Registry No. I, 50774-04-4; II, 52610-73-8; III, 52393-38-1; IV, 52393-39-2; V, 52393-40-5; VI, 52540-78-0; VII, 52483-66-6; $[Co(tmNH_2)_2]Cl_3$, 52393-41-6; C, 52393-58-5; D, 52438-81-0; A·2HCl, 52393-59-6; A·2HBr, 52393-60-9.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Synthesis of a Novel Pentacoordinate Glyoxime-Based Ligand and Preparation of Its Chlorocobalt(III) Complex[1a]

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Received March 20, 1974 AIC401901

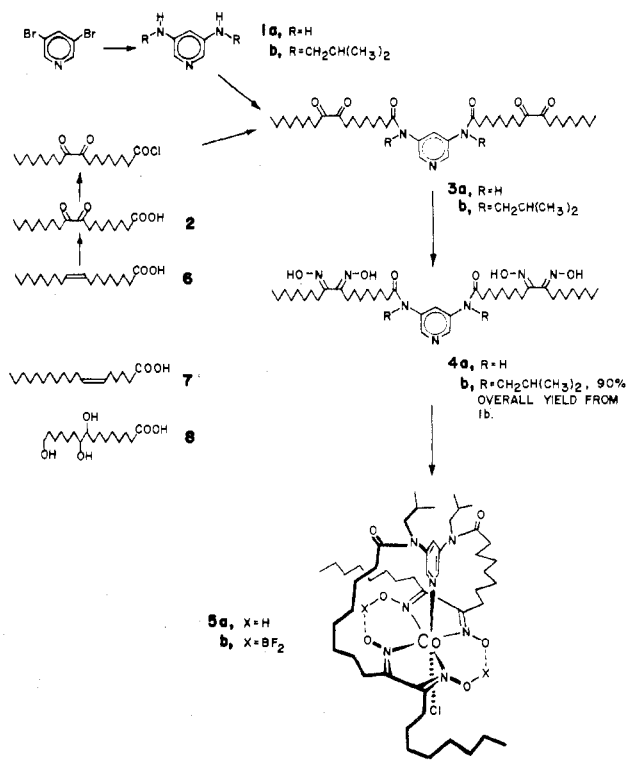
The synthesis and properties of the pentadentate, "basket-like" ligand *N,N'*-diisobutyl-*N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine (**4b**) are described, as well as the preparation and properties of its chlorocobalt(III) complex **5a**.

Cobaloximes have proved to be useful models for vitamin B_{12}.[2] In vitamin B_{12}, however, the fifth ligand, a 5,6-dimethylbenzimidazole, is covalently bound to the tetracoordinate planar corrin ligand. Several other important biological systems also consist of a metal atom with a square-planar, tetradentate N_4-coordinating ring system and another nitrogen-coordinating heterocyclic base as the axial fifth ligand, notable examples being the cobalt in vitamin B_{12}[3] and the iron in cytochrome *c*, hemoglobin, and myoglobin.[4]

Discussion and Results

Because of the dearth of synthetic pentacoordinate ligands and the interest[5] in the synthesis of these ligands as models for biological systems, we wish to report the simple, high-yield synthesis of the N_5-pentacoordinate ligand **4b**. Ligand **4b** has three major advantages over simpler glyoxime ligands. First, the ligand is quite soluble in most organic solvents. Ligand **4a** was also synthesized, but it was found to be quite insoluble. Introduction of the isobutyl groups on the amide nitrogens in **4b** markedly improves the solubility. A second advantage of ligand **4b** over simpler glyoximes is that, in a complex with the glyoxime functionalities of **4b** coordinated to the metal, the pyridine part of the ligand is held in the proximity of one of the axial coordination sites. This feature was designed into the system to help counteract the tendency of some metal dimethylglyoxime complexes to be either four- or six-coordinate, but not five-coordinate. If a metal complex of **4b** is only tetracoordinate, the pyridine base would be uncoordinated; but, it would still be held very close to its prospective axial coordination site. Thus, when another ligand approaches the opposite axial coordination site, the pyridine base of **4b** would be favorably disposed to form the hexacoordinate species.[5d,5f,6]

Scheme I



The third advantage of a ligand like **4** is the extreme flexibility offered for the synthesis of other modified ligands. Other fatty acid fragments could easily be substituted for the oleic acid derivative **2** in the synthetic scheme. In fact, fatty acids were used in the synthesis in order to take advantage of the functionality already correctly positioned by

(1) (a) Taken from the Ph.D. thesis of H. P. J., M.I.T., May 1974. (b) Camille and Henry Dreyfus Teacher-Scholar grant recipient; Alfred P. Sloan Fellow, 1973–1975. (c) National Science Foundation Predoctoral Fellow, 1970–1973; Goodyear Fellow 1973–1974.

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(6) The uv–visible spectra of the nickel(II) complex of ligand **4b** indicate that the pyridine is not coordinated. The nickel is tetracoordinate, as it is in most nickel(II) glyoxime complexes. The cobalt(III) complex **5a** of ligand **4b**, however, appears to involve coordination of the pyridine to the cobalt; *vide infra*.

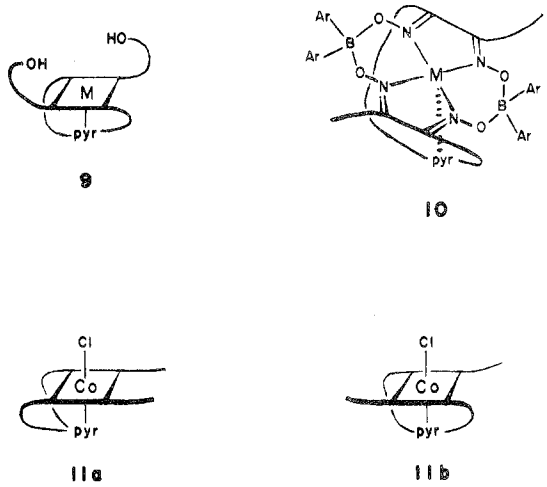
nature; thus, the cheap, readily available starting materials facilitated syntheses of the desired complex structures. For example, if petroselenic acid 7[7] is used instead of oleic acid **6** in the synthetic Scheme I, the resultant metal complex **11** would have the axial pyridine joined to the planar glyoxime system by a bridge of four methylene units instead of the seven methylene bridge in **4**. Thus, by simply substituting petroselenic acid for oleic acid, the complex **11** can be made to have a tighter "basket."[5b] Similarly, use of aleuritic acid[8] **8** instead of oleic acid in a modification of Scheme I would give a complex represented by **9**. In this case the functionality at the end of the aliphatic chains allows for closure of a bridge over the top of the complex to "put a handle on the basket" or to "turn the basket into a cage," depending on one's personal taste in metaphors. This second bridge over the top could be useful for the positioning of some functionality in close proximity to the metal or for introduction of steric hindrance.[9]

Even after the ligand **4b** has been coordinated to give complex **5a**, the system allows for even more flexibility *via* replacement of the protons in the oxime ring of **5a** by disubstituted boron.[10] When cobaloxime **5a** is treated with excess boron trifluoride etherate, the brown $(BF_2)_2$ adduct **5b** can be isolated by preparative tlc (1:1 ethyl acetate:hexane; R_f 0.7).[11] Other boron compounds can be used instead of boron trifluoride etherate to give boron adducts, such as **10**[10a,b] in which the aryl groups present steric obstructions above and below the glyoxime plane.[12]

All of these modifications are based on the glyoxime ligand **4**; however, the precursor bis(α-diketone) **3** can be used to prepare other completely different classes of ligands. For example, our preliminary studies indicate that it is possible to prepare a dihydrooctaaza[14]annulene[12a,13,14] macrocycle from **3b**, thus giving a pentadentate, basket-like dihydrooctaaza[14]annulene ligand.

Ligand **4b** forms a sort of "basket"[5b] around the cobalt atom in **5a**. This cobaloxime **5a** can exist as two possible isomers differing in whether the two chains that connect the axial pyridine to the planar glyoxime ligands come up on the same (as depicted in **11a**) or opposite (as depicted in **11b**) sides of the complex to give either C_s or C_2 symmetry, respectively. Thus far, attempts to identify complex **5a** as being either one of the two isomers or a mixture of both isomers have been unsuccessful. In Scheme I complex **5a** is shown as the C_2 symmetry form, although it could also be the C_s symmetry form.

Chart I



The synthesis of **1** was notable only for the brutal conditions required. The coupling of **1** and **2** to form the diamide **3** was complicated by the very low nucleophilicity of the nitrogens in **1**. This low nucleophilicity thwarted many of the usual amide-forming sequences, such as dicyclohexylcarbodiimide. Most attempted syntheses of the acid chloride of **2** were also unsuccessful due to the sensitivity of the α-diketone group to acid. Finally, a method utilizing thionyl chloride plus 1-2 equiv of pyridine in THF as solvent was found to give instantaneous formation of the acid chloride from the acid under the desired very mild, neutral conditions.[15] This thionyl chloride–pyridine–THF procedure appears to be a very convenient method for preparation of the acyl chloride of acid-sensitive acids. This reaction (complete in seconds) is much faster than use of the Lee reagent[16] (usually several hours). The reaction also proceeds at lower temperatures than those needed for the Lee reagent (usually refluxing carbon tetrachloride). As with all multidentate ligands, there is a possibility of polymer formation when complexes of **4b** are prepared. In order to minimize this possibility complexes such as **5a** are formed under fairly high dilution conditions.

Experimental Section

General Data. Melting points are uncorrected and were taken on a Thomas-Hoover capillary melting point apparatus. Uv spectra were taken on a Cary 14 recording spectrophotometer. Infrared spectra were taken on a Perkin-Elmer 237B spectrophotometer. Nmr spectra were obtained on a Varian T-60 spectrometer. Mass spectra were taken on an Hitachi Perkin-Elmer RMU-6 mass spectrometer. Elemental analyses were done by the M.I.T. Microchemical Laboratory and Midwest Microlab, Ltd.

3,5-Dibromopyridine was prepared by the method of Maier-Bode:[17] mp 110.5–110.7° [lit.[17] mp 110°]; uv max (C_2H_5OH) 277 mμ (ε 3210), shoulder 273 mμ (ε 2690), shoulder 285 mμ (ε 2500); ir (KBr disk) 2975, 1690, 1530, 1400, 1110, 1085, 1010, 880, 760, and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.03 (t, 1, J = 0.9 Hz, Ar H) and 8.60 (d, 2, J = 0.9 Hz, Ar H).

3,5-Diaminopyridine (1a) was prepared from 3,5-dibromopyridine by the method of Maier-Bode:[17] mp 110.5–111.5° [lit.[17] mp 110–111°]; nmr (DMSO-d_6) δ 4.8(4, NH_2), 6.1 (1, Ar H), and 7.3 (2, Ar H).

Anal. Calcd for $C_5H_7N_3$: C, 55.03; H, 6.47; N, 38.50. Found: C, 54.94; H, 6.51; N, 38.44.

(7) Obtained from Sigma Chemical Co., St. Louis, Mo. 63178.
(8) Obtained from Mann Research Laboratories, Inc., a subsidiary of B-D Laboratories, Inc., New York, N. Y. 10006.
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(11) Compound 5b was identified by ^1H and ^{19}F nmr and comparison of spectra with those of 5a.
(12) This concept of steric hindrance perpendicular to the plane of the complexing ligand has been exploited with notable success recently: (a) J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 95, 5757 (1973); (b) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *ibid.*, 95, 7868 (1973).
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(16) J. B. Lee, *J. Amer. Chem. Soc.*, 88, 3440 (1966).
(17) H. Maier-Bode, *Ber. Deut. Chem. Ges. B*, 69, 1534 (1936).

N,N'-Diisobutyl-3,5-diaminopyridine (1b). An 8.48-g sample of $CuSO_4 \cdot 5H_2O$ (0.034 mol) was dissolved in 100 ml of water and combined with 36.31 g of 3,5-dibromopyridine (0.153 mol) and 200 ml of isobutylamine (1.98 mol) (Aldrich Chemical Co.) in a stainless steel autoclave. The autoclave was flushed with N_2 and, after sealing, was heated to 150° for 37 hr. After adding 500 ml of ether to the cooled solution, the organic phase was washed with 50% NaOH, H_2O, and saturated NaCl solution. An 11.2-g amount of *N,N'*-diisobutyl-3,5-diaminopyridine (0.051 mol) was collected by distillation through a 30-cm Holtzman column: bp 184° (0.05 mm); mp 78–79.5°; uv max (C_2H_5OH) 228 mμ (ε 32,000) and 326 mμ (ε 7340); ir (CCl_4) 1215 (s), 1475, 1510, 1600 (s), 2875, 2930, 2965 (s), 3250 (2), and 3410 (w); nmr ($CDCl_3$) δ 0.95 (d, 12, *J* = 7 Hz, H_3C), 1.83 (m, 2), 2.87 (t, 4, *J* = 6 Hz, CH_2N), 4.09 (broad t, 2, NH), 6.11 (t, 1, *J* = 2.4 Hz, Ar H), and 7.45 ppm (d, 2, *J* = 2.4 Hz, Ar H); mass spectrum (70 eV) *m/e* (rel intensity) 221 parent (90), 179 (75), 178 (100), 56 (23), 50 (21).

Anal. Calcd for $C_{13}H_{23}N_3$: C, 70.54; H, 10.47; N, 18.98. Found: C, 70.56; H, 10.65; N, 18.73.

Also isolated during the distillation was *N*-isobutyl-3-amino-5-bromopyridine: bp 160° (0.05 mm); nmr ($CDCl_3$) δ 1.0 (d, 12, *J* = 8 Hz, H_3C), 1.8 (m, 1), 2.91 (t, 2, *J* = 6 Hz, CH_2N), 4.71 (broad, 1, NH), 7.02 (broad, 1, Ar H), and 8.0 ppm (broad, 2, Ar H); mass spectrum indicating the presence of one bromine atom (70 eV) *m/e* (rel intensity) 230 parent (21), 228 parent (23), 187 (96), 185 (100).

9,10-Diketostearic acid (2) was prepared from oleic acid by the procedure of Sharpless, *et al.*:[18] mp 85.0–85.5°; uv max (95% C_2H_5OH) 270 mμ (ε 47.2) and 425 mμ (ε 18.2) [lit.[19] mp 85–86°; uv max 270 mμ (log ε = 1.7)]; ir (KBr disk) 1690 and 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.90 (3, H_3C), 1.32 (m, 22, CH_2), 2.25 (m, 2, CH_2COOH), 2.75 (t, 4, *J* = 7 Hz, CH_2COCO), and 7.1 ppm (s, 1, COOH).

Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32. Found: C, 69.19; H, 10.63.

N,N'-Bis(9,10-diketostearoyl)-3,5-diaminopyridine (3a). A 205-mg sample of 9,10-diketostearic acid, 2 (0.656 mmol), and 177 mg of pyridine (2.24 mmol) in 6 ml of dry THF were cooled under N_2 in an ice bath. A 44-μl amount of thionyl chloride (0.612 mmol) was added, resulting in immediate formation of a white precipitate (pyridinium hydrochloride). A solution of 33 mg of 3,5-diaminopyridine (1a) (0.302 mmol) in 168 mg of pyridine (2.12 mmol) was added, forming more precipitate. After stirring of the slurry at room temperature for 2 days,[20] ether and water were added; some of the off-white solid did not dissolve. After removing the aqueous phase, the solid was filtered off and recrystallized from 50 ml of ethanol to give 153 mg of 3a (0.22 mmol, 72% yield). The solid 3a is insoluble in chloroform, ethanol, DMSO, acetonitrile, DMF, and acetone at room temperature, but it is soluble in pyridine; mp 169.5–169.8.

Anal. Calcd for $C_{41}H_{67}N_3O_6$: C, 70.55; H, 9.68; N, 6.02. Found: C, 70.66; H, 9.84; N, 5.97.

N,N'-Bis(9,10-diketostearoyl)-3,5-diaminopyridine (3a) (Alternate Method–Lee Reagent). A 4.26-g sample of 9,10-diketostearic acid, 2 (13.6 mmol), and 7.45 g of triphenylphosphine (28.4 mmol) in 75 ml of dry reductant-free carbon tetrachloride were refluxed under nitrogen for 70 hr. The solvent was "rotovapped" off and 125 ml of dry benzene was added. To this orange-yellow slurry was added 0.32 g of 3,5-diaminopyridine, 1a (2.93 mmol), dissolved in 25 ml of pyridine. After stirring of the mixture at room temperature for 2 days, 10 ml of methanol was added to quench any leftover acid chloride. The material is usually not isolated; rather, it is used directly for the preparation of 4a.

N,N'-Bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine (4a). A 1.48-g sample of 3a (2.12 mmol) was dissolved in 50 ml of pyridine. After addition of 4.0 g of hydroxylamine hydrochloride (57.5 mmol), the solution was heated at reflux for 30 min and then stirred at room temperature overnight. After addition of ether, the organic phase, which contained suspended solids, was washed with aqueous HCl until the washes remained acidic. After washing of the mixture with saturated NaCl solution, the ether phase was filtered; and the dark solids so obtained were dissolved in pyridine. Some insoluble sediment was removed by filtration of the dark pyridine solution. The addition of 3 volumes of ethanol precipitated 1.14 g of white solid 4a (1.51 mmol, 71% yield): mp 243–245° dec; nmr (pyridine-d_5) δ 0.85 (6, H_3C), 1.35 (36, CH_2), 1.82 (8, $CH_2CC(NOH)$), 2.4 (4, $CH_2C(O)N$), 3.1 (8, $CH_2C(NOH)$), 7.60 (1, Ar H), 9.15 (2, Ar H), 11.0 (2, C(O)NHAr), and 14.4 ppm (4, NO*H*) (all peaks are broadened to about 7 Hz).

Anal. Calcd for $C_{41}H_{71}N_7O_6$: C, 64.96; H, 9.44; N, 12.93. Found: C, 64.48; H, 9.57; N, 12.93.

N,N'-Diisobutyl-*N,N'*-bis(9,10-diketostearoyl)-3,5-diaminopyridine (3b). A solution of 5.65 g of 9,10-diketostearic acid, 2 (18.1 mmol), and 4.57 g of pyridine (57.8 mmol) in 90 ml of dry, freshly distilled THF was cooled in an ice bath. Upon addition of 1.13 ml of thionyl chloride (15.72 mmol) a white precipitate (py·HCl) immediately formed. To this slurry was added a solution of 1.43 g of *N,N'*-diisobutyl-3,5-diaminopyridine, 1b (6.47 mmol), in 6 ml of dry THF followed by 6.0 ml of dry pyridine. The slurry was stirred for 2 days,[20] after which time it was quenched by adding enough methanol to dissolve the solid and give a clear yellow solution. An analytical sample was prepared by preparative tlc (1:1 ethyl acetate:hexane): nmr ($CDCl_3$) δ 0.95 (d, 18, *J* = 4.5 Hz, H_3C), 1.34 (m, 48, CH_2), 2.14 (t, 4, *J* = 7 Hz, $CH_2C(O)N$), 2.75 (t, 8, *J* = 6 Hz, CH_2COCO), 3.57 (d, 4, *J* = 7 Hz, $CH_2N(Ar)CO$), 7.63 (broad s, 1, Ar H), and 8.58 ppm (broad s, 2, Ar H).

Usually this product is not isolated; but, rather, after removal of the solvent on a rotary evaporator at 20°, the resulting yellow solid is used directly in the next step.

N,N'-Diisobutyl-*N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine (4b). The yellow solid mixture of 3b and pyridinium hydrochloride prepared above was dissolved in 140 ml of dry pyridine. A 25.44-g amount of hydroxylamine hydrochloride (366 mmol) was added and the solution was refluxed for 1.1 hr. After cooling of the mixture in an ice bath, 500 ml of ether was added.

The organic phase was washed with water ten times and finally with saturated aqueous NaCl. The organic phase was "rotovapped" down with 43 g of silica gel. The product was purified by elution on a 7.6 cm × 60 cm column of silica gel[21] (1:1 ethyl acetate:hexane; R_f 0.8). The product was removed from the silica gel with ethyl acetate and then dried overnight at 40° under high vacuum to give 5.08 g of the white, waxy solid 4b (90% yield from 1b): mp 139.5–141.0°; uv max (EtOH) 228 mμ (ε 34,700); ir (KBr disk) 1635 cm^{-1} (C=N); nmr (DMSO-d_6) δ 0.83 (d, 18, *J* = 7 Hz, H_3C), 1.34 (m, 48, CH_2), 2.02 (broad t, 4, $CH_2C(O)N$), 2.5 ($CH_2C(NOH)$, partially obscured by DMSO-d_5), 3.39 (d, 4, *J* = 7 Hz, $CH_2N(Ar)CO$), 8.00 (broad s, 1, Ar H), 8.75 (broad s, 2, Ar H), and 11.48 ppm (s, 2, =NO*H*).

Anal. Calcd for $C_{49}H_{87}N_7O_6$: C, 67.63; H, 10.08; N, 11.27. Found: C, 67.55; H, 10.21; N, 11.28.

Chloro[*N,N'*-diisobutyl-*N,N'*-bis(9,10-hydroxyiminooximinatostearoyl)-3,5-diaminopyridine]cobalt(III) (5a). A 51.9-mg sample of ligand 4b (0.060 mmol) and 0.056 ml of a 1.00 *N* NaOH solution were dissolved in 50 ml of ethanol. A second solution was prepared by dissolving 14.2 mg of $CoCl_2 \cdot 6H_2O$ (0.060 mmol) in 50 ml of ethanol. The complex was formed under high-dilution conditions by simultaneously adding, at the rate of 8–10 drops/min, these two solutions to 100 ml of well-stirred ethanol in 55° heating bath. The resulting golden solution was taken to dryness at 40° on a rotary evaporator. The material was purified by preparative tlc (R_f 0.6; 4% ethanol in $CHCl_3$) to give 46.7 mg of complex 5a (0.049 mmol, 81% yield) as a brown glass which was quite soluble in many organic solvents, such as CH_2Cl_2, ether, C_2H_5OH, pyridine, and CCl_4. A high-resolution mass spectrum failed to yield any useful information: uv max (C_2H_5OH) 255 mμ (ε 31,500), 222 mμ (ε 37,000); ir (CCl_4) 1675 (C=N) and 3480 cm^{-1} (O–H); nmr ($CDCl_3$) (all peaks broadened to about 7 Hz) δ 0.90 (d, 18, H_3C), 1.30 (48, CH_2), 2.02 (4, $CH_2C(O)N$), 2.49 (8, $CH_2C(NOH)$), 3.52 (4, $CH_2N(Ar)CO$), 7.57 (1, Ar H), 8.24 (2, Ar H), and 17.8 ppm (2, –O–H···O–, 100 Hz wide).

Anal. Calcd for $C_{49}H_{85}ClCoN_7O_6$: C, 61.14; H, 8.90; Cl, 3.68; Co, 6.12; N, 10.18; mol wt 962. Found: C, 61.50; H, 9.00; Cl, 3.54; Co, 5.6; N, 10.00; mol wt 960 in acetone.

Acknowledgment. We are grateful to the National

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(20) The long reaction times for acylation of 1a and 1b are necessary because 1a and 1b are both stronger bases than pyridine; therefore, they precipitate out as the hydrochlorides, thus giving rise to heterogeneous reaction conditions.

(21) Woelm silica gel for dry-column chromatography supplied by Waters Associates, Framingham, Mass. 01701.

Science Foundation (Grant GP-30485X), Hoffmann-La Roche, Chevron Research, and the Mobil Foundation for support of this research.

Registry No. Isobutylamine, 75-64-9; 3,5-dibromopyridine, 625-92-3; *N,N'*-diisobutyl-3,5-diaminopyridine, 52165-28-3; *N*-isobutyl-3-amino-5-bromopyridine, 52165-29-4; 9,10-diketostearoyl chloride, 52165-30-7; 3,5-diaminopyridine, 4318-78-9; *N,N'*-bis(9,10-diketostearoyl)-3,5-diaminopyridine, 52165-31-8; *N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine, 52165-32-9; *N,N'*-diisobutyl-*N,N'*-bis(9,10-diketostearoyl)-3,5-diaminopyridine, 52165-33-0; *N,N'*-diisobutyl-*N,N'*-bis(9,10-dihydroxyiminostearoyl)-3,5-diaminopyridine, 52165-34-1; chloro[*N,N'*-diisobutyl-*N,N'*-bis(9,10-hydroxyiminooxyminatostearoyl)-3,5-diaminopyridine]cobalt(III), 52216-80-5.

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Mass Spectrometric Study of Polydentate Schiff Base Coordination Complexes. II. Cobalt(II), Nickel(II), and Copper(II) Complexes of *N,N'*-Bis(salicylidene)heptanediamine, *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl)amine, *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl) Ether, and *N,N'*-Bis(salicylidene)-3,3'-bis(aminopropyl) Sulfide

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Received April 3, 1974 AIC402200

Positive and negative ion mass spectra have been measured for the coordination compounds of cobalt(II), nickel(II), and copper(II) with SALHTDA,[1] SALDPT,[2] SALDAPE,[3] and SALDAPS.[4] Intense molecular ions were detected in both the positive and negative ion mass spectra. Fragmentation patterns are reported and many decomposition reactions are confirmed by metastable transitions. Ionization potentials of the uncomplexed ligand and the metal complexes are reported. The measured ionization potentials reflect the nature of the bonding of the ligand to the metal ion. Parent molecular negative ions are formed *via* direct electron capture at near-zero electron energies.

Introduction

The significance of metal coordination compounds in biological systems is recognized.[5] In many instances metal coordination compounds of Schiff bases have been suggested as models to describe energy transfer in naturally occurring systems. In such instances the coordination sphere about the metal ion is believed to play an important role in determining the nature of the model system.

In a similar way the importance of Schiff base ligand donor atoms in influencing the ionization potentials and mass spectral fragmentation patterns has been demonstrated.[6] In previous studies[6] tetradentate model ligand systems were investigated. The strength of the donor atoms (N and O) was found to influence directly the magnitude of the ionization potential of the metal-Schiff base complex and the formation of various parent molecular negative ions.

In this paper positive and negative ion mass spectra and ionization potentials of cobalt(II), nickel(II), and copper(II) complexes of potentially pentadentate Schiff base ligands are reported. The donor atom containing chain that joins azomethine linkages is found to influence the ionization potential. In addition evidence is presented regarding the formation of five-coordinate species in the gas phase.

Experimental Section

Mass spectra and ionization potentials for positive ions and resonance-capture appearance potentials for negative ions were obtained using an Hitachi Perkin-Elmer RMU-7 mass spectrometer described earlier.[7] Samples were introduced into the mass spectrometer using the direct insertion probe. Samples were heated to 190–210° to effect sublimation. The ion source temperature was maintained at about 10–20° above the solid inlet temperature. Upon removal from the mass spectrometer, all samples, except Co(SALDAPE), showed no evidence of thermal decomposition. In the case of Co(SALDAPE) decomposition appeared to begin at about 200°, so spectra and ionization measurements were carried out at about 180–190°. Data acquisition for the energetic measurements was accomplished using the MADCAP IV data acquisition program and a Digital PDP8/I computer. The electron energy scales were calibrated with Xe and Kr for positive ions (ionization potentials 12.13 and 13.99 eV, respectively)[8] and SF_6 for negative ions (0.08 eV).[9] Mass calibration at 50 eV and at other electron energies was accomplished using perfluorokerosene.[7]

Ionization efficiency curves for the parent molecular ions were parallel to the curve for the calibrant ions Xe^+ and Kr^+ so the semilogarithmic method[10] was used. The data in Table V represent the averages of no less than 10 separate measurements, and the quoted precision represents one standard deviation. It is anticipated that the accuracy of the ionization potentials is better than 0.5 eV. The vertical ionization potential measured here will deviate from the true adiabatic value if the potential energy representations for the neutral complex, ML, and the singly charged complex ion, ML^+, differ significantly. In such an instance the measured electron impact value would represent the formation of ML^+ in an excited electronic and/or vibrational state.

Complexes of SALDPT were prepared by the method of Sacconi and Bertini.[11] The other complexes were synthesized by a general procedure which involved adding a stoichiometric amount of an appropriate metal(II) acetate dissolved in ethanol to a refluxing

(1) SALHTDA = *N,N'*-bis(salicylidene)heptanediamine.
(2) SALDPT = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl)amine.
(3) SALDAPE = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl) ether.
(4) SALDAPS = *N,N'*-bis(salicylidene)-3,3'-bis(aminopropyl) sulfide.
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