospecific Linear NSNN Tetradentate Ligands. 1. Synthesis of Ligands That Adopt the Cis-β Coordination Geometry

PAUL J. TOSCANO and LUIGI G. MARZILLI*

Received November 16, 1982

The syntheses of four linear tetradentate ligands containing a sulfur atom and an amide nitrogen atom as internal donor atoms and either amine or pyridine terminal donor groups are reported. The ligands include geeH (*N*-[2-((2-aminoethyl)thio)ethyl]-2-aminoacetamide), pygeH (*N*-((2-pyridyl)methyl)-2-((2-aminoethyl)thio)acetamide), egeH (*N*-(2-aminoethyl)-2-((2-aminoethyl)thio)acetamide), and egpyH (*N*-(2-aminoethyl)-2-[((2-pyridyl)methyl)thio]acetamide). Co(III) complexes of these ligands were prepared, and chromatographic and spectroscopic evidence is presented which indicates that only one geometric isomer is formed. A single-crystal X-ray diffraction study of $Co(gee)(NO_2)_2 \cdot H_2O$ ($C_6H_{14}CoN_5S \cdot H_2O$) was undertaken to establish its stereochemistry. The complex crystallized in space group $C2/c$ with $a = 20.832$ (6) Å, $b = 7.823$ (3) Å, $c = 15.570$ (4) Å, $\beta = 95.19$ (2)°, and $Z = 8$. The structure was solved by conventional Patterson and Fourier methods for 2786 independent reflections having $2\theta_{Mo K\alpha} = 58.7°$ and $I > 3\sigma(I)$. Full-matrix least-squares refinement led to a final R value of 0.033. The tetradentate gee ligand adopts the cis-β coordination geometry about the cobalt atom. Arguments based upon ligand structural similarities, spectroscopic techniques, and interconversion reactions of the complexes are presented which suggest that all four ligands bind to Co(III) stereospecifically in the cis-β geometry for all complexes prepared in this study.

Introduction

In recent years, the study of metal complexes containing flexible tetradentate ligands has been an area of active interest.[1-5] Investigations have involved evaluation of factors governing the overall geometry of the complexes, their reactions, and the stereochemistry of the reaction products.[1-5] Cobalt(III) complexes of such ligands have been found to promote hydrolysis of amino acid esters, peptides, and other carbonyl compounds.[3-6] In some cases, peptide formation has been observed.[7] In addition, since metal complexes of a particular stereochemistry may be optically active and chiral

(1) Brubaker, G. R.; Schaefer, D. P.; Worrell, J. H.; Legg, J. I. *Coord. Chem. Rev.* **1971**, *7*, 161.
(2) McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 165.
(3) Hay, R. W.; Morris, P. J. *Met. Ions Biol. Syst.* **1976**, *5*, 173.
(4) Buckingham, D. A. In "Biological Aspects of Inorganic Chemistry"; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977 p 141.
(5) Phipps, D. A. *J. Mol. Catal.* **1979**, *5*, 81.
(6) (a) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 2772. (b) Kimura, E.; Young, S.; Collman, J. P. *Inorg. Chem.* **1970**, *9*, 1183. (c) Buckingham, D. A.; Davis, C. E.; Foster, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 5571. (d) Bentley, K. W.; Creaser, E. H. *Biochem. J.* **1973**, *135*, 507. (e) Oh, S. K.; Storm, C. B. *Biochemistry* **1974**, *13*, 3250. (f) Kimura, E. *Inorg. Chem.* **1974**, *13*, 951. (g) Bentley, K. W.; Creaser, E. H. *Ibid.* **1974**, *13*, 1115.
(7) (a) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 4539. (b) Collman, J. P.; Kimura, E. *Ibid.* **1967**, *89*, 6096.

0020-1669/83/1322-3342$01.50/0

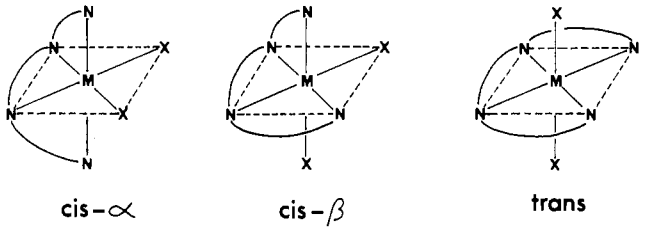


Figure 1. Possible coordination geometries for a linear tetradentate ligand in an octahedral system.

centers may be incorporated into the backbone of the tetradentate ligand,[8-10] such metal ion promoted reactions can occur stereospecifically.[11-14]

Perhaps the most studied complexes of this genre are the Co(III) complexes of triethylenetetramine (trien, NNNN donor set) and 1,8-diamino-3,6-dithiaoctane (eee, NSSN donor set). The trien ligand suffers somewhat from the fact that it does not bind stereospecifically to the cobalt atom; isomers result (up to three geometrical isomers are possible: cis-α, cis-β, and trans, see Figure 1), but they are fairly easily separated.[15] Further isomers which are less easily separated may result as a consequence of the stereochemistry about the "planar" secondary amino group in the cis-β geometry.[16] On the other hand, the eee ligand binds to cobalt only in the cis-α fashion;[17] however, this ligand contains two thioether donors which reduce the ligand field about the metal. The ability of Co^{III}(eee) complexes to promote the hydrolysis of peptides has been questioned.[18]

Complexes with cis-β geometry have proved to be the most reactive and useful. In light of the continued interest in stereospecific complexes of Co(III)[1-5,8-10] and their application to peptide synthesis,[19] we have investigated the preparations of Co(III) complexes which contain linear tetradentate ligands (gee, ege, pyge, egpy) having an NSNN donor atom set consisting of terminal amine or pyridine groups and internal amide and thioether donors, which were designed to adopt the cis-β geometry. In addition these ligands avoid the problem of stereochemistry about the internal donor atoms mentioned above for trien. We also present the visible and NMR spectra and chemical interconversions of the complexes. Finally the structure of one complex was determined by single-crystal X-ray diffraction techniques to unequivocably establish its stereochemistry.

Experimental Section

Techniques. ^{1}H NMR spectra were obtained on either a JEOL MH-100 spectrometer operating at 100 MHz or a Varian EM-390 spectrometer operating at 90 MHz. Spectra obtained in $CDCl_3$ or Me_2SO-d_6 solution were referenced to tetramethylsilane, while spectra obtained in D_2O solution were referenced to 3-(trimethylsilyl)propionic acid, sodium salt. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer operating at 20 MHz with a deuterium lock. ^{13}C NMR spectra in $CDCl_3$ or Me_2SO-d_6 solution were referenced to tetramethylsilane. A Cary 14 spectrophotometer was employed for visible spectra at ambient temperature. All melting points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc. (Atlanta, GA).

Synthesis of Ligands and Metal Complexes. Materials. Phosphorus pentachloride, *N*-phthaloylglycine, *N*-(2-bromoethyl)phthalimide, thiourea, 2-bromoethylamine hydrobromide, triethylamine, 2-(aminomethyl)pyridine, chloroacetyl chloride, *N*-((benzyloxy)carbonyl)-glycine, benzyl chloroformate, ethyl chloroformate, methyl thioglycolate, ethylenediamine, and 2-picolyl chloride hydrochloride were obtained from Aldrich. 2-Mercaptoethylamine hydrochloride was purchased from Sigma. Cobalt(III) chloride hexahydrate and 32% HBr/acetic acid were obtained from Fisher. Other inorganic salts and solvents were obtained from standard sources and used without further purification.

Preparation of Co(gee)$(NO_2)_2$. Method A. (i) *N*-Phthaloylglycyl Chloride. This compound was prepared by the method of Sheehan and Frank[20] from phthalylglycine and PCl_5; mp 83–84.5 °C (lit.[20] mp 83–85 °C).

(ii) *N*-(2-Bromoethyl)-2-phthalimidoacetamide (2). A solution of *N*-phthaloylglycyl chloride (20.0 g, 89.4 mmol) in *p*-dioxane (120 mL) was added dropwise over 30–45 min to a stirred, cooled (0–5 °C) mixture of 2-bromoethylamine hydrobromide (18.42 g, 90.0 mmol), NaOH (3.58 g, 90.0 mmol), and MgO (5.39 g, 134.0 mmol). After the addition was complete, the ice bath was removed, the stirred suspension was allowed to warm to room temperature over a period of 1 h, and then concentrated HCl was added to pH 1; the white product was filtered, washed well with water, and dried over silica gel. Yields averaged 75%. An analytical sample was obtained by recrystallization from hot 95% ethanol; mp 189–190 °C. Anal. Calcd for $C_{12}H_{11}BrN_2O_3$: C, 46.33; H, 3.56; N, 9.00. Found: C, 46.38; H, 3.74; N, 8.98. ^{1}H NMR ($CDCl_3$): δ 7.75–7.90 (m, 4 H, aryl), 6.27 (br, 1 H, NH), 4.37 (s, 2 H, NCH_2CO), 3.45–3.70 (m, 4 H, NCH_2CH_2Br).

(iii) *N*-(2-Mercaptoethyl)phthalimide. This compound was prepared by the method of Tulecki et al.[21] from *N*-(2-bromoethyl)phthalimide and thiourea except for the following modifications. The solution of the above two reagents was heated at reflux in 90% ethanol overnight rather than the 4 h called for in the literature. The intermediate isothiuronium salt was hydrolyzed without isolation. The final product was purified by stirring the crude hydrolysis product in diethyl ether and filtering insoluble impurities. Pure mercaptan was obtained by evaporating the diethyl ether; mp 74–75 °C (lit.[21] mp 74–75.5 °C). ^{1}H NMR ($CDCl_3$): δ 5.80 (m, 4 H, aryl), 3.89 (t, 2 H, NCH_2), 2.85 (m, 2 H, SCH_2), 1.44 (t, 1 H, SH).

(iv) *N*-[2-[(2-Phthalimidoethyl)thio]ethyl]-2-phthalimidoacetamide (phth^2-geeH) (3). To a solution of *N*-(2-mercaptoethyl)phthalimide (10.64 g, 51.4 mmol) in Me_2SO (160 mL) was added NaOH (2.05 g, 51.4 mmol) in water (40 mL), quickly followed by solid *N*-(2-bromoethyl)-2-phthalimidoacetamide (16.00 g, 51.4 mmol). The resulting solution was heated and stirred for 1.5 h at 60–65 °C. The reaction mixture was cooled and CH_2Cl_2 (400 mL) added. This mixture was extracted with 2 N NaOH (2 × 300 mL) and water (1 × 400 mL). The CH_2Cl_2 fraction was separated and dried over

(8) (a) Bosnich, B.; Phillip, A. T. *J. Chem. Soc. A* **1970**, 264. (b) Worrell, J. H.; MacDermott, T. E.; Busch, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 3317.
(9) (a) Yoshikawa, S.; Sekihara, T.; Goto, M. *Inorg. Chem.* **1967**, *6*, 169. (b) Goto, M.; Saburi, M.; Yoshikawa, S. *Ibid.* **1969**, *8*, 358. (c) Asperger, R. G. *Ibid.* **1969**, *8*, 2127. (d) Bosnich, B.; Kneen, W. R. *Ibid.* **1970**, *9*, 2191. (e) Saburi, M.; Sawai, T.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1086.
(10) (a) Cragel, J., Jr.; Brubaker, G. R. *Inorg. Chem.* **1972**, *11*, 303. (b) Brubaker, G. R.; Euler, R. A. *Ibid.* **1972**, *11*, 2357. (c) Goto, M.; Matshushita, H.; Saburi, M.; Yoshikawa, S. *Ibid.* **1973**, *12*, 1498. (d) Bosnich, B.; Harrowfield, J. M. *Ibid.* **1975**, *14*, 847, 853, 861. (e) Suzuki, T. M.; Kimura, T.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 77. (f) Muir, M. M.; Rechani, P. R.; Diaz, J. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 317.
(11) (a) Yamaguchi, M.; Yamamatsu, S.; Oikawa, H.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1981**, *20* 3179. (b) Ajioka, M.; Yano, S.; Matsuda, K.; Yoshikawa, S. *J. Am. Chem. Soc.* **1981**, *103*, 2459. (c) Yamaguchi, M.; Yano, S.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 691. (d) Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1980**, *19*, 2010.
(12) (a) Job, R. *Inorg. Chim. Acta* **1980**, *40*, 59. (b) Glusker, J. P.; Carrell, H. L.; Job, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 5741.
(13) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1967**, *6*, 796.
(14) Golding, B. T.; Gainsford, G. J.; Herlt, A. J.; Sargeson, A. M. *Tetrahedron* **1976**, *32*, 389.
(15) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787.
(16) (a) Anderson, B. F.; Bell, J. D.; Buckingham, D. A.; Cresswell, P. J.; Gainsford, G. J.; Marzilli, L. G.; Robertson, G. B.; Sargeson, A. M. *Inorg. Chem.* **1977**, *16*, 3233. (b) Buckingham, D. A.; Dwyer, M.; Gainsford, G. J.; Ho, V. J.; Marzilli, L. G.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *Ibid.* **1975**, *14*, 1739.
(17) Worrell, J. H.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1563, 1572.
(18) Rhee, M.-J.; Storm, C. B. *J. Inorg. Biochem.* **1979**, *11*, 17.
(19) (a) Clark, C. R.; Tasker, R. F.; Buckingham, D. A.; Knighton, D. R.; Harding, D. R. K.; Hancock, W. S. *J. Am. Chem. Soc.* **1981**, *103*, 7023. (b) Knighton, D. R.; Harding, D. R. K.; Friar, M. J.; Hancock, W. S.; Reynolds, G. D.; Clark, C. R.; Tasker, R. F.; Buckingham, D. A. *Ibid.* **1981**, *103*, 7025.
(20) Sheehan, J. C.; Frank, V. S. *J. Am. Chem. Soc.* **1949**, *71*, 1856.
(21) Tulecki, J.; Dabrowski, J.; Kalinowska-Torz, J. *Diss. Pharm. Pharmacol.* **1966**, *18*, 473; *Chem. Abstr.* **1967**, *67*, 63971.

$MgSO_4$, filtered, and reduced in volume to ~50 mL on a rotary evaporator. Petroleum ether was added slowly to induce crystallization. If an oil formed, crystallization was induced by cooling at −10 °C. The yield of crude product was ~50%. Residual Me_2SO was removed by recrystallization from hot 95% ethanol; mp 161–162 °C. Anal. Calcd for $C_{22}H_{19}N_3O_5S\cdot H_2O$: C, 58.02; H, 4.65; N, 9.23; S, 7.03. Found: C, 58.03; H, 4.65; N, 9.23; S, 7.08. ^1H NMR ($CDCl_3$): δ 7.64–7.92 (m, 8 H, aryl), 6.87 (br, 1 H, NH), 4.42 (s, 2 H, NCH_2CO), 3.89 (t, 2 H, $(CO)_2NCH_2$), 3.51 (m, 2 H, $CONHCH_2$), 2.80 (overlapping triplets, 4 H, CH_2SCH_2). ^{13}C NMR ($CDCl_3$): C=O, 168.46, 167.86, 166.32; aryl (only 5 of 6 resonances resolved), 134.19, 132.16, 131.94, 123.58, 123.48; NCH_2, 40.71, 38.69, 37.42; SCH_2, 32.01, 30.61.

(v) Deprotection of phth²-geeH: Co(gee)$(NO_2)_2\cdot H_2O$. Phth²-geeH (6.56 g, 15.0 mmol) was suspended in absolute ethanol (120 mL), and hydrazine hydrate (1.5 mL, 30.0 mmol) was added. The mixture was heated at reflux for 2 h, cooled, and filtered. The volume of the filtrate was reduced as much as possible on a rotary evaporator, and the previously collected solid was added, followed by 2 N HCl (75 mL). The suspension was heated at 50–60 °C for 30 min and then cooled at 0–5 °C overnight. The precipitated phthalhydrazide was removed by filtration. Though much effort was expended, the isolation of solid geeH·2HCl from the filtrate was found to be erratic and counterproductive to maximizing the yield of cobalt complex. Consequently, the geeH·2HCl was converted to product in situ. The filtrate was evaporated to near dryness on a rotary evaporator. Methanol (40 mL) was added to the residue and sodium chloride removed by filtration. $CoCl_2\cdot 6H_2O$ (3.57 g, 15.0 mmol) was added to the filtrate, followed by $NaNO_2$ (7.0 g, 101 mmol) in water (10 mL). (Note: The $NaNO_2$ solution must be added very slowly to avoid excessive foaming from the acid decomposition of NO_2^-.) The reaction mixture was stirred for 3 h, during which time Co(gee)$(NO_2)_2$ precipitated. The crude product was collected, washed with a little water, and air-dried. The complex is soluble in Me_2SO, slightly soluble in hot water, and virtually insoluble in other common solvents. The complex was recrystallized from boiling water. Crystals suitable for X-ray and elemental analyses were grown by slowly cooling a hot, saturated (filtered) aqueous solution of the complex. These crystals contained one molecule of water as shown by the diffraction studies and elemental analysis. The best method of purification, however, is via conversion to the dichloro complex (vide infra) and reconversion to the dinitro complex. (As mentioned later, the dinitro complex prepared in this manner contains two molecules of water). Anal. Calcd for $C_6H_{16}N_5O_6SCo\cdot H_2O$: C, 20.88; H, 4.67; N, 20.29. Found: C, 20.97; H, 4.46; N, 20.39. Vis spectrum (H_2O): λ_{max} 456 nm (ε 407). ^{13}C NMR (Me_2SO-d_6): δ 176.64, 48.28, 45.75, 42.71, 38.15, 32.39.

Method B. (i) *N*-(2-Bromoethyl)-2-[((benzyloxy)carbonyl)amino]acetamide (6). This compound was prepared via the "mixed anhydride" method, using either of two procedures for the analogous chloro derivative. The first method is a modification of the procedure of Mel'nik, et al.[22] *N*-((benzyloxy)carbonyl)glycine (12.0 g, 57.4 mmol) and triethylamine (5.75 g, 57.0 mmol) were dissolved in DMF (180 mL) and cooled to −10 °C. Ethyl chloroformate (6.18 g, 57.0 mmol) was added, and the mixture was stirred in the cold for 10 min. Then 2-bromoethylamine hydrobromide (11.64 g, 57.0 mmol) dissolved in DMF (120 mL) was added to the reaction mixture, followed quickly by triethylamine (5.75 g, 57.0 mmol), and stirring continued for 2 h (−5 to −10 °C). As much DMF as possible was removed on a rotary evaporator. The residue was dissolved in $CHCl_3$ (90 mL) and extracted with water (200 mL). The $CHCl_3$ fraction was dried over $MgSO_4$ and concentrated to a small volume on a rotary evaporator. The product was precipitated by slow addition of petroleum ether. Yields varied from 30 to 50%.

A second method based on the procedure of Chakrabarti and Friedman[23] was discovered later. This method, which uses lower boiling solvents and gives higher yields, was preferred. A solution of *N*-((benzyloxy)carbonyl)glycine (10.45 g, 50 mmol) and triethylamine (5.45 g, 54 mmol) in THF (120 mL) was cooled to 0–5 °C. Ethyl chloroformate (5.68 g, 52.5 mmol) was added, and the mixture was stirred in the cold for 30 min. Then a mixture of 2-bromoethylamine hydrobromide (15.38 g, 75 mmol) and triethylamine (8.00 g, 79 mmol) in $CHCl_3$ (150 mL) was added and stirring continued for 1 h at ice-bath temperature followed by 3 h at room temperature. The reaction mixture was filtered, and the solvents were removed on a rotary evaporator. The residue was dissolved in $CHCl_3$ (200 mL), and the solution was extracted with 1 N HCl (100 mL). The $CHCl_3$ fraction was dried over Na_2SO_4 and most of the $CHCl_3$ removed on a rotary evaporator. Petroleum ether was slowly added, and the precipitated white solid was collected and air-dried. Yields averaged 75%. An analytical sample was obtained from hot 95% ethanol/petroleum ether; mp 113–115 °C. Anal. Calcd for $C_{12}H_{15}BrN_2O_3$: C, 45.73; H, 4.80; N, 8.89. Found: C, 45.77; H, 4.81; N, 8.75. ^1H NMR ($CDCl_3$): δ 7.37 (s, 5 H, aryl), 6.68 (br, 1 H, NH), 5.68 (br, 1 H, NH), 5.15 (s, 2 H, $ArCH_2$), 3.87 (d, 2 H, NCH_2CO), 3.3–3.7 (m, 4 H, NCH_2CH_2Br).

(ii) 2-[((Benzyloxy)carbonyl)amino]ethanethiol. This compound was prepared via the method of Atkinson et al.[24] from 2-mercaptoethylamine hydrochloride and benzyl chloroformate; mp 42–43 °C (lit.[24] mp 43 °C). ^1H NMR ($CDCl_3$): δ 7.35 (s, 5H, aryl), 5.33 (br, 1 H, NH), 5.10 (s, 2 H, $ArCH_2$), 3.33 (q, 2 H, NCH_2), 2.62 (m, 2 H, SCH_2) 1.35 (t, 1 H, SH).

(iii) *N*-[2-((2-(((Benzyloxy)carbonyl)amino)ethyl)thio)ethyl]-2-[((benzyloxy)carbonyl)amino]acetamide (Z^2-geeH) (7). To a solution made by addition of ethanol (40 mL) to aqueous NaOH (0.76 g, 19 mmol, in 5 mL) was added 2-[((benzyloxy)carbonyl)amino]ethanethiol (4.00 g, 19 mmol), followed quickly by *N*-(2-bromoethyl)-2-[((benzyloxy)carbonyl)amino]acetamide (5.97 g, 19 mmol). The reaction mixture was heated at reflux for 4 h and cooled, and most of the ethanol was removed on a rotary evaporator. A 0.1 N NaOH solution (100 mL) was added to the residue and the resulting suspension stirred for 5 min. The white product was collected, washed well with water, and air-dried; yield 65–70%. An analytical sample was obtained from hot absolute ethanol; mp 112–113 °C. Anal. Calcd for $C_{22}H_{27}N_3O_5S$: C, 59.32; H, 6.11; N, 9.43. Found: C, 59.33; H, 6.15; N, 9.39. ^1H NMR ($CDCl_3$): δ 7.33 (s, 10 H, aryl), 6.75 (br, 1 H, NH), 5.72 (br, 1 H, NH), 5.42 (br, 1 H, NH), 5.12 (s, 2 H, $ArCH_2$), 5.10 (s, 2 H, $ArCH_2$), 3.82 (d, 2 H, NCH_2CO), 3.37 (overlapping m, 4 H, NCH_2), 2.62 (t, 4 H, CH_2SCH_2, accidental equivalence). ^{13}C NMR ($CDCl_3$): C=O, 169.26, 156.62; aryl, 136.48, 128.59, 128.14; OCH_2, 67.26, 66.91; aliphatic, 44.75, 40.53, 38.69, 32.28, 31.77 (there are 18 magnetically inequivalent carbon atoms, but only 12 resonances are resolved).

(iv) *N*-[2-((2-Aminoethyl)thio)ethyl]-2-aminoacetamide Dihydrobromide (geeH·2HBr) (4). Z^2-geeH (3.0 g, 6.7 mmol) was placed in 32% HBr/acetic acid (12 mL), and the mixture was stirred for 3 h. During this time, CO_2 evolved and a hard gum formed. Absolute diethyl ether (50 mL) was added and the mother liquor decanted. The solid in the flask was treated with absolute ethanol (30 mL), the flask was stoppered, and the mixture was stirred overnight. The powder that formed was collected, washed with a little absolute diethyl ether, and dried over silica gel; yield 75%. An analytical sample was obtained from hot absolute ethanol; mp 140–142 °C. Anal. Calcd for $C_6H_{15}N_3OS\cdot 2HBr$: C, 21.26; H, 5.05; N, 12.39. Found: C, 21.21; H, 5.10; N, 12.37. ^1H NMR (D_2O): δ 3.83 (s, 2 H, NCH_2CO), 3.52 (t, 2 H, ND_2CH_2), 3.26 (t, 2 H, $CONDCH_2$), 2.7–3.0 (overlapping t, 4 H, CH_2SCH_2).

(v) Co(gee)$(NO_2)_2$. To a solution of geeH·2HBr (1.02 g, 3 mmol) and $NaNO_2$ (1.04 g, 15 mmol) in water (4 mL) was added methanol (8 mL) followed by $CoCl_2\cdot 6H_2O$ (0.714 g, 3 mmol). The mixture was stirred for 6 h, and the precipitated product was collected and washed successively with water, acetone, and diethyl ether. The ^{13}C NMR spectrum of this material was identical with that of the complex synthesized via method A above.

Method C. (i) *N*-(2-Bromoethyl)-2-aminoacetamide Hydrobromide (8). *N*-(2-bromoethyl)-2-[((benzyloxy)carbonyl)amino]acetamide (8.0 g) was stirred in 32% HBr/acetic acid for 3 h. If solid product precipitated during this time, absolute diethyl ether (100 mL) was added to the flask and the product collected and dried over silica gel. If no solid formed, absolute diethyl ether (100 mL) was added to form an oil. The mother liquor was then decanted and absolute ethanol (40 mL) added to the oil with swirling. In general, the oily residue dissolved, and then with continued swirling, a powder precipitated. The product was collected, washed with absolute diethyl ether, and dried over silica gel; yield 85–90%. An analytical sample was obtained

(22) Mel'nik, S. Ya.; Mairanovskii, V. G.; Miropol'skaya, M. A.; Samokhvalov, G. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *38*, 1445.
(23) Chakrabarti, J. K.; Friedman, O. M. *J. Med. Chem.* **1967**, *10*, 285.
(24) Atkinson, J. G.; Girard, Y.; Rokach, J.; Rooney, C. S.; McFarlane, C. S.; Rackham, A.; Share, N. N. *J. Med. Chem.* **1979**, *22*, 99.

from hot absolute ethanol; mp 161–163 °C. Anal. Calcd for $C_4H_9BrN_2O\cdot HBr$: C, 18.34; H, 3.85; N, 10.69. Found: C, 18.36; H, 3.89; N, 10.69. ^1H NMR (D_2O): δ 3.85 (s, 2 H, NCH_2CO), 3.60 (m, 4 H, NCH_2CH_2Br).

(ii) Co(gee)$(NO_2)_2$. To a solution of NaOH (1.92 g, 48 mmol) in water (4 mL) was successively added ethanol (35 mL), 2-mercaptoethylamine hydrochloride (1.82 g, 16 mmol), and *N*-(2-bromoethyl)-2-aminoacetamide hydrobromide (4.2 g, 16 mmol). The mixture was heated at reflux for 3 h and cooled, and the ethanol was removed on a rotary evaporator. Methanol (20 mL) was added to the residue, and sodium salts were removed by filtration. A solution of $NaNO_2$ (3.32 g, 48 mmol) in water (10 mL) was added to the filtrate, followed by $CoCl_2\cdot 6H_2O$ (3.82 g, 16 mmol). Air was bubbled through the reaction mixture for 3 h, and a tan powder, which proved to be very impure product, separated. After recrystallization of this powder from boiling water, the product (0.95 g) obtained had a ^{13}C NMR spectrum identical with that of the complex synthesized in method A above.

Preparation of Co(pyge)$(NO_2)_2$. (i) *N*-((2-Pyridyl)methyl)-2-chloroacetamide (10). This compound was prepared via a modification of the method of Yamazaki et al.[25] A mixture of NaOH (9.31 g, 233 mmol), water (133 mL), diethyl ether (80 mL), and 2-(aminomethyl)pyridine (7.0 g, 64.8 mmol) was cooled (0–5 °C). A solution of chloroacetyl chloride (14.5 g, 128 mmol) in diethyl ether (20 mL) was added dropwise over a period of 30–45 min. After addition was complete, stirring was continued for 30 min at ice-bath temperature, followed by 1 h at room temperature. The reaction mixture was transferred to a separatory funnel and shaken, and the ether layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 75 mL), and the combined ether and CH_2Cl_2 fractions were quickly dried over $MgSO_4$ and filtered. The filtrate was concentrated on a rotary evaporator to a yellow oil, which decomposed readily. The compound was prepared as needed and used without further purification; yield 85%. ^1H NMR ($CDCl_3$): δ 7.25–8.92 (multiplets, 5 H, pyridyl and NH), 4.73 (d, 2 H, NCH_2), 4.25 (s, 2 H, $ClCH_2$).

(ii) *N*-((2-Pyridyl)methyl)-2-chloroacetamide Hydrochloride (10·HCl). Chloroacetyl chloride (12.54 g, 111 mmol) was added dropwise to a stirred, cooled (0–5 °C) solution of 2-(aminomethyl)pyridine (12.0 g, 111 mmol) in CH_2Cl_2 (180 mL). After addition was complete, the reaction mixture was stirred at ice-bath temperature for 1.5 h, followed by 1.5 h at room temperature. The white solid that formed was collected and washed with petroleum ether; yield 90%. An analytical sample was obtained from hot absolute ethanol; mp 134–136 °C. Anal. Calcd for $C_8H_9ClN_2O\cdot HCl$: C, 43.46; H, 4.56; N, 12.67. Found: C, 43.42; H, 4.59; N, 12.66. ^1H NMR (D_2O): δ 7.8–8.8 (multiplets, 4 H, pyridyl), 4.83 (s, 2 H, NCH_2), 4.28 (s, 2 H, $ClCH_2$).

(iii) Co(pyge)$(NO_2)\cdot H_2O$. This complex was prepared by utilizing either *N*-((2-pyridyl)methyl)-2-chloroacetamide or its hydrochloride. The procedure that employs the hydrochloride will be outlined. If the free base is used, 1 equiv less of NaOH is employed.

Ethanol (65 mL) was added to a solution of NaOH (5.43 g, 136 mmol) in water (15 mL), followed by *N*-((2-pyridyl)methyl)-2-chloroacetamide hydrochloride (10.0 g, 45.2 mmol) and 2-mercaptoethylamine hydrochloride (5.14 g, 45.2 mmol). The reaction mixture was heated at reflux for 3 h and cooled, and the solvent was removed on a rotary evaporator. Methanol (65 mL) was added to the residue, and NaCl was removed by filtration. A solution of $NaNO_2$ (9.37 g, 136 mmol) in water (35 mL) was added to the filtrate followed by $CoCl_2\cdot 6H_2O$ (10.77 g, 45.2 mmol). Air was bubbled through the reaction mixture for 4 h. The orange product was washed successively with water and acetone; yield 65–70%. The product was recrystallized from hot 9:1 methanol–water. Anal. Calcd for $C_{10}H_{14}N_5O_5SCo\cdot H_2O$: C, 30.55; H, 4.10; N, 17.81. Found: C, 30.48; H, 4.15; N, 17.78. Vis spectrum (H_2O): λ_{max} 460 nm (ε 452). ^{13}C NMR (Me_2SO-d_6): δ 175.67, 167.26, 150.44, 139.00, 123.75, 122.22, 52.72, 43.71, 39.26, 36.94.

Preparation of Co(ege)$(NO_2)_2\cdot 3H_2O$. (i) *N*-(2-Aminoethyl)-2-mercaptoacetamide (12). This compound was prepared by a modification of the method of Atkinson et al.[26] Originally, a solution of methyl thioglycolate (5.3 g, 50 mmol) and ethylenediamine (3.0 g, 50 mmol) in absolute methanol (20 mL) was stirred overnight. The white product that formed was collected and washed with a little methanol and petroleum ether. Yields averaged 50–60%. Higher yields were obtained in the following manner. A solution of methyl thioglycolate (10.6 g, 100 mmol) and ethylenediamine (6.0 g, 100 mmol) in absolute methanol (30 mL) was kept in a stoppered flask at 0–5 °C for 2 days. When the reaction mixture was seeded with material obtained by the first procedure, yields in excess of 80% were routinely obtained. The compound decomposes slowly at room temperature but can be stored for several months at 0–5 °C with only minimal loss of purity; mp 119–121 °C (lit.[26] mp 120–122 °C).

(ii) Co(ege)$(NO_2)_2\cdot 3H_2O$. Ethanol (320 mL) was added to a solution of NaOH (9.60 g, 240 mmol) in water (40 mL), followed by *N*-(2-aminoethyl)-2-mercaptoacetamide (16.00 g, 120 mmol) and 2-bromoethylamine hydrobromide (24.48 g, 120 mmol). The reaction mixture was heated at reflux for 3 h and cooled, and the solvent was removed on a rotary evaporator. Methanol (160 mL) was added to the residue and NaBr removed by filtration. A solution of $NaNO_2$ (24.72 g, 360 mmol) in water (80 mL) followed by $CoCl_2\cdot 6H_2O$ (28.40 g, 120 mmol) was added to the filtrate. Air was bubbled through the reaction mixture overnight, and the orange product that precipitated was collected and air-dried. Occasionally, no precipitate formed; in this case, water (200 mL) was added to the reaction solution. Scratching with a spatula induced crystallization; yield 35–40%. A hot 9:1 methanol–water solution of the product which was filtered through Celite gave purified product. Anal. Calcd for $C_6H_{14}N_5O_5SCo\cdot 3H_2O$: C, 18.90; H, 5.29; N, 18.37. Found: C, 18.86; H, 5.32; N, 18.27. Vis spectrum (H_2O): λ_{max} 453 nm (ε 413). ^{13}C NMR (Me_2SO-d_6): 175.17, 45.58, 45.36, 43.93, 40.26, 35.81.

Preparation of Co(egpy)$(NO_2)_2\cdot H_2O$. Ethanol (200 mL) was added to a solution of NaOH (6.04 g, 151 mmol) in water (25 mL), followed by *N*-(2-aminoethyl)-2-mercaptoacetamide (10.1 g, 75.5 mmol) and 2-picolyl chloride hydrochloride (12.37 g, 75.5 mmol). The reaction mixture was heated at reflux for 6 h and cooled, and the solvent was removed on a rotary evaporator. Methanol (200 mL) was added to the residue and NaCl removed by filtration. A solution of $NaNO_2$ (15.6 g, 226 mmol) in water (100 mL) was added to the filtrate, followed by $CoCl_2\cdot 6H_2O$ (17.93 g, 75.5 mmol). Air was bubbled through the reaction mixture overnight, and the orange product was collected and washed with water. A second crop was obtained by adding water (30 mL) to the filtrate. The total yield of product was 18.77 g (66%). The complex was recrystallized from hot 9:1 methanol–water. Anal. Calcd for $C_{10}H_{14}N_5O_5SCo\cdot H_2O$: C, 30.55; H, 4.10; N, 17.81. Found: C, 30.66; H, 4.18; N, 17.68. Vis spectrum (H_2O): λ_{max} 459 nm (ε 452). ^{13}C NMR (Me_2SO-d_6): 175.31, 163.59, 150.55, 139.57, 125.17, 124.55, 45.96 (probably accidental equivalence of two resonances), 42.23, 41.24.

Interconversion Reactions of the Cobalt Complexes. (A) gee Complexes. (i) Co(gee)$Cl_2\cdot HCl$. Co(gee)$(NO_2)_2$ (3.0 g) was heated and stirred in concentrated HCl (50 mL) for 45 min. The reaction mixture was cooled at 0–5 °C and the purple product collected and washed successively with acetone and diethyl ether. A small second crop could be obtained by allowing the filtrate to evaporate at room temperature. Excess HCl was removed by treatment of the crude product with absolute methanol at reflux for 3 h. The product gave an analysis as a monohydrochloride. Anal. Calcd for $C_6H_{14}Cl_2N_3OSCo\cdot HCl$: C, 21.04; H, 4.41; N, 12.27. Found: C, 21.43; H, 4.17; N, 12.42.

(ii) Co(gee)$(NO_2)_2\cdot 2H_2O$. Methanol (25 mL) was added to a solution of $NaNO_2$ (0.68 g, 9.8 mmol) in water (10 mL), followed by Co(gee)$Cl_2\cdot HCl$ (0.50 g, 1.5 mmol). The mixture was heated for 1.5 h and then stirred overnight at room temperature. The orange product was collected and washed successively with water, acetone, and diethyl ether. The ^{13}C NMR spectrum of the product was identical with that of the complex prepared via method A above. However, the visible spectrum indicated that this product is a dihydrate (method A yielded a monohydrate); yield 0.46 g (84.5%).

(iii) Co(gee)$(N_3)_2$. Methanol (7 mL) was added to a solution of NaN_3 (0.64 g, 9.8 mmol) in water (10 mL), followed by Co(gee)$Cl_2\cdot HCl$ (0.50 g, 1.5 mmol). The mixture was heated and stirred for 20 m and then filtered hot. The filtrate was allowed to evaporate at room temperature. The brown-violet product was collected and washed successively with acetone and diethyl ether; yield 0.18 g (37.6%). Anal. Calcd for $C_6H_{14}N_9OSCo$: C, 22.58; H, 4.42; N, 39.50. Found: C, 22.60; H, 4.48; N, 39.47. Vis spectrum (H_2O): λ_{max} 530 nm (ε 402).

(25) Yamazaki, T.; Nagata, M.; Ogawa, K.; Nohara, F. *Yakugaku Zasshi* **1967**, *87*, 668; *Chem. Abstr.* **1967**, *67*, 90770.

(26) Atkinson, E. R.; Handrick, G. R.; Bruni, R. J.; Granchelli, F. E. *J. Med. Chem.* **1965**, *8*, 29.

(B) pyge Complexes. (i) Co(pyge)Cl_2·H_2O. Co(pyge)$(NO_2)_2$ (3.0 g) was heated and stirred in concentrated HCl (50 mL) for 1 h and then stirred overnight at room temperature. The purple product that formed was collected and washed successively with acetone and diethyl ether. A substantial second crop (~25% size of first crop) could be obtained by allowing the filtrate to evaporate at room temperature. Excess HCl was removed as for Co(gee)Cl_2·HCl above. Anal. Calcd for $C_{10}H_{14}Cl_2N_3OSCo·H_2O$: C, 32.28; H, 4.33; N, 11.29. Found: C, 32.07; H, 4.15; N, 10.82.

(ii) Co(pyge)$(NO_2)_2$. Methanol (10 mL) was added to a solution of $NaNO_2$ (0.88 g, 12.8 mmol) in water (15 mL), followed by Co(pyge)Cl_2·H_2O (0.75 g, 2.0 mmol). The mixture was heated and stirred for 45 min in a beaker covered with a watch glass. The watch glass was removed, and heating and stirring were continued for 30 min. The reaction vessel was cooled at 0–5 °C, and the orange product that deposited was collected and washed successively with water, acetone, and diethyl ether; yield 0.62 g (82.3%). The ^{13}C NMR spectrum was identical with that of the directly prepared product. However, the visible spectrum indicated that this product was anhydrous (the directly prepared product contained one water of hydration).

(iii) Co(pyge)$(N_3)_2$. Methanol (10 mL) was added to a solution of NaN_3 (0.85 g, 13.1 mmol) in water (15 mL), followed by Co(pyge)Cl_2·H_2O (0.75 g, 2.0 mmol). The mixture was heated and stirred for 20 min in a beaker covered with a watch glass. The watch glass was removed, and heating and stirring were continued for 10 min. The reaction mixture was cooled at 0–5 °C, and the brown-purple product was collected and washed successively with water, acetone, and diethyl ether; yield 0.65 g (88.6%). Anal. Calcd for $C_{10}H_{14}N_9OSCo$: C, 32.71; H, 3.84; N, 34.33. Found: C, 32.69; H, 3.86; N, 34.24. Vis spectrum (H_2O): λ_{max} 530 nm (ϵ 471).

(iv) Co(pyge)(ox)·4H_2O. Oxalic acid dihyrate (0.28 g, 2.22 mmol) and NaOH (0.16 g, 4.0 mmol) were dissolved in hot water (10 mL). Co(pyge)Cl_2·H_2O (0.75 g, 2.0 mmol) was added to the hot, stirred solution, which immediately turned deep red. Heating and stirring were continued for 20 min. Then the solution was filtered hot and cooled at −10 °C for 30 min. The wine red product was collected and washed successively with acetone and diethyl ether; yield 0.58 g (65.5%). Anal. Calcd for $C_{12}H_{14}N_3O_5SCo·4H_2O$: C, 32.52; H, 5.00; N, 9.48. Found: C, 32.48; H, 4.98; N, 9.47. Vis spectrum (H_2O): λ_{max} 506 nm (ϵ 471).

(v) Co(pyge)$(CN)_2$·3H_2O. Methanol (10 mL) was added to a solution of KCN (0.28 g, 4.3 mmol) in water (15 mL), followed by Co(pyge)Cl_2·H_2O (0.75 g, 2.0 mmol). The mixture was warmed and stirred gently for 15 min, and an orange solution resulted. Then stirring was continued for 1.5 h at room temperature, and the yellow powder that formed was collected and successively washed with acetone and diethyl ether; yield 0.20 g (25.7%). Anal. Calcd for $C_{12}H_{14}N_5OSCo·3H_2O$: C, 37.03; H, 5.18; N, 17.99. Found: C, 37.06; H, 5.14; N, 17.95. Vis spectrum (H_2O): λ_{max} 422 nm (ϵ 449).

(vi) [Co(pyge)(tn)]Cl_2·H_2O. A mixture of Co(pyge)Cl_2·H_2O (0.75 g, 2.0 mmol) and 1,3-diaminopropane (0.16 g, 2.2 mmol) in methanol (15 mL) was gently warmed and stirred for 1 h. The pale red-orange powder that formed was collected and washed successively with a little methanol and acetone; yield 0.50 g (56.0%). Anal. Calcd for $C_{13}H_{24}Cl_2N_5OSCo·H_2O$: C, 34.99; H, 5.87; N, 15.69. Found: C, 35.12; H, 6.26; N, 15.68. Vis spectrum (H_2O): λ_{max} 496 nm (ϵ 378).

(C) ege Complexes. (i) Co(ege)Cl_2·0.5H_2O. Co(ege)$(NO_2)_2$ (3.0 g) was heated and stirred in concentrated HCl (50 mL) for 45 min. The reaction mixture was cooled at 0–5 °C, and the purple product was collected and washed successively with acetone and diethyl ether. A second crop could be obtained by evaporating the filtrate at room temperature. Excess HCl was removed as for Co(gee)Cl_2·HCl above. Anal. Calcd for $C_6H_{14}Cl_2N_3OSCo·0.5H_2O$: C, 22.87; H, 4.80; N, 13.34. Found: C, 22.65; H, 4.35; N, 13.10.

(ii) Co(ege)$(NO_2)_2$·3H_2O. Methanol (10 mL) was added to a solution of $NaNO_2$ (1.01 g, 14.6 mmol) in water (15 mL), followed by Co(ege)Cl_2·0.5H_2O (0.75 g, 2.4 mmol). The mixture was heated and stirred for 20 min and the resulting orange solution filtered hot. The filtrate was allowed to evaporate to ~$^1/_2$ volume at room temperature, and the orange product was collected and washed successively with a little water, acetone, and diethyl ether; yield 0.62 g (67.8%). The ^{13}C NMR and visible spectra of the product were identical with those of the directly prepared complex above.

(iii) Co(ege)$(N_3)_2$. Methanol (10 mL) was added to a solution of NaN_3 (0.95 g, 14.6 mmol) in water (15 mL), followed by Co(ege)Cl_2·0.5H_2O (0.75 g, 2.4 mmol). The mixture was heated and stirred for 20 min, and the resulting purple solution was filtered hot. The filtrate was set aside for crystallization, and the deep violet crystals that deposited were collected and successively washed with a little water, acetone, and diethyl ether; yield 0.61 g (79.7%). Anal. Calcd for $C_6H_{14}N_9OSCo$: C, 22.58; H, 4.42; N, 39.50. Found: C, 22.77; H, 4.49; N, 39.41. Vis spectrum (H_2O): λ_{max} 532 nm (ϵ 387).

(iv) Co(ege)(ox)·H_2O. Co(ege)Cl_2·0.5H_2O (0.75 g, 2.4 mmol) was added to a solution of oxalic acid dihydrate (0.33 g, 2.62 mmol) and NaOH (0.21 g, 5.25 mmol) in water (10 mL). The mixture was heated and stirred for 20 min and the resulting red solution filtered hot. The filtrate was allowed to evaporate at room temperature. The deep red product was collected and successively washed with acetone and diethyl ether; yield 0.62 g (74.5%). Anal. Calcd for $C_8H_{14}N_3O_5SCo·H_2O$: C, 28.16; H, 4.73; N, 12.32. Found: C, 28.39; H, 4.75; N, 12.39. Vis spectrum (H_2O): λ_{max} 508 nm (ϵ 349).

(v) Co(ege)$(CN)_2$·1.5H_2O. Methanol (10 mL) was added to a solution of KCN (0.32 g, 4.9 mmol) in water (15 mL), followed by Co(ege)Cl_2·0.5H_2O (0.75 g, 2.4 mmol). The mixture was heated and stirred for 15 min, and the resulting orange-yellow solution was filtered hot. The filtrate was allowed to evaporate at room temperature, and the yellow powder that formed was collected and washed successively with acetone and diethyl ether; yield 0.08 g (10.6%). Anal. Calcd for $C_8H_{14}N_5OSCo·1.5H_2O$: C, 30.58; H, 5.45; N, 22.29. Found: C, 30.56; H, 5.46; N, 22.12. Vis spectrum (H_2O): λ_{max} 423 nm (ϵ 364).

X-ray Crystallographic Study of Co(gee)$(NO_2)_2$·H_2O. The single-crystal structural determination of Co(gee)$(NO_2)_2$·H_2O was performed by Crystalytics Co. (Lincoln, NE). A single, dark red crystal, shaped like a parallelepiped having dimensions 0.21 × 0.30 × 0.78 mm, was glued to the end of a thin glass fiber. The crystal was monoclinic, space group $C2/c$-C_{2h}^6, with a = 20.832 (6) Å, b = 7.823 (3) Å, c = 15.570 (4) Å, β = 95.19 (2)°, and Z = 8 at 20 °C (μ_a(Mo K$\bar{\alpha}$)[27a] = 1.60 mm^{-1}; d_{calcd} = 1.81 g cm^{-3}). Intensity measurements were made on a computer-controlled four-circle Nicolet Autodiffractometer using 1.2° wide ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. A total of 3477 independent reflections having $2\theta \leq 58.7°$ (the equivalent of 1.2 limiting Cu K$\bar{\alpha}$ spheres) were measured in 3 concentric shells of increasing 2θ. A scanning rate of 6.0°/min was employed for the scan between ω settings 0.60° respectively above the below the calculated K$\bar{\alpha}$ doublet value ($\lambda_{K\bar{\alpha}}$ = 0.71073 Å) for those reflections having $3° \leq 2\theta_{Mo K\bar{\alpha}} \leq 43°$; a scanning rate of 4.0°/min was used for reflections having $43° \leq 2\theta_{Mo K\bar{\alpha}} \leq 58.7°$. Each of these 1.2° scans was divided into 19 equal (time) intervals, and those 15 contiguous intervals that had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan, were measured at ω settings 1.2° above and below the calculated K$\bar{\alpha}$ doublet value for each reflection. The data were empirically corrected for absorption effects with use of ψ scans for six reflections having 2θ between 8.2° and 32.0° and were then reduced to relative squared amplitudes, $|F_0|^2$, by means of standard Lorentz and polarization corrections.

The cobalt atom was located from a Patterson synthesis; the 18 remaining non-hydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the Co atom (R_1 = 0.501 for 1271 independent reflections having $2\theta_{Mo K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$). Isotropic unit-weighted full-matrix least-squares refinement for the 19 non-hydrogen atoms gave R_1(unweighted, based on F) = 0.077 and R_2 (weighted) = 0.081; anisotropic refinement converged to R_1 = 0.047 and R_2 = 0.055 for 1271 reflections having $2\theta_{Mo K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. These and all subsequent structure factor calculations employed recent tabulations of atomic form factors[27b] and an anomalous dispersion correction to the scattering factors of the cobalt and sulfur atoms.[27c]

The hydrogen atom positions were located from a difference Fourier synthesis calculated at this point. All subsequent cycles of least-squares refinement employed anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. The final cycles of empirically weighted full-matrix least-squares refinement gave R_1 = 0.033 and R_2 = 0.013 for 236 parameters with 2786 independent reflections having $2\theta_{Mo K\bar{\alpha}} \leq 58.7°$ and $I > 3\sigma(I)$. The largest peak (0.80 e/Å^3) in the final difference Fourier was 0.79 Å from the Co atom; the next largest peak of 0.59 e/Å^3 was essentially

(27) "International Tables for Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 55–66; (b) pp 99–101; (c) pp 149–150.

Table I. Atomic Coordinates for Non-Hydrogen Atoms in $Co(gee)(NO_2)_2 \cdot H_2O$

	x	y	z
Co	0.12958 (1)	0.30035 (4)	0.12810 (2)
S	0.20486 (3)	0.47427 (9)	0.19079 (4)
O(1)	0.1440 (1)	0.2432 (4)	0.3049 (1)
O(2)	0.0840 (1)	0.0636 (4)	0.2393 (1)
O(3)	0.2465 (1)	0.1610 (3)	0.0974 (1)
O(4)	0.1722 (1)	−0.0237 (3)	0.0922 (2)
O(5)	−0.0379 (1)	0.5515 (3)	0.1129 (1)
N(1)	0.1461 (1)	0.4080 (3)	0.0161 (1)
N(2)	0.0677 (1)	0.4721 (3)	0.1468 (1)
N(3)	0.0559 (1)	0.1726 (3)	0.0741 (1)
N(4)	0.1175 (1)	0.1915 (3)	0.2375 (1)
N(5)	0.1896 (1)	0.1244 (3)	0.1039 (1)
C(1)	0.1738 (1)	0.5813 (3)	0.0237 (1)
C(2)	0.2277 (1)	0.5840 (4)	0.0957 (2)
C(3)	0.1509 (1)	0.6244 (4)	0.2375 (1)
C(4)	0.0852 (1)	0.6378 (3)	0.1872 (1)
C(5)	0.0081 (1)	0.4465 (3)	0.1133 (1)
C(6)	−0.0040 (1)	0.2738 (3)	0.0717 (1)
O(w)	0.4386 (2)	0.3907 (3)	0.1070 (1)

at the noise level. Final non-hydrogen positional parameters are collected in Table I. Anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom positional and thermal parameters, and final observed and calculated structure factors have been deposited as supplementary material.

Results and Discussion

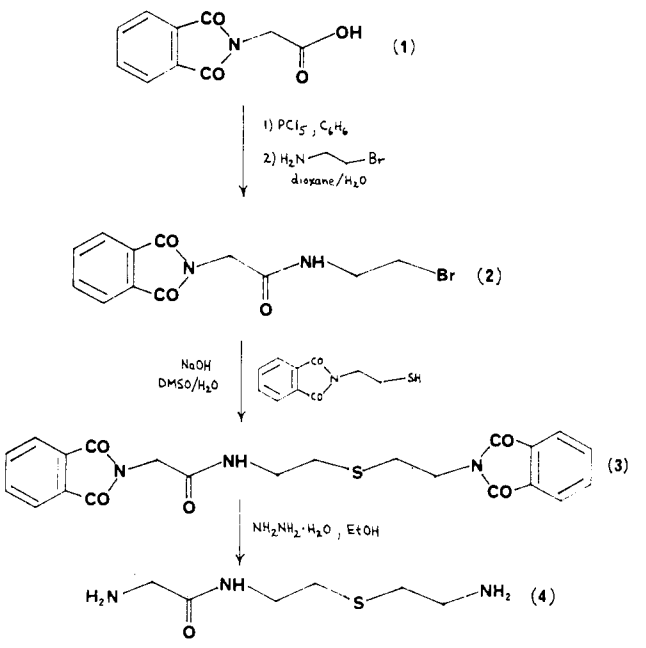
Strategy. Previous attempts at synthesis of tetradentate ligands that would stereospecifically coordinate to cobalt in the cis-β mode have concentrated on introducing optically active centers at suitable positions in the backbone of the ligand.[9b,d,10a,e] However, it is difficult to predict which geometrical isomer one might obtain. Sometimes the cis-β Co(III) complexes would rearrange to the trans geometry upon heating in methanol.[9b,d,10a]

Perhaps the simplest way to design a tetradentate ligand that will stereospecifically coordinate to cobalt is to make use of internal donor atoms of known stereochemical preference. It is well-known that a S donor atom at the junction of two five-membered chelate rings (in which at least one of the adjacent donor atoms is N or O) prefers to bind pyramidally, probably due to the relatively longer Co–S bond.[17,28a] It is also known that amide N atoms do not coordinate to metals unless they are deprotonated.[28b,29] In this case, the deprotonated amide N atom and the donor atoms of the ligand adjacent to it are constrained to lie in the same plane upon coordination.[28b] We thus expected that a linear tetradentate ligand incorporating a sulfur and amide nitrogen as internal donor atoms and amine or pyridine groups as terminal donors would stereospecifically coordinate to cobalt in the cis-β fashion.

Syntheses of Ligands and Dinitrocobalt Complexes. The syntheses of the tetradentate ligands in this study involved stepwise incorporation of fragments containing the donor atoms from readily available starting materials (see Experimental Section). In general, a key intermediate compound was prepared from two fragments, followed by condensation with a third fragment to produce the ligand either in protected or unprotected form. The stepwise synthetic approach was necessitated by the unsymmetrical nature of the ligands.

The geeH ligand was prepared in modest yields with use of different protecting groups (see Schemes I and II). In each synthetic method, the key compound was a 2-bromoethyl amide. In the case of the phthalyl protecting group (Scheme I), protected acid **1** was converted to acid chloride with PCl_5. The protected acid chloride was treated with 2-bromoethylamine to give protected 2-bromoethylamide (**2**). The condensation of **2** and phthalyl-protected 2-mercaptoethylamine was initially attempted with NaOEt in ethanol. However, yields of protected geeH (**3**) were low (<25%). An unwanted byproduct appeared to be a 2-substituted oxazoline (by ^{13}C NMR). Such intramolecular cyclization products are known to result from 2-haloethyl amides under basic conditions.[30,31] When the condensation was performed in a mixture of Me_2SO and water, the yield of **3** was increased to 50%. The protected geeH (**3**) was deprotected with hydrazine hydrate to give geeH (**4**). Attempts to isolate **4** as an acid salt were erratic, so the ligand was reacted in situ with $CoCl_2 \cdot 6H_2O$ in the presence of $NaNO_2$ to give $Co(gee)(NO_2)_2$.

Scheme I

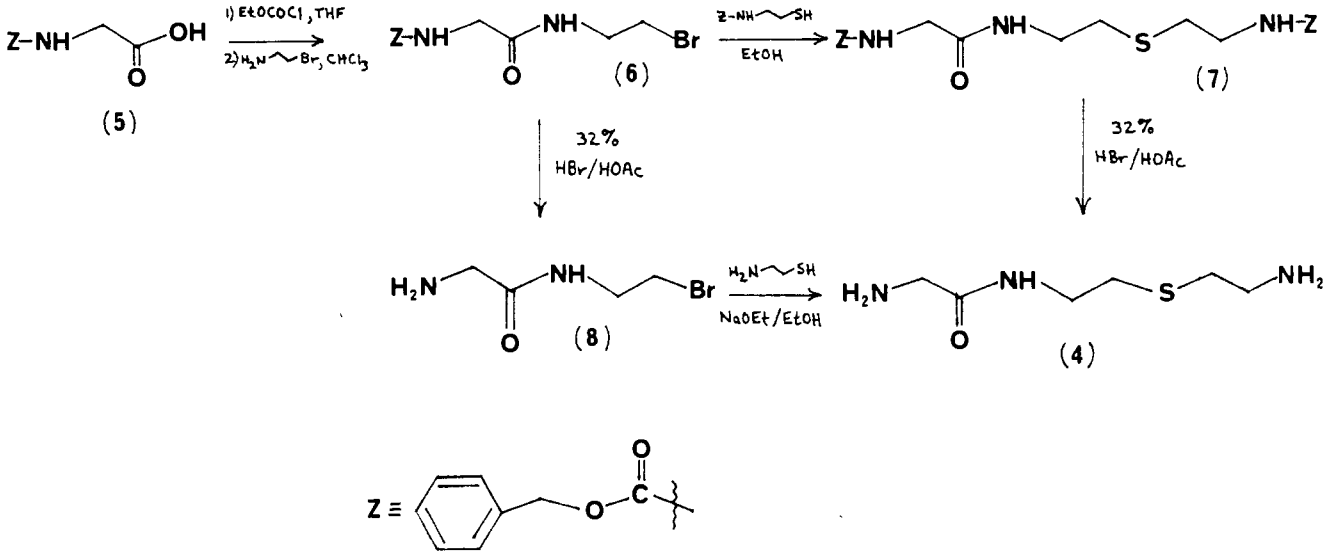


The (benzyloxy)carbonyl (Z) protecting group was also employed (see Scheme II). Protected acid **5** was converted to the 2-bromoethyl amide **6** via the mixed-anhydride method. The protected geeH ligand **7** was formed by treating **6** with Z-protected 2-mercaptoethylamine. Free geeH·2HBr (**4**·HBr) was obtained by the action of 32% HBr/HOAc on **7**. $Co(gee)(NO_2)_2$ was then obtained by combining the free ligand with $CoCl_2 \cdot 6H_2O$ and $NaNO_2$. Alternatively, **6** could be deprotected to give the 2-bromoethyl amide **8**, which was treated with 2-mercaptoethylamine to give geeH (**4**). The geeH formed in this manner was reacted in situ with $CoCl_2 \cdot 6H_2O$ and $NaNO_2$ to give $Co(gee)(NO_2)_2$. The methods involving protected ligands **3** and **7** were preferred, however, since the protected compounds could be isolated and freed from undesired byproducts (such as the oxazoline).

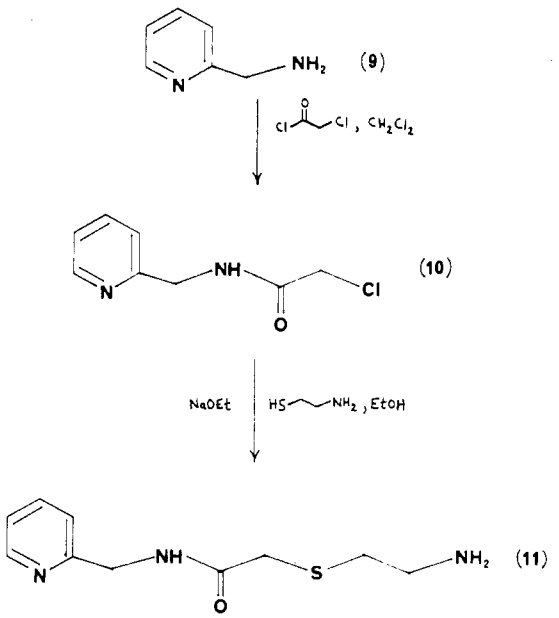
The key compound for the synthesis of pygeH was *N*-((2-pyridyl)methyl)-2-chloroacetamide (or its hydrochloride) (**10**), which was prepared by condensing 2-(aminomethyl)pyridine (**9**) with chloroacetyl chloride (see Scheme III). 2-Mercaptoethylamine was condensed with **10** to give pygeH (**11**), which was reacted in situ with $CoCl_2 \cdot 6H_2O$ and $NaNO_2$ to form $Co(pyge)(NO_2)_2$. This ligand and its Co(III) complex were previously prepared by Toprak[32] et al. in a synthetic

(28) (a) Buckingham, D. A. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; Vol. 1, p 3. (b) Freeman, H. C. In ref 28a, p 121.
(29) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257.
(30) Frump, J. A. *Chem. Rev.* **1971**, *71*, 483.
(31) Derner, O. C.; Ham, G. E. "Ethylenimine and Other Aziridines"; Academic Press: New York, 1969.
(32) Toprak, M.; Gellert, E.; Bekaroglu, O. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 372.

Scheme II



Scheme III



scheme requiring five steps. The overall yield of Co(III) complex was 3%, and a reaction requiring 15 days was among the synthetic steps. Our method represents a vast improvement in that overall yields of Co(III) complex of 60% were routinely obtained in a two-step synthesis which may be performed within 1 day.

The ligands egeH (**13**) and egpy (**14**) were prepared in situ by alkylating *N*-(2-aminoethyl)-2-mercaptoacetamide (**12**) with the appropriate alkylating agent (see Scheme IV). The dinitro Co(III) complexes of these ligands were then obtained similarly as for geeH and pygeH.

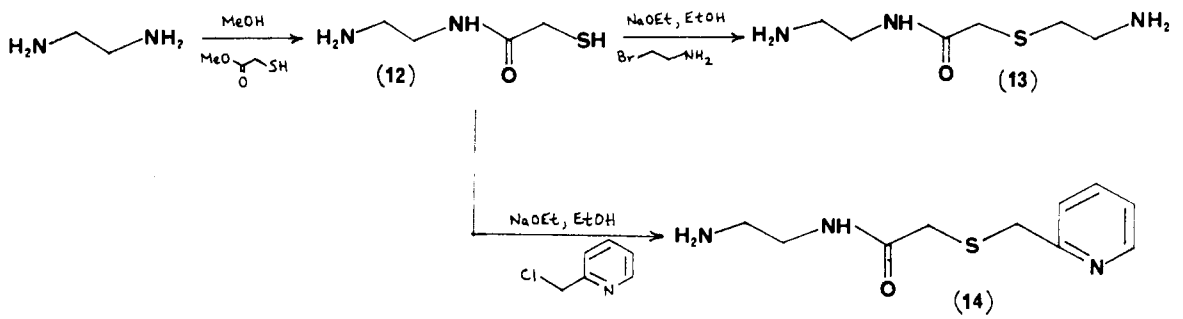
Table II. Bond Lengths in $Co(gee)(NO_2)_2 \cdot H_2O$

type	length, Å	type	length, Å
Co-S	2.233 (1)	C(5)-C(6)	1.510 (4)
Co-N(1)	1.994 (2)	C(5)-O(5)	1.261 (3)
Co-N(2)	1.902 (2)	N(1)-C(1)	1.474 (3)
Co-N(3)	1.957 (2)	N(2)-C(4)	1.473 (3)
Co-N(4)	1.941 (2)	N(3)-C(6)	1.474 (3)
Co-N(5)	1.920 (2)	N(2)-C(5)	1.318 (3)
S-C(2)	1.812 (3)	N(4)-O(1)	1.210 (3)
S-C(3)	1.822 (3)	N(4)-O(2)	1.222 (4)
C(1)-C(2)	1.513 (3)	N(5)-O(3)	1.232 (3)
C(3)-C(4)	1.518 (3)	N(5)-O(4)	1.222 (3)

Interconversion Reactions of the Cobalt Complexes. $CoL(NO_2)_2$ (where L = gee, ege, and pyge) complexes were smoothly converted to violet $CoLCl_2$ by the action of concentrated HCl. For L = egpy, a green solution resulted, from which no solid product could be obtained. Upon addition of water, the green color changed to pink, indicating that reduction to Co(II) may have occurred.

The crude $CoLCl_2$ (L = gee, ege, and pyge) complexes gave satisfactory elemental analyses only after purification in boiling methanol to remove excess HCl. The purified $CoLCl_2$ complexes were converted to various $CoLX_2$ (where X = NO_2, N_3, CN; X_2 = ox, tn) complexes, which were characterized by elemental analysis and spectroscopic techniques (see below). The complexes eluted as single spots on silica gel (TLC) in two different solvent systems (3:1 acetone–water and absolute methanol).

Visible Spectra. The visible spectra of the dinitro, diazido, and oxalato complexes are similar to those for analogous cobalt complexes of NNNN[33] and NSSN[17,34] donor sets. The as-



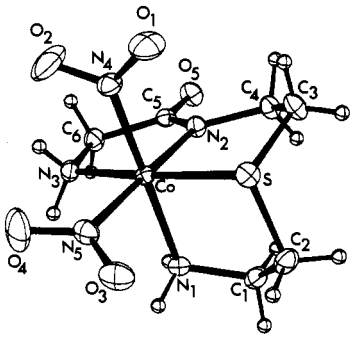


Figure 2. Molecular structure and numbering scheme for Co(gee)$(NO_2)_2 \cdot H_2O$ (the water molecule of hydration is not illustrated).

signment of the gross stereochemistry about the metal is not possible, however, since often there is very little difference (<10 nm) between the λ_{max} values for cis-α and cis-β isomers. Visible spectra for dichloro complexes were not obtained due to rapid hydrolysis. Sometimes the cis-α configuration has been assigned on the basis of the characteristic tetragonal splitting of the $^1T_1$ state. No splitting was observed in the absorption spectra of the complexes in this study, but this absence cannot be confidently used to prove the geometrical arrangement of the ligands.

NMR Spectra. In general, the ^1H NMR spectra of the cobalt compounds were too complex to meaningfully assign their overall stereochemistry. However, in the case of complexes with ligands containing a pyridine moiety, the H-2(py) resonance (at δ 8.5–9.0) was well separated from other resonances. Only one such resonance (broad pseudodoublet) appeared to be present in these compounds.

^{13}C NMR spectra of several complexes, including representative compounds for each ligand, were analyzed and also indicated that only one isomer was present in each case. Ligands ranged from the strongly electron-donating CN^- to the weakly donating Cl^- and oxalato. The chemical shifts were dependent on the ligands as has been observed in the cobaloxime system.[35] In each case, only one set of ligand resonances was observed; if more than one isomer were present, at least some resonances would probably be different as has been observed in the ^{13}C NMR spectra of diethylenetriamine cobalt complexes.[36] However, the geometry of the isomer present cannot be deduced from the spectra.

X-ray Crystallography. A single-crystal X-ray diffraction study of Co(gee)$(NO_2)_2 \cdot H_2O$ was performed. The numbering scheme for non-hydrogen atoms is given in Figure 2, and bond lengths and angles may be found in Tables II and III.

The gee ligand adopts the expected cis-β geometry about the Co atom. The bond lengths in the ligand are within expected values. The Co–S distance of 2.233 (1) Å is very similar to the values of 2.22 and 2.24 Å found in *cis-β*-[Co(ete)NO_2Cl]Cl[37] (where ete = 1,9-diamino-3,7-dithianonane) and 2.244 and 2.248 Å found in *u-fac*-[Co(daes)$_2$]Cl_3[38] (where daes = bis(2-aminoethyl) sulfide). The Co–N(1) (trans to NO_2) distance of 1.994 (2) Å is almost identical with that found in the above-mentioned ete complex (1.99 Å) as is the Co–N(3) (trans to S) distance of 1.957 (2) Å, which is 1.96 Å in the ete complex. The Co–N(2) distance of 1.902 (2) Å is about halfway between the values of 1.87[39] and 1.92 Å found in different studies of the *mer*-[Co(glygly)$_2$] anion complex (glygly = glycylglycine dianion). The Co–NO_2 bond lengths of 1.941 (2) (trans to NH_2) and 1.920 (2) Å (trans to amide) are within the usual values found in such Co(III) complexes.[41]

Table III. Bond Angles in Co(gee)$(NO_2)_2 \cdot H_2O$

type	angle, deg	type	angle, deg
S-Co-N(1)	87.44 (6)	N(1)-Co-N(2)	90.46 (8)
S-Co-N(2)	87.80 (6)	N(1)-Co-N(3)	91.75 (8)
S-Co-N(3)	172.58 (6)	N(1)-Co-N(4)	177.36 (8)
S-Co-N(4)	91.44 (6)	N(1)-Co-N(5)	87.97 (8)
S-Co-N(5)	94.51 (7)	N(2)-Co-N(3)	84.83 (8)
Co-S-C(2)	99.04 (9)	N(2)-Co-N(4)	91.88 (8)
Co-S-C(3)	97.65 (8)	N(2)-Co-N(5)	177.14 (9)
C(2)-S-C(3)	103.8 (1)	N(3)-Co-N(4)	89.66 (9)
Co-N(2)-C(4)	122.8 (1)	N(3)-Co-N(5)	92.83 (9)
Co-N(2)-C(5)	117.4 (2)	N(4)-Co-N(5)	89.74 (9)
C(4)-N(2)-C(5)	119.4 (2)	Co-N(4)-O(1)	122.0 (2)
Co-N(1)-C(1)	114.6 (1)	Co-N(4)-O(2)	119.9 (2)
Co-N(3)-C(6)	111.5 (2)	O(1)-N(4)-O(2)	118.1 (2)
N(1)-C(1)-C(2)	109.3 (2)	Co-N(5)-O(3)	119.8 (2)
N(2)-C(4)-C(3)	109.7 (2)	Co-N(5)-O(4)	121.3 (2)
N(3)-C(6)-C(5)	111.2 (2)	O(3)-N(5)-O(4)	118.9 (2)
C(1)-C(2)-S	111.5 (2)	N(2)-C(5)-C(6)	114.8 (2)
S-C(3)-C(4)	113.5 (2)	N(2)-C(5)-O(5)	126.2 (2)
		O(5)-C(5)-C(6)	118.9 (2)

Bond angles within the complex reveal some distortion within the five-membered chelate rings, particularly about the S atom. The Co–S–C(2) and Co–S–C(3) angles are only 99.04 (9) and 97.65 (8)°, respectively, while the C(2)–S–C(3) angle is 103.8 (1)°. These angles represent a considerable departure from expected tetrahedral values. The trigonal amide nitrogen, N(2), is slightly unsymmetrically bound to the Co atom with Co–N(2)–C(4) and Co–N(2)–C(5) angles of 122.8 (1) and 117.4 (2)°, respectively.

Conclusion

Of the four tetradentate ligands synthesized in this study, three appear to form relatively stable Co(III) complexes. The ligands are by design unsymmetrical, and it is therefore even more difficult than usual to assign a stereochemistry to the complexes by spectroscopic methods although ^{13}C NMR spectroscopy strongly points to the formation of only one isomer. The X-ray structure of one complex, Co(gee)$(NO_2)_2$, establishes the geometry of this complex as the expected cis-β mode. The conversion of this complex to the dichloro derivative and its reconversion to the same dinitro compound is suggestive that the cis-β geometry is preserved in the other gee complexes. The formation of only one geometric isomer is an advantage compared to the situation in NNNN systems such as trien. Although stable complexes are formed by such ligands, numerous isomers of the resulting complexes can be formed, particularly in reactions with unsymmetrical bidentate ligands such as amino acids and peptides. Preliminary studies indicate that, even with unsymmetrical bidentate ligands, the isomer problem with the NSNN systems studied here is greatly diminished.

Studies are in progress to establish the stereochemistry of some of the other complexes in these series and to determine the applicability of these complexes to peptide hydrolysis and peptide synthesis. Studies of ligand substitution reactions could also be of interest particularly in view of the presence of an amide group in the ligands, although we do not plan to pursue such studies at this time.

Acknowledgment. This work was supported by NIH Grant GM 29225. We are grateful for this support.

(33) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1965**, *4*, 45.
(34) Bosnich, B.; Kneen, W. R.; Phillip, A. T. *Inorg. Chem.* **1969**, *8*, 2567.
(35) Stewart, R. C.; Marzilli, L. G. *Inorg. Chem.* **1977**, *16*, 424.
(36) Ha, F. C.; House, D. A.; Blunt, J. W. *Inorg. Chim. Acta* **1979**, *33*, 269.
(37) Murray-Rust, J.; Murray-Rust, P. *Acta Crystallogr., Part B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2606.
(38) Hammershøi, A.; Larsen, E.; Larsen, S. *Acta Chem. Scand., Part A* **1978**, *A32*, 501.
(39) Barnet, M. T.; Freeman, H. C.; Buckingham, D. A.; Hsu, I.-N.; van der Helm, D. *J. Chem. Soc., Chem. Commun.* **1970**, 367.
(40) Gillard, R. D.; McKenzie, E.; Mason, R.; Robertson, G. B. *Nature (London)* **1966**, *209*, 1347.
(41) Herak, R; Juranic, N.; Celap, M. B. *J. Chem. Soc., Chem. Commun.* **1980**, 660.

Note Added in Proof.

The crystal structure of $[Co(NH_3)_2(L\text{-ala-gly-gly})]$ has been reported (Evans, E. J.; Hawkins, C. J.; Rodgers, J.; Snow, M. R. *Inorg. Chem.* **1983**, *22*, 34). The Co–N(amide) bond lengths average about 1.87 and 1.86 Å. A recent review on transition-metal complexes containing a metal–amide bond has appeared (Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385).

Registry No. **2**, 87156-80-7; **3**, 87156-81-8; **4**·2HBr, 87156-84-1; **5**, 1138-80-3; **6**, 87156-82-9; **7**, 87156-83-0; **8**·HBr, 87156-85-2; **9**, 3731-51-9; **10**, 46120-62-1; **12**, 62-47-5; Co(gee)$(NO_2)_2$·H_2O, 87156-86-3; Co(gee)Cl_2·HCl, 87156-88-5; Co(gee)$(N_3)_2$, 87156-89-6; Co(pyge)$(NO_2)_2$, 87205-49-0; Co(pyge)Cl_2, 87156-90-9; Co(pyge)$(N_3)_2$, 87156-91-0; Co(pyge)(ox), 87174-19-4; Co(pyge)$(CN)_2$, 87156-92-1; [Co(pyge)(tn)]Cl_2, 87156-93-2; Co(ege)$(NO_2)_2$, 87156-87-4; Co(ege)Cl_2, 87156-94-3; Co(ege)$(N_3)_2$, 87156-95-4; Co(ege)(ox), 87156-96-5; Co(ege)$(CN)_2$, 87156-97-6; Co(egpy)$(NO_2)_2$, 87156-98-7; *N*-(2-mercaptoethyl)phthalimide, 4490-75-9; 2-bromoethylamine hydrobromide, 2576-47-8; triethylamine, 121-44-8; 2-[((benzyloxy)carbonyl)amino]ethanethiol, 68642-94-4; 2-mercaptoethylamine hydrochloride, 156-57-0; chloroacetyl chloride, 79-04-9; hydrazine hydrate, 7803-57-8; 2-picolyl chloride hydrochloride, 6959-47-3; methyl thioglycolate, 2365-48-2; ethylenediamine, 107-15-3; phthalylglycyl chloride, 6780-38-7.

Supplementary Material Available: Crystal structure analysis report and tables of anisotropic thermal parameters for the non-hydrogen atoms, parameters for the hydrogen atoms, R_f values, calculated and observed structure factor amplitudes, and short contacts involving hydrogen atoms (23 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

Synthesis and Characterization of Anionic Halogen-Containing Rhodacarboranes. Crystal and Molecular Structure of the Hydrogen-Bonded Ion Pair $[HPPh_3][closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$

LIMIN ZHENG,[1] R. THOMAS BAKER, CAROLYN B. KNOBLER, JOHN A. WALKER, and M. FREDERICK HAWTHORNE*

Received March 1, 1983

The title compound was obtained in low yield from the reaction of *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (**1**) and BBr_3 and was characterized by an X-ray diffraction study. Red crystals of $[HPPh_3][closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]\cdot 1.5C_6H_6$, $[HPPh_3][\mathbf{3}]\cdot 1.5C_6H_6$, were triclinic, space group $P\bar{1}$, with $a = 12.591$ (5) Å, $b = 13.299$ (4) Å, $c = 17.568$ (5) Å, $\alpha = 111.77$ (2)°, $\beta = 94.41$ (3)°, $\gamma = 61.24$ (3)°, and $Z = 2$. The structure was solved by conventional heavy-atom techniques to a final discrepancy index of $R = 0.046$ for 6054 independent observed reflections. The rhodacarborane anion is pseudooctahedral about the rhodium atom, and the phosphonium cation is near the rhodium-bound bromine atoms with Br···H distances of 3.06 (6) and 2.70 (6) Å. It was suggested on the basis of NMR spectral data and solubility properties that ion pairing may also be significant for $[HPPh_3][\mathbf{3}]$ in solution. It was found that K[18-crown-6][**3**] could be prepared in high yield from the anionic rhodacarborane K[18-crown-6][*closo*-3,3-$(Ph_3P)_2$-3,1,2-$RhC_2B_9H_{11}$] and bromoform. The iodo analogue of $\mathbf{3}^-$ could be isolated as the $(n\text{-}C_4H_9)_4N^+$ salt, in high yield, from the reaction of *closo*-3-Ph_3P-3,3-NO_3-3,1,2-$RhC_2B_9H_{11}$, $(n\text{-}C_4H_9)_4NI$, and NaI in dichloromethane/water. The chloro analogue of complex **3** could be prepared as the $[Et_4N]^+$ salt from the reaction of the 16-electron complex $[Et_4N][closo\text{-}3\text{-}Ph_3P\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ (generated in situ) with CH_2Cl_2 in 60% yield.

Introduction

We recently reported the reaction of *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (**1**) with benzoyl peroxide, which afforded the asymmetric (phosphine)rhodacarborane dimer $[closo\text{-}(Ph_3P)RhC_2B_9H_{11}]_2$ (**2**) in modest yields (ca. 40%).[2] In order to conduct a more thorough study of the chemical reactivity and catalytic properties of this dimeric complex we sought a more efficient conversion of **1** to **2** employing Lewis acids (A), as shown in eq 1.

$$(Ph_3P)_2(H)RhC_2B_9H_{11} + A \rightarrow {}^1/_2H_2 + APPh_3 + [(Ph_3P)RhC_2B_9H_{11}]_2 \quad (1)$$

While the reactions of **1** with diborane and boron trifluoride did indeed proceed as per eq 1,[3] that with boron tribromide produced in low yield a bromine-containing (phosphine)-rhodacarborane that was shown by X-ray crystallography to be the ionic complex $[HPPh_3][closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$, $[HPPh_3][\mathbf{3}]$. Subsequent to the characterization of $[HPPh_3][\mathbf{3}]$ improved synthetic methods were developed that allowed the isolation of $\mathbf{3}^-$ with a variety of supporting counterions in good yields. Moreover, it was found that the iodo and chloro analogues of $\mathbf{3}^-$ could be easily prepared. Herein we report the details of these studies.

Results and Discussion

The reaction of complex **1** with a 5-fold excess of BBr_3 in benzene at 25 °C for 48 h yielded a mixture of products. Column chromatography on Florisil with benzene elution yielded first a purple fraction and then a red fraction. The purple fraction was shown to consist of complex **2** and an unknown component. Red crystals could be isolated from the red fraction and were ultimately shown to be the ionic complex $[HPPh_3][closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]\cdot 1.5C_6H_6$, $[HPPh_3][\mathbf{3}]\cdot 1.5C_6H_6$, by X-ray crystallography (vide infra). Although the elemental analyses correctly indicated the composition of $[HPPh_3][\mathbf{3}]$, the recognition of the ionic nature of this complex was clouded by its ready solubility in benzene and an osmometric molecular weight measurement in benzene that showed that this salt must exist as a tight ion pair in this solvent. As the mass, IR, and NMR spectra did not fully elucidate the nature of this red complex, an X-ray diffraction study was undertaken and showed the complex to be $[HPPh_3][\mathbf{3}]\cdot 1.5C_6H_6$.

The molecular structure of $[HPPh_3][\mathbf{3}]$ is shown in Figure 1, and some relevant bond distances and angles are presented

(1) On leave from East China Institute of Textile Science and Technology, Shanghai, The Peoples Republic of China.
(2) Baker, R. T.; King, R. E., III; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266.
(3) The reaction of complex 1 with diborane and boron trifluoride produced **2** in yields of 74 and 60%, respectively. Baker, R. T. Ph.D. Thesis, University of California, Los Angeles. Numbering of compounds in this paper: **1**, *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$; **2**, $[closo\text{-}(Ph_3P)RhC_2B_9H_{11}]_2$; **3**, $[closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}Br_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$; **4**, *closo*-3,3-$(Ph_3P)_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$; **5**, *closo*-3-$Ph_3P$-3,3-$NO_3$-3,1,2-$RhC_2B_9H_{11}$; **6**, $[closo\text{-}3,3\text{-}(Ph_3P)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$; **7**, $[closo\text{-}3\text{-}Ph_3P\text{-}3,3\text{-}I_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$.

0020-1669/83/1322-3350$01.50/0