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Vitamin B_{12} and Coenzyme B_{12} Models. 1. Synthesis and Physical Characterization of Alkyl- and (Non-alkyl)cobalt(III) Complexes of 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime

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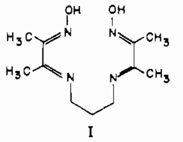
A quadridentate tetraaza ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime, has been synthesized by the condensation of *o*-phenylenediamine with diacetyl monoxime. The free ligand is neutral and coordinates with cobalt through its nitrogen donors in the equatorial position with the loss of one of the oxime protons with the concomitant formation of an intramolecular hydrogen bond. The dichloro and dibromo complexes have been synthesized by the direct reaction of the ligand with the respective cobalt(II) halide hexahydrate. If use is made of the axial lability of the dibromo complex [Co(DODOHbzo)Br_2], pseudohalogeno complexes [YCo(DODOHbzo)Br], where Y = CN^-, SCN^-, or N_3^-, Lewis base complexes [LCo(DODOHbzo)Br]A, where L = pyridine or imidazole and A = ClO_4^- or PF_6^-, and the so-called cyanocobalamin models [CNCo(DODOHbzo)L]Br, where L = pyridine or imidazole, have been synthesized. Alkylcobalt(III) complexes [RCo(DODOHbzo)L]ClO_4, where R = CH_3^-, $C_2H_5^-$, $(CH_3)_2CH^-$, $C_6H_5CH_2^-$, or $C_6H_{11}^-$ and L = pyridine, imidazole, or triphenylphosphine, which serve as vitamin B_{12} coenzyme models, have been synthesized by the oxidative-addition reaction of the in situ generated Co(I) form of the dibromo complex with RX in an inert atmosphere. Thus eleven (non-alkyl)cobalt(III) complexes and nine alkylcobalt(III) complexes have been synthesized and characterized by elemental analysis, conductivity measurements, magnetic susceptibility, and infrared, ^1H NMR, and electronic spectroscopy. Evidence for the formation of hydrogen bonding in the complexes has been obtained by synthesizing the BF_2 derivative of the dibromo complex by replacing the hydrogen-bonded proton by the BF_2 group. In solution the axially bound halide ions in the dihalo complexes are replaced by the solvent molecules whereas in pseudohalogeno and Lewis base complexes the axial ligands remain intact with the metal ion. All complexes are diamagnetic except the pseudohalogeno complexes, which exhibit residual paramagnetism. All (non-alkyl)cobalt(III) complexes except [SCNCo(DODOHbzo)Br] undergo tetragonal distortion as evidenced by the splitting of the $^1T_{1g}$ and $^1T_{2g}$ levels of the pseudooctahedral symmetry and have been assigned a D_{4h} microsymmetry in analogy with the crystal field model of Wentworth and Piper. The ligand field parameters such as Dq^{xy}, Dq^z, and the tetragonal splitting parameter, D_t, have been computed, and the ligand field strength of the equatorial ligand is comparable with that of other macrocyclic ligands. The alkylcobalt(III) complexes exhibit Co–C CT transitions in the region (21.5–23.8) × 10^3 cm^{-1} and the energy of this transition decreases with increasing field strength of the axial base trans to the organic ligand.

Introduction

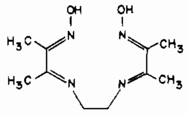
The isolation of vitamin B_{12} coenzyme by Barker in 1958[1] and the subsequent discovery by Lenhert and Hodgkin[2] that it contains an adenosyl group linked to cobalt by a direct Co–C σ-bond indicated for the first time the occurrence of organometallic reactions in biological systems. While vitamin B_{12} coenzyme and methylcobalamin are recognized to play important and distinctive biochemical roles, they are not accessible in quantity for studies under nonenzymatic conditions. This stimulated the search for simpler models, complexes that contain a stable Co–C bond axial to a planar equatorial ligand, which could simulate the reactions of the cobalt atom in the complicated corrin. The discovery of the vitamin B_{12}-like chemical properties of complexes of bis(dimethylglyoximato)cobalt, i.e., the cobaloximes, by Schrauzer and Kohnle in 1964,[3] demonstrated the feasibility of this approach and in turn stimulated the search for other models. The coordinating atoms of the equatorial ligand do not have to be necessarily nitrogen but may be substituted partially by oxygen. Subsequently, numerous other cobalt chelates were tested as possible vitamin B_{12} models, notably the propylene- and ethylenediimine complexes of diacetyl monoximes, and Schiff bases derived from salicylaldehyde and acetylacetone, particularly by Costa and his co-workers.[4]

Among the models reported thus far, Costa's cobalt chelates of I,[5] its ethylenediamine analogue II,[5b,6] and the related ligand III,[7] are the only monoanionic ligands like the naturally occurring corrin. However, although I was shown by electrochemical measurements to exhibit oxidation–reduction potentials closely resembling those of vitamin B_{12},[8] Schrauzer warned[9] that it is not a bona fide vitamin B_{12} model because, in contrast to vitamin B_{12}, on reductive alkylation it is easily overreduced, giving rise to neutral dialkyl derivatives, first described by Costa and coworkers.[10] The cobalt complex of ligand II, on the other hand, cannot be readily reduced to the Co(I) form under conditions applicable to vitamin B_{12} or to the cobaloximes. According to Schrauzer et al.,[6] this is due to their higher Co(II)/Co(I) reduction potential; reduction to the Co(I) derivatives was possible in nonaqueous solvents such as diglyme and pyridine, with sodium amalgam as the reductant.



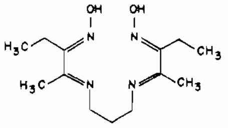
I

(DOH)$_2$pn



II

(DOH)$_2$en



III

C$_2$(DOH)$_2$ pn

As small structural changes have profound effects on the reactivity of the cobalt atom, it thus appeared desirable to study

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a model ligand that would be free of these disadvantages and contain a through-conjugated unsaturated ligand system that would render it more similar to vitamin B_{12}. We considered it likely that the replacement of the propylenediimine moiety in I by 1,2-phenylenediimine could produce a ligand whose cobalt complexes would be useful vitamin B_{12} model compounds.[11] We are glad to introduce a monoanionic conjugated quadridentate ligand with nitrogen as the atoms that coordinate with cobalt in the equatorial plane, leaving the axial sites vacant for coordination by a variety of monodentate ligands thereby paving the way for the synthesis of a number of (non-alkyl)- and alkylcobalt(III) complexes which can serve as models for B_{12} and its coenzyme. This paper highlights only the synthesis and physical characterization of representative alkyl- and (non-alkyl)cobalt(III) complexes of the new model as part of the research program we have initiated to design a new model and to study its suitability as a biological mimic of the primary bioinorganic system by establishing a quantitative comparison with coenzyme B_{12} and other well-studied models.

Experimental Section

Materials. Cobalt(II) chloride hexahydrate (E. Merck) and cobalt(II) bromide hexahydrate (Hopkin & Williams Ltd. LR) were used as such for the synthesis of the complexes.

Ethyl methyl ketone, isopropyl alcohol, and petroleum ether (all BDH, LR) were distilled once before use. Nitromethane, sodium borohydride, triphenylphosphine, and imidazole (BDH) were used as such. Boron trifluoride etherate (BDH) was distilled just before use.

Sodium perchlorate (E. Merck), sodium fluoroborate (Riedel), potassium hexafluorophosphate, benzimidazole, 1-methylimidazole, methyl iodide and iodocyclohexane supplied by Fluka were used as such. Pyridine (Sarabhai M. Chemicals) was refluxed over potassium hydroxide and distilled. Ethyl iodide (Loba-Chemie) and 40% hydrobromic acid (SD's) were used as received.

Diacetyl monoxime (2,3-butanedione monoxime) was synthesized by the method of Semon and Damerell.[12]

DMSO-d_6 (99.9 atom % D) and $CDCl_3$ (100 atom % D) supplied by Sigma and DMSO-d_6 (99.5 atom % D) supplied by Stobler Isotope Chemicals were dried over 4-Å molecular sieves and used to record proton NMR spectra.

Synthesis of 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime, (DOH)$_2$bzo. 2,3-Butanedione monoxime (20.22 g, 0.2 mol) and freshly recrystallized *o*-phenylenediamine (10.81 g, 0.1 mol) were dissolved in 100 mL of warm water and refluxed for an hour whereupon bright yellow needles separated out. The solution was cooled to 5 °C, filtered and washed with cold methanol (0 °C) and recrystallized from warm ethanol, giving bright yellow needles (mp 176 °C). Yield: 80%. Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 61.30; H, 6.61; N, 20.42. Found: C, 61.02; H, 6.70; N, 19.84.

Synthesis of the Complexes. [Co(DODOHbzo)Br$_2$] (1). Method A. The free ligand, (DOH)$_2$bzo (5.485 g, 0.02 mol) and cobalt(II) bromide hexahydrate (6.5374 g, 0.02 mol) were dissolved in 100 mL of dry acetone with stirring. The dark green solution was filtered to remove undissolved particles and kept overnight at room temperature (30 °C). The dark green crystals, which separated out, were filtered and washed repeatedly with dry acetone or dry methanol followed by diethyl ether to get the green microcrystalline compound. Yield: 40%.

Method B. The ligand (5.485 g, 0.02 mol) and $CoBr_2{\cdot}6H_2O$ (6.5374 g, 0.02 mol) were dissolved in 100 mL of hot dry acetone. The solution was filtered and stirred vigorously for about 5 min. The resulting fine green crystalline compound, which separated out, was filtered rapidly through a G3 sintered funnel and washed with dry acetone followed by diethyl ether and dried under vacuum over anhydrous calcium chloride. Yield: 25%. Anal. Calcd for $C_{14}H_{17}N_4O_2Br_2Co$: C, 34.17; H, 3.48; N, 11.39; Co, 11.98; Br, 32.48. Found: C, 33.78; H, 3.21; N, 10.57; Co, 11.27; Br, 32.31.

[Co(DODOHbzo)Cl$_2$] (2). The ligand (5.485 g, 0.02 mol) and $CoCl_2{\cdot}6H_2O$ (4.758 g, 0.02 mol) were dissolved in 100 mL of hot dry acetone or ethanol. The green solution formed was filtered and the filtrate treated by any one of the two methods outlined for the synthesis of [Co(DODOHbzo)Br$_2$] to obtain the gray-green dichloro complex. Yield: 30%. Anal. Calcd for $C_{14}H_{17}N_4O_2Cl_2Co$: C, 41.71; H, 4.25; N, 13.90; Cl, 17.59; Co, 14.62. Found: C, 40.98; H, 4.06; N, 13.42; Cl, 17.38; Co, 13.94.

[Co(DODOHbzo)I$_2$] (3). To the green solution of the ligand (4.758 g, 0.02 mol) and $CoCl_2{\cdot}6H_2O$ (4.758 g, 0.02 mol) in 100 mL of hot acetone was added 2 mL of a saturated aqueous solution of KI, yielding a dark brown solution. This, on slow evaporation at room temperature (30 °C), yielded a dark brown crude product. This was filtered, dried in air, and recrystallized twice from cold acetone. The brown diiodo complex was dried in vacuum. Yield: 20%. Anal. Calcd for $C_{14}H_{17}N_4O_2I_2Co$: C, 28.69; H, 2.92; N, 9.56; Co, 10.06. Found: C, 28.71; H, 3.12; N, 9.83; Co, 10.26.

[SCNCo(DODOHbzo)Br] (4) and [N$_3$Co(DODOHbzo)Br] (5). A brown solution of [Co(DODOHbzo)Br$_2$] (2.46 g, 5 mmol) in 100 mL of hot aqueous methanol (1:5 v/v) was treated with potassium thiocyanate (0.4859 g, 5 mmol) (for **4**) and sodium azide (0.325 g, 5 mmol) (for **5**) in 2 mL of water with stirring. The volume of the solution was then reduced to one-fourth by slow evaporation and refrigerated at 0 °C overnight. The resulting dark brown crystalline compound, which separated out, was filtered through a G3 sintered funnel and washed once with cold water followed by cold (0 °C) alcohol, recrystallized from hot methanol twice, and dried under vacuum. Yield for **4**: 60%. Anal. Calcd for $C_{15}H_{17}N_5O_2SBrCO$: C, 38.31; H, 3.64; N, 14.89; Co, 12.53. Found: C, 37.68; H, 3.51; N, 15.02; Co, 12.33. Yield for **5**: 65%. Anal. Calcd for $C_{14}H_{17}N_7O_2BrCo$: C, 37.02; H, 3.77; N, 21.59; Co, 12.97. Found: C, 37.17; H, 3.91; N, 22.11; Co, 12.69.

[CNCo(DODOHbzo)Br] (6). An aqueous solution of potassium cyanide (0.3256 g, 5 mmol) was added to a solution of [Co(DODOHbzo)Br$_2$] (2.46 g, 5 mmol) in 100 mL of hot aqueous methanol (1:5 v/v) with stirring. The small amount of KCN that precipitated out was redissolved by addition of a little water. The resulting light brown solution was refluxed on a water bath for 2 h, the volume of the solution was then reduced to one-fourth by slow evaporation on a water bath, and the solution was cooled to room temperature (30 °C). The resulting brownish yellow compound, which separated out, was filtered, washed with cold water followed by dry alcohol, and dried in air. Recrystallization from DMF–methanol (1:1 v/v) yielded the brownish yellow crystalline cyano complex. Yield: 68%. Anal. Calcd for $C_{15}H_{17}N_5O_2BrCo$: C, 41.08; H, 3.91; N, 15.97; Co, 13.44. Found: C, 41.31; H, 3.97; N, 15.73; Co, 13.84.

[pyCo(DODOHbzo)Br]ClO$_4$ (7). To a solution of [Co(DODOHbzo)Br$_2$] (2.46 g, 5 mmol) in 100 mL of hot aqueous methanol (1:5 v/v) was added 2 mL of a saturated aqueous solution of sodium perchlorate followed by the addition of pyridine (0.395 g, 5 mmol) with stirring. The resulting yellowish brown crystalline compound, which separated out, was filtered immediately through a G3 sintered funnel, washed twice with dry methanol followed by diethyl ether, and dried under vacuum. Yield: 80%. Anal. Calcd for $C_{19}H_{22}N_5O_6BrClCo{\cdot}H_2O$: C, 37.49; H, 3.97; N, 11.51; Co, 9.68. Found: C, 37.21; H, 3.64; N, 11.20; Co, 9.94.

[IzCo(DODOHbzo)Br]PF$_6$ (8). This complex was synthesized by following the procedure employed for the synthesis of (**7**) with use of an alcoholic solution of imidazole (5 mmol) and an aqueous solution of potassium hexafluorophosphate. Brown microcrystals were obtained. Yield: 80%. Anal. Calcd for $C_{17}H_{21}N_6O_2BrPF_6Co$: C, 32.66; H, 3.39; N, 13.44; Co, 9.43. Found: C, 33.12; H, 3.45; N, 13.50; Co, 9.79.

[CNCo(DODOHbzo)py]Br (9). A solution of [Co(DODOHbzo)Br$_2$] (2.46 g, 5 mmol) in 100 mL of hot aqueous methanol (1:5 v/v) was treated with 2 mL of an aqueous solution of KCN (0.3256 g, 5 mmol). A small amount of water was added to redissolve the KCN that separated out. To this clear light brown solution was added pyridine (0.3955 g, 5 mmol), and the mixture was refluxed on a water bath for an hour. Evaporation of the solvent on a water bath led to the formation of a brownish yellow crystalline compound. When this was allowed to stand for 2 h at 30 °C, a large amount of product was formed, which was filtered, washed with water followed by dry alcohol, and dried in air. Recrystallization from DMF–CH_3OH (1:1 v/v) yielded an orange yellow crystalline compound. Yield: 60%. Anal. Calcd for $C_{20}H_{22}N_6O_2BrCo$: C, 46.44; H, 4.29; N, 16.25; Co, 11.39. Found: C, 46.31; H, 4.50; N, 16.13; Co, 12.00.

[CNCo(DODOHbzo)Iz]Br (10). This complex was synthesized by employing the procedure outlined for the synthesis of **9** with the use of 3 mL of a methanolic solution of imidazole (5 mmol). A yellow crystalline compound resulted. Yield: 60%. Anal. Calcd for $C_{18}H_{21}N_7O_2BrCo$: C, 42.7; H, 4.18; N, 19.37, Co, 11.64. Found: C, 43; H, 4.30; N, 20; Co, 12.

[Co{(DO)$_2$BF$_2$bzo}Br$_2$] (11). The hydrogen-bonded proton in [Co(DODOHbzo)Br$_2$] was replaced by BF$_2$ by reaction of the complex with boron trifluoride etherate by following the procedure of Schrauzer et al.[13]

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(11) In his studies on vitamin models with modified corrin, Murakami has emphasized the need to choose a set of model compounds with minimal (ideally one) alteration in structure to determine the structure–reactivity correlation. Therefore, designing a model system with more structural resemblances to the Costa model would be of great value since it enables a study of the structure–reactivity pattern with minimal structural parameters.

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A suspension of [Co(DODOHbzo)Br_2] (2.46 g, 5 mmol) in 100 mL of dry diethyl ether was stirred with a large excess of boron trifluoride etherate with a magnetic stirrer for 20 h in a stoppered round-bottom flask. The green dibromo complex turned chocolate brown as the reaction proceeded. The product was filtered, washed twice with aqueous methanol to remove any starting complex and then with dry alcohol followed by diethyl ether, and dried under vacuum. Yield: 85%. Anal. Calcd for $C_{14}H_{16}N_4O_2BF_2Br_2Co$: C, 31.15; H, 2.99; N, 10.38; Co, 10.92. Found: C, 30.97; H, 3.12; N, 10.13; Co, 10.31.

[CH_3Co(DODOHbzo)py]ClO_4 (12). The synthesis of the organocobalt derivatives was accomplished by the oxidative-addition reaction of the cobalt(I) form of the dibromo complex by following the procedure of Costa et al.[5b] and Schrauzer et al.[6]

A brown solution of [Co(DODOHbzo)Br_2] (4.92 g, 10 mmol) in 200 mL of hot aqueous methanol (1:5 v/v) taken in a 500-mL side-arm round-bottom flask was deaerated by flushing with oxygen-free dinitrogen for about 15 min at 10 °C. A slight excess of methyl iodide (2.8 g, 20 mmol) was added and stirred by a magnetic stirrer. An aqueous solution of a large excess of sodium borohydride was then added from a dropping funnel as quickly as possible in an atmosphere of dinitrogen. The brown solution became deep red with copious frothing and effervescence. The stirring was continued for another 5 min in an inert atmosphere and then for about 10 min in air.

The deep red solution was transferred to a 500-mL beaker and treated with a large excess of acetone with stirring. The unreacted $NaBH_4$ precipitated out and was filtered off, and the filtrate was again treated with acetone to precipitate any remaining unreacted $NaBH_4$ and filtered through a G3 sintered funnel. The red solution was then treated with 5 mL of a saturated aqueous solution of $NaClO_4$ followed by the addition of pyridine (0.791 g, 10 mmol). The resulting orange red solution was evaporated in a flash evaporator below 60 °C until crystals started separating out. The evaporation was continued until the volume was reduced to nearly 25 mL. The reaction vessel was kept at 0 °C, and the red crystalline compound was filtered. It was rapidly washed once with cold acetone (0 °C), dried under vacuum in the dark, and then recrystallized twice from chloroform–petroleum ether (1:4 v/v). The resulting yellow crystals were stored in the dark. Yield: 40%. Anal. Calcd for $C_{20}H_{25}N_5O_6ClCo{\cdot}H_2O$: C, 44.17; H, 5; N, 12.88; Co, 10.84. Found: C, 43.70; H, 5.11; N, 13.21; Co, 11.10.

[CH_3Co(DODOHbzo)Iz]ClO_4 (13), [CH_3Co(DODOHbzo)Me_2BIz]ClO_4 (14), and [CH_3Co(DODOHbzo)PPh_3]ClO_4 (15). These complexes were synthesized by employing the procedure outlined for the synthesis of **12** using a methanolic solution of [Co(DODOHbzo)Br_2] (10 mmol) and a methanolic solution of 10 mmol of the respective Lewis base. **13** was obtained as red crystals after being recrystallized thrice from chloroform–petroleum ether (1:10 v/v). Yield: 35%. Anal. Calcd for $C_{18}H_{24}N_6O_6ClCo{\cdot}H_2O$: C, 40.57; H, 4.92; N, 15.77; Co, 11.06. Found: C, 40.24; H, 5.10; N, 15.63; Co, 11.42. **14** was obtained as bright yellow microcrystals after being recrystallized from dry petroleum ether. Yield: 42%. Anal. Calcd for $C_{24}H_{40}N_6O_6Co{\cdot}H_2O$: C, 46.41; H, 6.82; N, 13.53; Co, 9.49. Found: C, 46.25; H, 6.66; N, 13.75; Co, 9.50.

15 was obtained as orange yellow crystals after being recrystallized twice from chloroform–petroleum ether (1:3 v/v). Yield: 45%. Anal. Calcd for $C_{33}H_{35}N_4O_6ClCo{\cdot}H_2O$: C, 56.94; H, 5.36; N, 8.05; Co, 8.47. Found: C, 56.85; H, 5.50; N, 7.98; Co, 8.78. All the compounds were stored in the dark.

[C_2H_5Co(DODOHbzo)py]ClO_4 (16), [C_2H_5Co(DODOHbzo)Iz]ClO_4 (17), [*i*-PrCo(DODOHbzo)py]ClO_4 (18), [C_6H_{11}Co(DODOHbzo)py]ClO_4 (19), and [$C_6H_5CH_2$Co(DODOHbzo)py]ClO_4 (20). These were synthesized by the procedure employed for the synthesis of **12**. In the case of **16** and **17** a slight excess of ethyl iodide (3.1 g, 20 mmol) and 10 mmol of the respective Lewis base were used. **16** was obtained as yellow crystals after being recrystallized thrice from chloroform–petroleum ether (1:5 v/v). Yield: 28%. Anal. Calcd for $C_{21}H_{27}N_5O_6ClCo{\cdot}H_2O$ (**16**): C, 45.21; H, 5.24; N, 12.55; Co, 10.56. Found: C, 44.96; H, 5.38; N, 12.08; Co, 10.23.

17 was obtained as orange red crystals after being recrystallized thrice from chloroform–petroleum ether (1:5 v/v). Yield: 25%. Anal. Calcd for $C_{19}H_{26}N_6O_6ClCo{\cdot}H_2O$: C, 41.73; H, 5.16; N, 15.37; Co, 10.78. Found: C, 42; H, 5.34; N, 15; Co, 11.

18 was synthesized as reddish yellow crystals by using isopropyl bromide (2.46 g, 20 mmol). Yield: 30%. Anal. Calcd for $C_{22}H_{29}N_5O_6ClCo{\cdot}H_2O$: C, 46.20; H, 5.46; N, 12.24; Co, 10.30. Found: C, 45.86; H, 5.52; N, 12.63; Co, 11.24.

19 was synthesized as red crystals after recrystallization from chloroform–petroleum ether (1:3 v/v) by using iodocyclohexane (4.2 g, 20 mmol). Yield: 43%. Anal. Calcd for $C_{26}H_{29}N_5O_6ClCo{\cdot}H_2O$: C, 50.37; H, 5.04; N, 11.30; Co, 9.50. Found: C, 50.81; H, 4.97; N, 11.48; Co, 10.

20 was synthesized as red glassy crystals after recrystallization from chloroform by using freshly distilled benzyl chloride (20 mmol). Yield: 45%. Anal. Calcd for $C_{26}H_{29}N_5O_6ClCo{\cdot}H_2O$: C, 50.37; H, 5.04; N, 11.30; Co, 9.51. Found: C, 50; H, 5.26; N, 11.25; Co, 9.87.

Physical Measurements. Conductance. The specific conductances of all non-alkyl derivatives were measured with 10^{-3} M solutions in electrochemically pure DMF at room temperature (30 °C) by using an ELICO Model CM-88 digital conductivity bridge and an ELICO Type CC-03 conductivity cell with a cell constant of unity. The conductances of alkyl derivatives were measured by using 10^{-3} M solutions in CH_3CN.

Magnetic Susceptibility. The magnetic susceptibilities of all compounds were measured by the Gouy method at room temperature (30 °C) on finely and uniformly ground solid samples. The sample tube was calibrated by using mercury tetrakis(thiocyanato)cobaltate(II) prepared by the method of Figgis and Nyholm.[14] The specific susceptibility χ^v of $Hg(NCS)_4$ was corrected to 30 °C by multiplying the decrease in χ^v by 0.628×10^{-2} per degree rise above 20 °C.[15] The measurement was repeated for each complex until consistent results were obtained. Corrections were applied for diamagnetic effects with Pascal constants.[16]

Electronic Absorption Spectra. UV and visible spectra were recorded either on a Hitachi Model 200-10 spectrophotometer with a Hitachi 200 recorder or on a Shimadzu UV 300 (Seisakusho Ltd. Kyoto, Japan) double-beam/difference/dual-wavelength recording spectrophotometer in the range 225–800 nm [(44.44–to 12.5) × 10^3 cm^{-1}] by using a matched pair of Teflon-stoppered quartz cells having a path length of 1 cm at 25 °C. The solutions were freshly prepared before recording.

Infrared Spectra. Infrared spectra were recorded in the solid state by using potassium bromide plates on a Perkin-Elmer 598 infrared spectrophotometer in the region from 4000 to 200 cm^{-1}. Spectroscopic grade KBr (Merck) was used to make KBr plates with the samples.

Nuclear Magnetic Resonance Spectra. 90-MHz ^1H NMR spectra were recorded on a Varian EM 390 NMR spectrometer. The NMR spectra of non-alkyl derivatives were recorded in DMSO-d_6 (99.5 atom % D or 99.9 atom % D) and those of alkyl derivatives in $CDCl_3$ (100 atom % D). Chemical shifts are reported downfield from an internal Me_4Si standard. All measurements were made at 20 °C.

Estimation of Carbon, Hydrogen, Nitrogen, and Cobalt. Carbon and hydrogen were estimated by using a Thomas CH-Analyzer 35 Carlo Erba 1106 instrument at the Central Drug Research Institute, Lucknow, India, and at the CIBA-GEIGY Research Centre, Bombay. Nitrogen was estimated by using a Coleman N-Analyzer 2y instrument at the CDRI, Lucknow, India. The cobalt content in the complexes was estimated by Kitson's method[17] (λ_{max} = 625 nm, ϵ = 1864 L mol^{-1} cm^{-1}).

Results

The elemental analyses of the ligand and the metal complexes already given in the Experimental Section are in reasonably good agreement with the proposed compositions.

Infrared Spectra. The infrared spectrum of the ligand shows no characteristic absorption assignable to either a C=O or NH_2 function. This confirms the formation of the ligand. The sharp band of medium intensity occurring at 1575 cm^{-1} is attributed to ν(C=N)[18] while a similar band at 1630 cm^{-1} is assigned to ν(C=C).[19] The strong as well as sharp band at 1220 cm^{-1} is due to the N–O stretching vibration.[18c,20]

The two broad medium-intensity bands appearing at about 3060 and 3200 cm^{-1} and the very weak band at 3280 cm^{-1} are due to the CH stretching vibrations.[21] The broad band at around 2900 cm^{-1} is assignable to ν(OH).[22] The very strong band of medium broadness at 1480 cm^{-1} and the weak band at 1430 cm^{-1} are assigned to the ring modes of ortho-disubstituted benzene.[18b] The

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Table I. Characteristic Infrared Absorption Bands (cm^{-1}) of (Non-alkyl)cobalt(III) Complexes[a]

	assignts						absorpn due to the axial ligands	
complex	ν(CH)	ν(OH)	ν(C=N)	ν(NO)	ν'(NO)	ν(Co—N)	band	assignts[b]
[Co(DODOHbzo)Br$_2$]	3040 w, b 3200 w, b	2900 b, s	1490 s, b	1220 vs, sp	1075 vs, sp	520 vs, sp		
[Co(DODOHbzo)Cl$_2$]	3040 b, w 3200 b, w	2420 b	1500 b	1225 vs, sp	1080 s, sp	515 vs, sp		
[Co(DODOHbzo)I$_2$]	3400 b	2380 b	1500 s, sp	1225 vs, sp	1090 vs, sp	525 vs, sp		
[Co[(DO)$_2$BF$_2$bzo]Br$_2$]	3450 s, b		1515 vs, sp	1210 vs, sp		510 vs, sp		
[CNCo(DODOHbzo)Br]		2400 b, w	1560 s, mb	1240 s, sp	1095 s, sp	525 s, sp	2160 s, sp 440 s, sp	ν(CN) ν(Co—C)
[SCNCo(DODOHbzo)Br]		2370 b, s	1545 s, mb	1230 s, sp	1090 s, sp	520 s, sp	2150 s, sp 740 s, sp	ν(CN) ν(CS)
[N$_3$Co(DODOHbzo)Br]		2400 b, s	1565 s, mb	1230 s, mb	1085 s, sp	520 s, sp	2030 s, sp 760 w, mb	ν_a(NNH) δ(NNN)
[(py)Co(DODOHbzo)Br]ClO$_4$	3040 sp, w		1560 s, sp	1240 vs, sp	1095 sh	525 s, sp	700 s, sp 425 w, sp	CH in-plane def CH out-of-plane def
[IzCo(DODOHbzo)Br]PF$_6$[c]	3300 vs, b 3120 s, sp	2380 w, b	1550 s, mb	1230 vs, sp	1090 s, sp	520 s, sp	1490 sh 1500 sh 920 w, sp	ring str mode of Iz ring mode of Iz
[CNCo(DODOHbzo)py]Br[d]	3440 s, b 2920 sp, w 3040 w, b		1560 s, sp	1230 vs, sp	1080 s, sp	525 s, sp	2145 s, sp	ν(CN)
[CNCo(DODOHbzo)Iz]Br[e,f]	3380 ms, b 3040 w, b 2980 w, mb		1550 vs, mb	1235 vs, sp	1090 s, mb	520 vs, sp	2130 s, sp	ν(CN)

[a] Medium: KBr disk. Abbreviations: s = strong, sp = sharp, vs = very strong, sh = shoulder, w = weak, b = broad, ms = medium strong, mb = medium broad. [b] For references, see text. [c] The ν(NH) of imidazole appears as a sharp and strong band at 3120 cm^{-1}. [d] The CH in-plane and out-of-plane deformation vibrations of the pyridine ring are not well-resolved. [e] The ν(NH) of imidazole overlaps with the ν(CH). [f] The ring modes of imidazole are not well resolved.

sharp bands of medium intensity at 1375 and 1445 cm^{-1} are due to the symmetric and asymmetric deformation vibrations, respectively, of the methyl groups.[18c]

The strong sharp bands appearing at 1260, 1180, and 1130 cm^{-1} are assignable to ν(C–C), ν(C–N), or the coupled vibration between these modes. The metal-sensitive strong as well as sharp band at 765 cm^{-1} may be attributed to C=N—O deformation vibration. The metal-dependent strong as well as sharp bands appearing at 990, 920, and 910 cm^{-1} can be ascribed to the deformation vibrational modes of the ligand in analogy to the infrared spectral studies on metalloporphyrins by Boucher and Katz[23] and by Ogoshi et al.[21] The infrared spectrum of the ligand is depicted in Figure 1A.

The characteristic infrared absorption bands of the ligand are shifted and lowered in intensity on complex formation, and new vibrational bands characteristic of the complex appear. The broad band of medium intensity occurring at 2900 cm^{-1} in the free ligand is shifted to 2400 cm^{-1} in [Co(DODOHbzo)Br$_2$]. This is attributed to the ν(OH) of the hydrogen bond.[22] The ν(N–O) of the dibromo complex is observed at 1220 cm^{-1} as in the free ligand. The symmetric and asymmetric deformation vibrations of the methyl groups occur at 1370 and 1435 cm^{-1}, respectively. An unique feature is the occurrence of new strong and sharp bands at 1075 and 520 cm^{-1} in the dibromo complex that are not found in the ligand. In agreement with the detailed infrared studies on cobaloximes by Yamazaki and Hohokabe,[18c] the former band is assigned to ν'(NO) and the latter to the ν(Co–N) vibrations. The infrared spectrum of [Co{(DO)$_2$bzoBF$_2$}Br$_2$] resembles that of the dibromo complex except for the occurrence of new bands characteristic of the BF$_2$ group and the absence of the ν(OH) and ν'(NO) bands. The weak band at 1175 cm^{-1} and the strong sharp band at 826 cm^{-1} are attributed to the B–O stretching modes while the weak bands occurring at 1026 and 1006 cm^{-1} are ascribed to the B–F stretching modes of the BF$_2$ derivative.[24] The infrared spectra of [Co(DODOHbzo)Br$_2$] and [Co{(DO)$_2$bzoBF$_2$}Br$_2$] are shown in parts B and C, respectively, of Figure 1.

In [CNCo(DODOHbzo)Br] ν(CN) occurs at 2160 cm^{-1}. This enhancement in the ν(CN) frequency of the cyanide ion upon coordination can be attributed to its better σ-donor and poorer π-acceptor properties.[25] In addition to ν(CN), the cyano complex exhibits a weak band of medium broadness at 440 cm^{-1}, absent in the free ligand. This band may therefore be ascribed to ν(Co–C). The value falls within the region, 600–300 cm^{-1}, of ν(M–C) vibration for various hexacyano complexes.[26] [SCNCo(DODOHbzo)Br] exhibits a very strong sharp band at 2150 cm^{-1} assignable to ν(CN) of the coordinated thiocyanate. The higher value of ν(CN) may probably be due to the formation of thiocyanato complex. The strong band of medium broadness at 740 cm^{-1} may be attributed to the ν(CS) vibration. The azido complex [N$_3$Co(DODOHbzo)Br] exhibits a strong absorption band at 2030 cm^{-1} and weak bands of medium broadness at 760 and 295 cm^{-1} assignable to the ν_a(NNN),[27] δ(NNN) and ν(Co–N)(N$_3$) vibrations respectively. The complex [CNCo(DODOHbzo)Iz]Br exhibits a sharp and strong band at 3120 cm^{-1} and a strong band of medium broadness at around 3400 cm^{-1} assignable to the ν(NH) and ν(CH) vibrations of the coordinated imidazole. The infrared spectral data for the (non-alkyl)cobalt(III) complexes are given in Table I.

The ν(O–H···O) band observed at 2400 cm^{-1} in the (non-alkyl)cobalt(III) complexes appears as a broad, weak band at 2400 cm^{-1} in both [CH$_3$Co(DODOHbzo)Iz]ClO$_4$ and [C$_2$H$_5$Co(DODOHbzo)Iz]ClO$_4$. The weak bands appearing at 1500 and 1445 cm^{-1} in these complexes are ascribed to the ring-stretching modes of imidazole.[28] The ring mode of coordinated imidazole appears at 945 and 940 cm^{-1} in [CH$_3$Co(DODOHbzo)Iz]ClO$_4$ and [C$_2$H$_5$Co(DODOHbzo)Iz]ClO$_4$, respectively. This observation is in conformity with that of Davis and Smith[29] that this vibration, which appears at 935 cm^{-1} in the free imidazole, is shifted to higher frequency upon complexation. The coordinated pyridine ring

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(25) The C≡N stretching frequency of the free cyanide ion occurs at 2080 cm^{-1}. Upon coordination to a metal, the ν(CN) shifts to higher frequency due to the better σ-donor and poorer π-acceptor properties of the cyanide ion. See: ref 26; p 259.

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(27) The azide ion in KN$_3$ exhibits ν_a(NNN) and ν_s(NNN) at 2041 and 1344 cm^{-1}, respectively. The azido complex [N$_3$Co(DODOHbzo)Br] exhibits a strong as well as a sharp absorption band at 2030 cm^{-1} assignable to ν_a(NNN), and the ν_s(NNN) vibration found in the free azide ion disappears.

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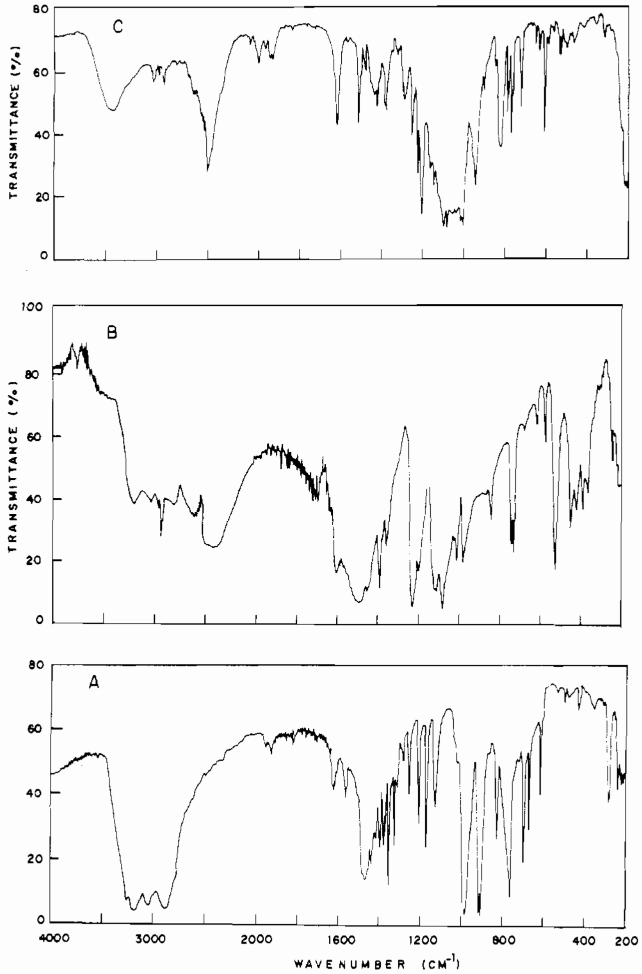

Figure 1. Infrared spectra of (A) $(DOH)_2bzo$, (B) $[Co(DODOHbzo)Br_2]$ and (C) $[Co\{(DO)_2bzoBF_2\}Br_2]$.

exhibits the ν(CH) vibrations in the region 3020–3080 cm^{-1} and the coupled ν(C=C) and ν(C=N) vibrations at 1600 cm^{-1}. The CH deformation, in-plane deformation, and out-of-plane deformation vibrations of the coordinated pyridine appear consistently in all the complexes at 765, 700, and 425 cm^{-1}, respectively.[18c,30] The (Co–N) band occurs in all the alkylcobalt(III) complexes at 520 cm^{-1}, showing that the organic ligands do not have much effect on the Co–N bond with the equatorial ligand. All complexes containing perchlorate anion exhibit strong unsplit absorptions at ~1100 and 620 cm^{-1}. The absence of splitting of the ν_3 band at 1100 cm^{-1} or the ν_4 band at 620 cm^{-1} indicates that the perchlorate anion is not coordinated.[31] $[IzCo(DODOHbzo)Br]PF_6$ exhibits strong sharp bands at ~835 and 565 cm^{-1} characteristic of the uncoordinated hexafluorophosphate anion.[32] $[PyCo(DODOHbzo)Br]ClO_4$ and all alkyl complexes exhibit infrared absorption bands characteristic of lattice water. The antisymmetric and symmetric OH stretching of lattice water appears at 3550–3220 cm^{-1} and its OH bending at 1630–1600 cm^{-1}.[33] It also exhibits an absorption band in the region 600–300 cm^{-1}.[34] Thus the ν_a(OH) + ν_s(OH) of the lattice water appears as a broad band around 3450 cm^{-1}. The absorption characteristic of HOH bending is not observed, which may be due to coupling with the ν(C=C) + ν(C=N) of the pyridine ring at 1600 cm^{-1}. These complexes exhibit another absorption at 440 cm^{-1} characteristic of lattice water.[34] The infrared spectra of all these complexes exhibit absorptions such as ν(CH), ν(C=N), ν(NO), and symmetric and asymmetric deformation vibrations of the methyl groups characteristic of the ligand framework. The ν'(NO) band is obscured by the ν_3 band of ClO_4^- at ~1100 cm^{-1}. In a few cases this band appears as a shoulder. The infrared spectral data for the alkylcobalt(III) complexes are given in Table II.

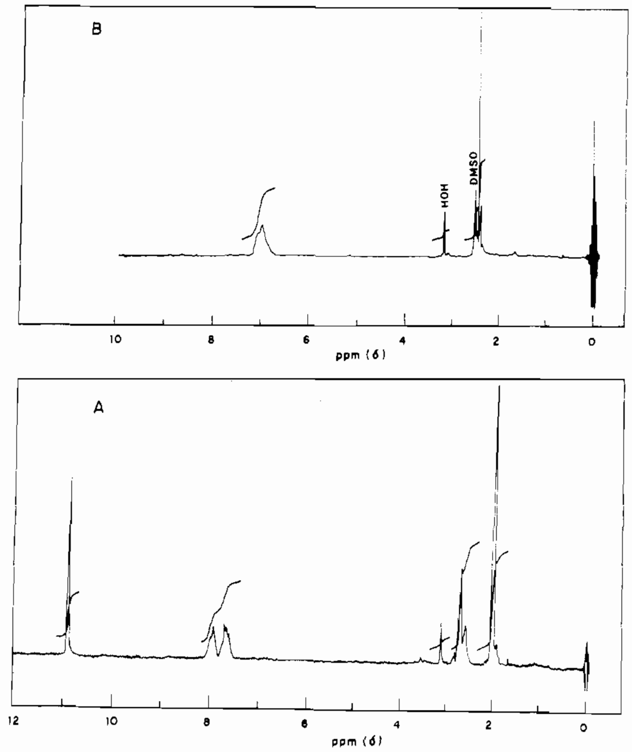

Figure 2. ^1H NMR spectra of (A) $(DOH)_2bzo$ and (B) $[Co(DODOHbzo)Br_2]$.

^{1}H NMR Spectra. The proton magnetic resonance spectrum of the ligand gives sharp singlets at 1.96 and at 2.66 ppm corresponding to the two types of methyl protons. The aromatic protons give broad multiplets centered at 7.8 ppm, and the two oxime protons give sharp singlets at 10.86 ppm. The ^{1}H NMR spectrum of the ligand is shown in Figure 2A. In most of the complexes only a singlet is observed for the 12 methyl protons. The aromatic protons (4 H) always give broad multiplets centered between 6.5 and 7.0 ppm. The 90-MHz ^{1}H NMR spectrum of $[Co(DODOHbzo)Br_2]$ is depicted in Figure 2B. In the case of non-alkyl pyridine complexes the α and β proton signals are not well-resolved, whereas in the case of alkylcobalt(III) complexes, the α and β protons of the coordinated pyridine give weak multiplets and the γ proton signal appearing inbetween the α and β protons overlaps with the signal of the aromatic protons of the equatorial ligand. The 12 methyl protons of the equatorial ligand give a sharp singlet between 2 and 1.5 ppm. The hydrogen-bonded proton signal is observed for the alkylcobalt(III) complexes at ~17.5 ppm whereas it is not detected for the non-alkyl complexes. The ^{1}H NMR spectral data for the complexes are given in Table III.

Molar Conductivity. The molar conductivity of $[Co(DODOHbzo)Br_2]$ found to be 40 Ω^{-1} cm^2 mol^{-1} immediately after the solution was prepared in DMF was found to alter with time. After 12 h it exhibits a Λ_M of 87.5 Ω^{-1} cm^2 mol^{-1}, a value well within the range for a 1:1 electrolyte in DMF.[35] The variation in the molar conductivity reveals that the axial bromide ions are replaced by the solvent molecules. Since the replacement of the bromide ions by the solvent is not completed within a short time, Λ_M is found to increase with time. When the conductance was measured after the solution was allowed to stand overnight, a

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Table II. Characteristic Infrared Absorption Bands (cm^{-1}) of Coenzyme B$_{12}$ Models[a]

complex	assignts[b] ν(CH)	ν(C=N)	ν(NO)	ν(CO—N)	absorpn due to axial base band	assignts
[CH$_3$Co(DODOHbzo)py]ClO$_4$	2910 s, sp	1555 s, mb	1235 vs, sp	520 s, sp	765 s, sp	CH def
	3050 sp, vw				700 s, sp	CH in-plane def
	3120 sp, vw				425 s, w	CH out-of-plane def
					1600 s	ν(C=C) + ν(C=N)
[CH$_3$Co(DODOHbzo)Iz]ClO$_4$	2860 w, sb	1550 s, mb	1230 vs, sp	520 vs, sp	1500 w	ring str mode of Iz
	2900 s, sp				1445 w	
	3040 w, mb				945 sp, w	ring mode of Iz
					3150 sp	ν(NH)
[CH$_3$Co(DODOHbzo)PPh$_3$]ClO$_4$	2920 s, sp	1555 s, mb	1240 vs, sp	525 vs, sp		
	3000 w, mb					
	3070 sp, w					
[CH$_3$Co(DODOHbzo)Me$_2$BIz]ClO$_4$	2930 s, sp	1550 s, mb	1235 vs, sp	525 vs, sp	3130 s, sp	ν(NH)
	3235 w, b					
	3300 w, b					
[C$_2$H$_5$Co(DODOHbzo)py]ClO$_4$	2880 sp, w	1560 s, mb	1235 vs, sp	525 vs, sp	765 s, sp	CH def
	2940 s, sp				700 s, sp	CH in-plane def
	3000 w, b				425 s, w	CH out-of-plane def
					1605 sp, w	ν(C=C) + ν(C=N)
[C$_2$H$_5$Co(DODOHbzo)Iz]ClO$_4$	2860 s, sp	1565 vs, mb	1230 vs, sp	529 vs, sp	1500 w	ring str mode of Iz
	2920 s, sp				1445 w	
	3040 mb, w				945 sp, w	ring mode of Iz
					3120 sp	ν(NH)
[*i*-PrCo(DODOHbzo)py]ClO$_4$	2865 w, sp	1550 s, mb	1230 vs, sp	520 s, sp	765 s, sp	CH def
	2940 w, sp				700 s, sp	CH in-plane def
	2980 s, sp				425 s, w	CH out-of-plane def
					1600 sp, w	ν(C=C) + ν(C=N)
[C$_6$H$_5$CH$_2$Co(DODOHbzo)py]ClO$_4$	2950 s, sp	1560 s, mb	1239 vs, sp	520 s, sp	765 s, sp	CH def
	3020 s, sp				700 s, sp	CH in-plane def
	3080 sh				425 s, w	CH out-of-plane def
					1600 w	ν(C=C) + ν(C=N)
[C$_6$H$_{11}$Co(DODOHbzo)py]ClO$_4$	2850 s, sp	1550 s, mb	1230 vs, sp	520 s, sp	765 s, sp	CH def
	2920 vs, sp				700 s, sp	CH in-plane def
					425 s, w	CH out-of-plane def
					1600 sp, w	ν(C=C) + ν(C=N)

[a] Medium: KBr disk. Abbreviations: s = strong, sp = sharp, sh = shoulder, vs = very strong, b = broad, m = medium, w = weak. [b] The ν'(NO) band is obscured by the ν_3 band of ClO$_4^-$ at ~1100 cm^{-1}.

Table III. ^{1}H NMR Spectral Data for the Alkyl- and (Non-alkyl)cobalt(III) Complexes[a]

complex	chem shift, ppm aliphatic proton	aromatic proton
[Co(DODOHbzo)Br$_2$]	2.36 s (12 H)	7 m (4 H)
[Co(DODOHbzo)Cl$_2$]	2.33 s (12 H)	6.3 m (4 H)
[Co[(DO)$_2$bzoBF$_2$]Br$_2$]	2.35 s (12 H)	6.7 m (4 H)
[(py)Co(DODOHbzo)Br]ClO$_4$[b]	2.33 s (12 H)	7.61 m (2 H), 8.16 m (7 H)
[IzCo(DODOHbzo)Br]PF$_6$[b]	2.34 s (12 H)	6.5 m (1 H), 7.06 m (1 H), 7.31 m (5 H), 7.53 m (2 H)
[CNCo(DODOHbzo)Iz]Br[b]	2.26 s (12 H)	6.76 m, 7.26 m, 7.56 m
[CH$_3$Co(DODOHbzo)PPh$_3$]ClO$_4$	1.16 d (3 H), 1.76 s (12 H), 17.46 (1 H)	7 m (19 H)
[C$_2$H$_5$Co(DODOHbzo)py]ClO$_4$[c]	0.33 t (3 H), 1.7 s (2 H), 2 s (12 H), 17.6 (1 H)	7 m (2 H), 7.45 m (5 H), 8.2 m (2 H)
[*i*-PrCo(DODOHbzo)py]ClO$_4$[c]	0.6 t (3 H), 1.4 s (1 H), 2 s (12 H), 17.5 (1 H)	7 m (2 H), 7.43 m (5 H), 8.32 m (2 H)
[C$_6$H$_5$CH$_2$Co(DODOHbzo)py]ClO$_4$[c]	1.87 s (12 H), 2.7 s (2 H), 17.6 (1 H)	6.7 m (2 H), 7 m (5 H), 7.4 (2 H), 8.23 m (6 H)
[C$_6$H$_{11}$Co(DODOHbzo)py]ClO$_4$[c,d]	1.4 m (11 H), 2 s (12 H), 17.4 (1 H)	7 m (2 H), 7.43 m (5 H), 8.3 m (2 H)

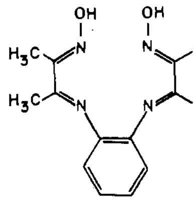
[a] Solvent: DMSO-d_6 for (non-alkyl)cobalt(III) complexes and CDCl$_3$ for alkylcobalt(III) complexes. [b] The signals due to the aromatic protons of the equatorial ligand and the axial base overlap and, due to low solubility of the complexes, the aromatic proton signals are not well resolved. [c] The α- and β-proton signals of the coordinated pyridine are well resolved (see text). [d] The cyclohexane protons give very broad multiplet.

nearly constant value of 163.7 Ω^{-1} cm^2 mol^{-1} was obtained. This value corresponds to that of a 1:2 electrolyte in DMF,[35] showing that the axial bromide ions are gradually replaced by the solvent molecules leading first to the 1:1 electrolyte, [Co(DODOHbzo)Br(DMF)]Br and finally to the 1:2 electrolyte, [Co(DODOHbzo)(DMF)$_2$]Br$_2$. The dichloro and diiodo complexes also exhibit the same behavior. The donor capacity of dimethyl sulfoxide and its high viscosity limit its utility as a solvent for conductivity measurements. The molar conductivities of the other (non-alkyl)cobalt(III) complexes in DMF fall in the range 65–90 Ω^{-1} cm^2 mol^{-1} and those of the alkylcobalt(III) complexes in acetonitrile fall in the range of 130–150 Ω^{-1} cm^2 mol^{-1}, showing that they are 1:1 electrolytes.[35]

Magnetic Susceptibility. For all the complexes except the pseudohalogeno ones the χ_M^{corr} value is found to be a negative quantity ranging from -970×10^{-12} to -3085×10^{-12}, indicating that these complexes are diamagnetic. The pseudohalogeno complexes exhibit a residual paramagnetism with magnetic moments, μ_{eff}, of 0.45, 0.32, and 0.21 μ_B for [CNCo(DODOHbzo)Br], [SCNCo(DODOHbzo)Br] and [N$_3$Co(DODOHbzo)Br], respectively.

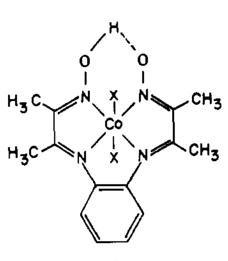
Discussion

Synthesis of (Non-alkyl)- and Alkylcobalt(III) Complexes. The free ligand (IV) is a neutral compound that complexes as a monoanion with cobalt with the loss of an oxime proton with the concomitant formation of an intramolecular hydrogen bond. The ligand coordinates with the metal through its nitrogen donors in the equatorial position, leaving the two axial sites vacant for coordination by a number of monodentate ligands. In the case



IV

(DOH)$_2$bzo



V

[Co(DODOHbzo)X$_2$]

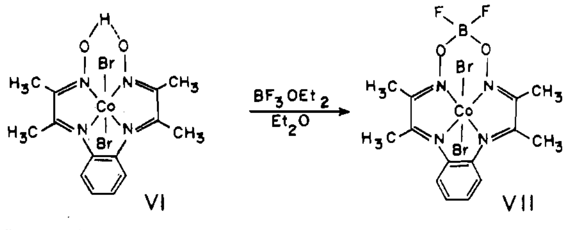
X = Cl$^-$, Br$^-$ or I$^-$

of dihalo complexes, the two halide ions are coordinated to the metal ion in the axial sites, thereby forming six-coordinate complexes (V).

In all of the dihalo complexes cobalt is found to be in the 3+ oxidation state as inferred from magnetic susceptibility and electronic absorption spectra (vide infra). While the complexes were synthesized from cobalt(II) salts, the oxidation of cobalt(II) to cobalt(III) was effected by air without the help of any external oxidizing agent. The ease with which cobalt(III) complexes are formed by the ligand may be attributed to the ability of the ligand to accommodate the smaller cobalt(III) ion more readily than the larger cobalt(II) ion in its central cavity. This is in agreement with the observation of Jackels et al.[18a] that the metal ion site in a macrocyclic ligand becomes smaller with increasing unsaturation. In the ligand under investigation the unsaturation extends to all four donor atoms, causing the cavity available to accommodate the metal ion to become smaller, thereby favoring cobalt(III) over cobalt(II).

In aqueous methanol, aqueous ethanol, or aqueous acetone both the dichloro and dibromo complexes yield brown transparent solutions. Upon the addition of hydrochloric acid or hydrobromic acid, the original complex was precipitated. This observation illustrates that in solution the axially coordinated halide ions are reversibly replaced by water molecules. Besides conductivity, evidence for the replacement of axially coordinated halide ions by solvent molecules is afforded by the instantaneous precipitation of silver halide from aqueous alcoholic or aqueous acetone solution of the complexes by silver nitrate. The reaction was complete and was utilized to estimate the halide ions present in [Co(DODOHbzo)Cl$_2$] and [Co(DODOHbzo)Br$_2$] with high precision and reproducibility.[36] The estimated amounts of chloride and bromide ions present in the dichloro and dibromo complexes are given in the Experimental Section. To date no study has been reported that makes use of the lability of coordinated halides in complexes of macrocyclic or nonmacrocyclic ligand systems to estimate the halides reliably.

Indirect evidence for the presence of hydrogen bond in the complex [Co(DODOHbzo)Br$_2$] is obtained by treating it with boron trifluoride etherate. This reagent readily reacts with the O–H···O bridge in the molecule, affording an extremely stable compound containing an O–BF$_2$–O bridge:



VI VII

[Co(DODOHbzo)Br$_2$] (green)

[Co{(DO)$_2$bzoBF$_2$}Br$_2$] (chocolate brown)

Schrauzer,[24] in his studies on bis(dimethylglyoximato)nickel(II), replaced the two hydrogen-bonded protons by BF_2 groups for the first time by treating the hydrogen-bonded complex with boron trifluoride etherate. Later, Schrauzer and Windgassen[13] in their studies on methylaquocobaloximes and Magnuson and Weber[37] in studies on alkylcobalt complexes of (DODOHpn) replaced the hydrogen-bonded proton by BF_2 group by the same method. In the present investigation as well, the synthesis of the BF_2 derivative of the dibromo complex was accomplished by stirring the heterogeneous mixture of [Co(DODOHbzo)Br$_2$] in dry ether with $BF_3\cdot OEt_2$ for 20 h. The broad band appearing at 2400 cm^{-1} in [Co(DODOHbzo)Br$_2$] assignable to ν(OH) disappears in the BF_2 derivative. This shows the presence of O–H···O bridge in the original dibromo complex. The strong and sharp band appearing at 1075 cm^{-1} assignable to ν'(NO) for the dibromo complex disappears in the BF_2 analogue.

The synthesis of coenzyme B_{12} model complexes having an organic ligand bonded to the cobalt by means of a Co–C σ-bond in one of the axial coordination sites can be accomplished by one of the three different types of reactions, namely, carbanion transfer to a cobalt(III) complex from an organometallic compound, usually a Grignard reagent or an organolithium compound;[4a,d,f,5a,b,38] addition of an aryl or alkyl radical to a cobalt(II) complex;[39] and nucleophilic attack of a cobalt(I) complex on alkyl, acyl,[4b,c,e,40] vinyl[40a,41] or aryl halides.[4c,9b,42] The low solubility of the dihalo complexes in tetrahydrofuran or ether limits the utility of the first method, whereas the nonfeasibility of synthesizing cobalt(II) complexes of (DOH)$_2$bzo limits that of the second method. Therefore the organocobalt(III) complexes were synthesized by the reaction of the reactive cobalt(I) nucleophile generated by treating an aqueous alcoholic solution (1:5 v/v) of [Co(DODOHbzo)Br$_2$] with sodium borohydride with the appropriate alkyl halide in an inert atmosphere. The in situ generated cobalt(I) nucleophile reacts with the carbonium ion present in the solution and is reoxidized to cobalt(III). The reaction was found to be instantaneous as indicated by the rapid color change of the brown reaction solution to orange-red due to the formation of the alkyl derivative. When the reaction was carried out at ambient temperature (30 °C), the yields of the alkyl derivatives were found to be too low and they were often difficult to isolate. At 0–10 °C, the formation of the alkyl derivatives was enhanced as indicated by the high yield of the resulting complexes possibly due to the greater stability of the cobalt(I) species at lower temperatures. Therefore the syntheses of all organocobalt(III) complexes were carried out at or below 10 °C. All of these alkyl derivatives could be isolated as solids only after reaction with a Lewis base

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(36) [Co(DODOHbzo)I$_2$] in aqueous alcohol or acetone upon treatment with $AgNO_3$ gives pale yellow AgI. But no quantitative study has been undertaken. To get reproducible results in the quantitative determination of halide ions, the solution of the complex was stirred for 3 min after the addition of $AgNO_3$ and allowed to stand for about 30 min at ambient temperature.

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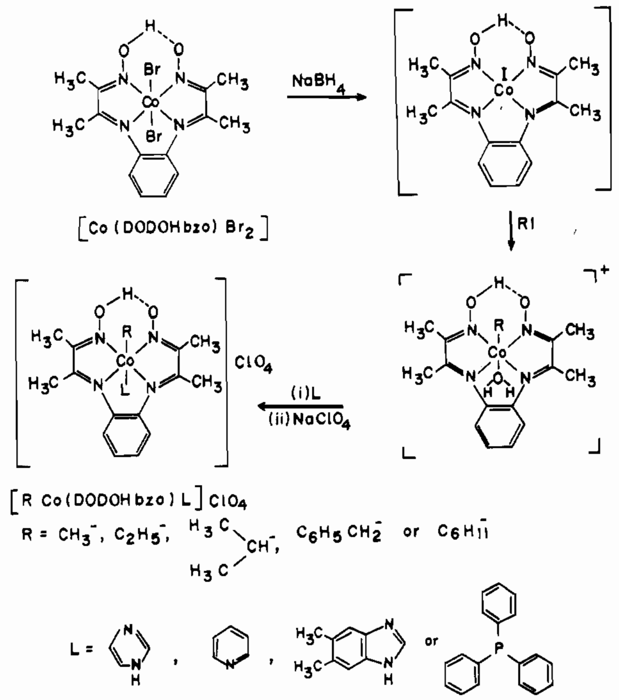
Scheme I. Generation of Co(I) Nucleophile and Its Subsequent Oxidative-Addition Reaction with R$^+$



followed by the addition of an aqueous solution of sodium perchlorate. The generation of cobalt(I) species and its subsequent oxidative addition reaction with R$^+$ may be schematically represented as depicted in Scheme I.

Residual Paramagnetism of Cobalt(III) Complexes. The magnetic moment expected for Co^{3+} ion in an octahedral high-spin complex (T$_{2g}^5$) is about 5.8 μ_B at 300 K. A high-spin octahedral complex of cobalt(II) having $^4T_{1g}$ as the ground term is expected to give a magnetic moment of about 6.5 μ_B at 300 K or probably somewhat lower if the symmetry of the ligand field departs from the O_h symmetry. An octahedral low-spin complex of bivalent cobalt may be presumed to possess the electronic configuration $t_{2g}^6e_g^1$ with a ^2E_g ground term, and the magnetic moment is expected to be about 1.8–1.85 μ_B.[43] The low residual paramagnetism observed for the pseudohalogeno complexes indicates the presence of a low-spin cobalt(III) ion with a $d^6(t_{2g}^6,e_g^0)$ configuration. This observation is in broad agreement with the generalization of Figgis and Lewis[43] that the great majority of cobalt(III) complexes are of the low-spin type and are either diamagnetic or show a small positive susceptibility. In octahedral spin-paired cobalt(III) complexes the $^1A_{1g}$ term of the t_{2g}^6 configuration lies lowest and the second-order Zeeman effect accounts for the small residual paramagnetism[44] observed for the pseudohalogeno complexes. Residual paramagnetism can also arise by the quenching of diamagnetism caused by the distortion of groups by their neighbors due to the existence of electronic energy levels very close to that of the ground state.[45] However, the presence of traces of Co(II) due to the reduction of Co(III) leading to small paramagnetism cannot be ruled out.

Electronic Absorption Spectra and Computation of the Ligand Field Parameters. The point charge model predicts that the electronic spectra of octahedral metal complexes with the low-spin d^6 configuration will be characterized by two bands, which may be assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively.[46] On descent in symmetry to D_{4h} (tetragonal centric) or C_{4v} (tetragonal acentric), corresponding to a tetragonal distortion, the degeneracy of the octahedral $^1T_{1g}$ and $^1T_{2g}$ levels is removed. Experimentally this lowering of symmetry is manifested in a splitting of the low-lying d–d absorption band. Wentworth and Piper[47] have developed a crystal field model for the d–d transition of a d^6 ion in D_{4h} symmetry. When the symmetry is lowered from O_h to D_{4h}, the first band in the octahedral environment, $^1A_{1g} \rightarrow {}^1T_{1g}$, splits into two bands, namely $^1A_{1g} \rightarrow {}^1E_g{}^a$ (ν_E) and $^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_A), and the second band, $^1A_{1g} \rightarrow {}^1T_{2g}$, splits into $^1A_{1g} \rightarrow {}^1E_g{}^b$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ (ν_{II}). The splitting of the ν_{II} band has never been observed, probably due to the onset of charge-transfer bands or due to the ligand field.[47] Thus when the symmetry is lowered to D_{4h}, more than two bands are expected, usually three, assignable to $^1A_{1g} \rightarrow {}^1E_g{}^a$, $^1A_{1g} \rightarrow {}^1A_{2g}$, and $^1A_{1g} \rightarrow ({}^1B_{2g} + {}^1E_g{}^b)$. The tetragonal splitting of the excited states of low-spin d^6 cobalt(III) is depicted in Figure 3.

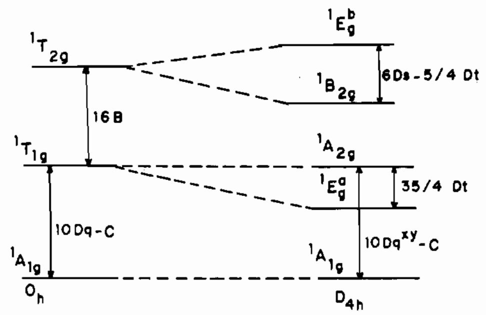


Figure 3. Energy level diagram for a low-spin d^6 ion in O_h and D_{4h} symmetry.

The splitting of the $^1T_{1g}$ state of the octahedral symmetry in a D_{4h} microsymmetry is associated with a single tetragonal splitting parameter D_t. A positive D_t indicates that the in-plane ligand field is stronger than the axial field and vice versa. The splitting of the $^1T_{1g}$ becomes larger as the difference in the ligand field strength between the in-plane ligand and the axial ligand increases. Application of the crystal field model of Wentworth and Piper enables the computation of the ligand field strength of the equatorial ligand, Dq^{xy}, and that of the axial ligand, Dq^z, by using eq 1–3.

$$10Dq^{xy} = {}^1A_{1g} \rightarrow {}^1A_{2g}\ (\nu_A) + C \qquad (1)$$

$$D_t = {}^4\!/_{35}(10Dq^{xy} - {}^1A_{1g} \rightarrow {}^1E_g{}^a - C) \qquad (2)$$

$$Dq^z = Dq^{xy} - {}^7\!/_4 D_t \qquad (3)$$

The interelectronic repulsion parameter C is taken to be 3800 cm^{-1}, a value shown by Wentworth and Piper to be roughly independent of the field strength.

In order to apply the crystal field model of Wentworth and Piper to interpret the electronic transitions and to compute the ligand field strengths, D_{4h} symmetry has to be assumed for the low-spin d^6 cobalt(III) complexes discussed in the foregoing sections. This amounts to assuming that the four macrocyclic nitrogen atoms are coordinated in a square-planar array and impose equivalent ligand fields on the metal ion. This assumption obviously does not hold true for all the complexes under study. However, many of the derivatives do display the three predicted bands, thereby indicating the close approximation to D_{4h} symmetry. Therefore, in the present study, the D_{4h} crystal field model has been chosen by virtue of the spectral characteristics of the majority of the complexes being analogous to those of complexes with D_{4h} microsymmetry. Other low-spin cobalt(III) macrocyclic systems lacking true D_{4h} symmetry have been usefully treated by assuming the D_{4h} model.[18a]

The dihalo and pseudohalogeno complexes exhibit two bands in the visible region, one in the near-UV region and one or two bands in the UV region characteristic of tetragonally distorted cobalt(III) complexes.[48] The electronic spectral band assignments

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Table IV. Electronic Spectral Band Assignments ($cm^{-1} \times 10^3$) and Ligand Field Parameters for the (Non-alkyl)cobalt(III) Complexes[a]

complex	$^1A_{1g} \to {}^1E_g{}^a$ (ν_E)	$^1A_{1g} \to {}^1A_{2g}$ (ν_A)	$^1A_{1g} \to ({}^1E_g{}^b + {}^1B_{2g})$ (ν_{II})	other bands[b]	ligand field params,[c] cm^{-1} Dq^{xy}	Dq^z	D_t
$[Co(DODOHbzo)Br_2]$	17.54	22.73	25.97	34.25, 39.22	2653	1615	593
$[Co(DODOHbzo)Cl_2]$	17.86	23.4	27.4	37.3, 36.66	2720	1612	633
$[N_3Co(DODOHbzo)Br]$	17.86	22.73	26.68	37	2653	1679	557
$[(py)Co(DODOHbzo)Br]ClO_4$	17.64	22.83	27	38	2663	1625	593
$[IzCo(DODOHbzo)Br]PF_6$	17.54	22.94	27.4	37.59	2674	1594	617

[a] Spectra were recorded by using a 10^{-3} M solution in DMF in the visible region and in methanol in the UV region. [b] The change-transfer transitions and/or the π–π^* transition of the ligand framework. [c] Computed by using the crystal field model of Wentworth and Piper.[47] See also ref 18a and 48e.

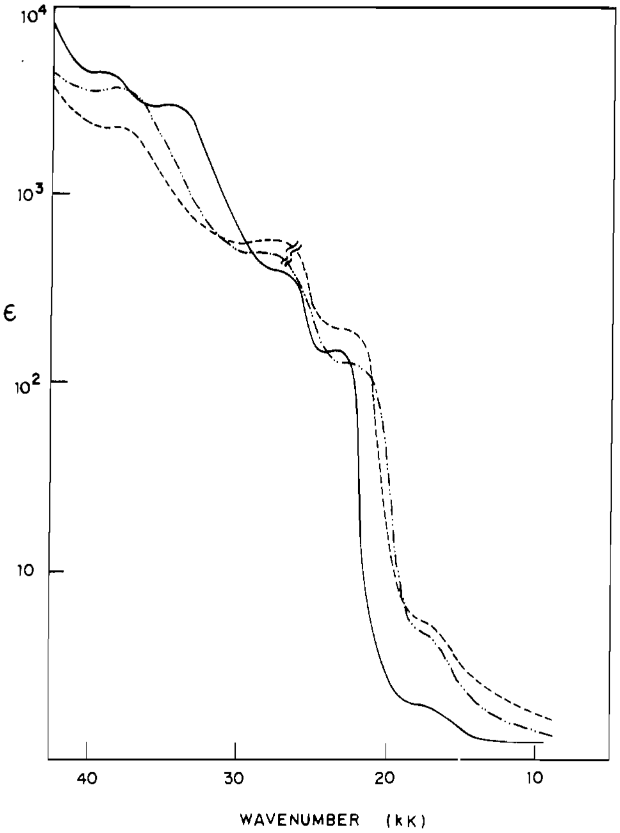

Figure 4. Electronic absorption spectra of $[Co(DODOHbzo)Br_2]$ (solid line) $[(py)Co(DODOHbzo)Br]ClO_4$ (dashed line) and $[IzCo(DODOHbzo)Br]PF_6$ (dotted line) in DMF (visible region) and in methanol (UV region) at 25 °C.

for the dihalo, pseudohalogeno, and Lewis base complexes are given in Table IV, and typical spectra are given in Figure 4. The dibromo complex $[Co(DODOHbzo)Br_2]$ exhibits a strong band at 17.54×10^3 cm^{-1} and a weak band at 22.73×10^3 cm^{-1}, both in methanol and in DMF, assignable to the $^1A_{1g} \to {}^1E_g{}^a$ and $^1A_{1g} \to {}^1A_{2g}$ transitions, respectively. The bands are broadened to a greater extent in DMF than in methanol probably due to slow replacement of the coordinated bromide ions by the DMF molecules. The calculated ligand field parameters such as Dq^{xy}, D_t and Dq^z based on these band assignments are 2653, 593, and 1615 cm^{-1} respectively. The field strength of the axial ligand reflects the sum of the field strengths contributed by both axial ligands. Thus additivity is assumed for the dihalo complexes, for example, $Dq^z(X + X) = {}^1/_2[Dq^z(X) + Dq^z(X)]$. For the Lewis base complexes of the type, $[LCo(DODOHbzo)Br]A$, the $Dq^z(L + Br) = {}^1/_2[Dq^z(L) + Dq^z(Br)]$. But in such cases where there are two ligands coordinating to a metal ion through the axial sites, it is customary to report the value of Dq^z calculated from eq 1–3, as a measure of the axial field strength.[48b,e] In the case of Lewis base complexes, though the value of Dq^z does not reflect the actual field strength of the base alone, the additive value is used as a measure of the field strength of the respective Lewis base since the contribution of the bromide, present in all such complexes, is constant.

The dichloro complex $[Co(DODOHbzo)Cl_2]$, exhibits three absorptions at 16.67, 17.86, and 23.42×10^3 cm^{-1} with ε values 51.6, 52, and 1.21×10^3 L mol^{-1} cm^{-1}, respectively. The occurrence of these bands in the visible region is also characteristic of tetragonally distorted cobalt(III) complexes.[48a] It would be unrealistic to assign the first two bands to the $^1A_{1g} \to {}^1E_g{}^a$ and $^1A_{1g} \to {}^1A_{2g}$ transitions, respectively, since such an assignment would result in Dq^{xy} and Dq^z values of 2165 and 1927 cm^{-1}, respectively, as against the corresponding values of 2652 and 1616 cm^{-1} for $[Co(DODOHbzo)Br_2]$. Though the ligand field strength of Cl^- is higher than that of Br^-, it is surprising that the tetragonal splitting caused by the former is only 136 cm^{-1} as against 593 cm^{-1} for the latter. This is contrary to the observation that the tetragonal splitting is higher when the field strength of the axial ligand is higher. The ligand field strength of the equatorial ligand obtained from the above spectral assignments of the dichloro complex is much lower than that of ethylenediamine (2530 cm^{-1}),[47] which is contrary to the observation of Jackels et al.,[18a] Sadasivan et al.,[49] and Tait et al.[48b] that the ligand field strengths of the macrocycles increase with the degree of unsaturation. The assignment of the second and third bands at 17.86 and 23.42×10^3 cm^{-1} to the $^1A_{1g} \to {}^1E_g{}^a$ and $^1A_{1g} \to {}^1A_{2g}$ transitions respectively leads to Dq^{xy} and Dq^z values of 2720 and 1612 cm^{-1}, respectively. These values closely agree with the corresponding values calculated for other complexes. The D_t value of 633 cm^{-1} so obtained is also higher than that of the dibromo complex (593 cm^{-1}).

The diiodo complex $[Co(DODOHbzo)I_2]$, exhibits only one absorption band in the visible region at 22.57×10^3 cm^{-1} with $\epsilon = 6.59 \times 10^3$ L mol^{-1} cm^{-1}, and this is tentatively assigned to the ν_A transition. The other band expected in the visible region, assignable to the ν_E transition, is obscured. Though the assignment of the band at 22.57×10^3 cm^{-1} to the ν_A transition ascribes a Dq^{xy} value of 2637 cm^{-1}, which is comparable with the corresponding values computed for other complexes, it is unsound to assign this band to this transition because of its higher molar absorptivity. The very high intensity of this band may be due to the reducing nature of the iodide ion and/or it may arise from intensity stealing from the even more intense third band nearby. A very similar spectral behavior was observed for the diiodo complexes of other macrocycles such as CR and TIM.[18a]

The complexes $[N_3Co(DODOHbzo)Br]$, $[CNCo(DODOHbzo)Br]$, $[pyCo(DODOHbzo)Br]ClO_4$, and $[IzCo(DODOHbzo)Br]PF_6$ exhibit both ν_E and ν_A absorptions as does the dibromo complex. $[pyCo(DODOHbzo)Br]ClO_4$ exhibits the $^1A_{1g} \to {}^1E_g{}^a$ and $^1A_{1g} \to {}^1A_{2g}$ transitions at 17.64 and 22.83×10^3 cm^{-1}, respectively. This leads to the Dq^{xy}, Dq^z and D_t values 2663, 1624,

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Table V. Electronic Spectral Band Assignments ($cm^{-1} \times 10^3$) for the Organocobalt(III) Complexes[a]

complex	Co–C CT band[b]	other bands[c]
$[CH_3Co(DODOHbzo)py]ClO_4$	23	26.3, 35, 42.5
$[CH_3Co(DODOHbzo)Iz]ClO_4$	23.25	27, 33, 41.7
$[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$	23.8	26.7, 37
$[CH_3Co(DODOOHbzo)PPh_3]ClO_4$	22.57	26.3, 31.25, 39.2
$[C_2H_5Co(DODOHbzo)py]ClO_4$	22.3	26.3, 34.7
[*i*-pr Co(DODOHbzo)py]ClO_4	21.6	25.97, 30.3, 34.48
$[C_6H_5CH_2Co(DODOHbzo)py]ClO_4$	21.74	28.17, 36.2
$[C_6H_{11}Co(DODOHbzo)py]ClO_4$	21.5	30.3, 34.48

[a] Spectra were recorded in methanol at 25 °C. [b] Assignments were made after ref 50. [c] Absorptions due to the axial base, $\pi \rightarrow \pi^*$ transition of the ligand framework, and other CT transitions.

and 593 cm^{-1}, respectively. The lone-pair electron density on the imidazole tertiary nitrogen is higher than that on the pyridine nitrogen, and hence one would expect the field strength of imidazole to be greater than that of pyridine, but the Dq^z is 1594 cm^{-1} for imidazole, lower than that for pyridine. The thiocyanato complex, [SCNCo(DODOHbzo)Br], exhibits two absorptions at 15.95 and 22.72 × 10^3 cm^{-1} with molar absorptivities of 23 and 476 L mol^{-1} cm^{-1}, respectively. These low molar absorptivities are characteristic of d–d transitions, which indicate that the thiocyanato complex has pseudo-O_h symmetry, exhibiting the two expected d–d transitions, namely ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$.

Organocobalt(III) compounds are highly colored and generally give somewhat complex electronic spectra. All of these complexes exhibit only one band in the visible region between 21.6 and 23.8 × 10^3 cm^{-1} with molar absorptivities of 10^3 L mol^{-1} cm^{-1}. This band is assigned to the Co–C charge-transfer transition in analogy with the assignment of Schrauzer et al.,[50] who in their studies on the spectra of cobalamins and cobaloximes assigned the low-energy absorption between 400 and 500 nm to the Co–C charge-transfer (CT) transition based on extended, self-consistent HMO calculations.

Between 25 and 28.17 × 10^3 cm^{-1} there are two or three bands with molar absorptivities ranging from 6 × 10^3 to 10^4 L mol^{-1} cm^{-1}. Since the axial base may also absorb in this region it is of little diagnostic value so far as the axial Co–C bond is concerned. These bands may also be a combination of the $\pi \rightarrow \pi^*$ transition of the ligand framework and other CT transitions.

The Co–C CT band shifts to shorter wavelengths as the alkyl group becomes more electron withdrawing and the σ-donor ability of the axial base or the equatorial ligand increases.[51] For the complexes [R Co(DODOHbzo)py]ClO_4, this band shifts to higher energy region as the organic ligand is changed from C_6H_{11} (21.5 × 10^3 cm^{-1}) to CH_3 (23 × 10^3 cm^{-1}). The observed order is C_6H_{11} (21.5 × 10^3 cm^{-1}) < *i*-Pr (21.6 × 10^3 cm^{-1}) < $C_6H_5CH_2$ (21.7 × 10^3 cm^{-1}) < C_2H_5 (22.32 × 10^3 cm^{-1}) < CH_3 (23 × 10^3 cm^{-1}). When the alkyl group is fixed and the base trans to it is varied as in $[CH_3Co(DODOHbzo)L]ClO_4$, the Co–C CT band moves to higher energy in the order PPh_3 (22.57 × 10^3 cm^{-1}) < py (23 × 10^3 cm^{-1}) < Iz (23.25 × 10^3 cm^{-1}) < Me_2BIz (23.8 × 10^3 cm^{-1}). The order of the trans influence of these Lewis bases except 5,6-dimethylbenzimidazole is in the decreasing order of their ligand field strength computed from the spectral data of the respective Lewis base complexes of the type [LCo(DODOHbzo)Br]A. Thus, as the field strength of the axial base trans to the organic ligand increases, the Co–C CT transition is shifted to lower energy. The electronic spectral data of the organocobalt(III) complexes are given in Table V, and the electronic spectra of $[CH_3Co(DODOHbzo)py]ClO_4$ and $[C_2H_5Co(DODOHbzo)py]ClO_4$ are given in Figure 5.

It is interesting to compare the energy of the Co–C CT transition of various in-plane ligands. It has been observed by Schrauzer et al.[50] that the energy of the transition increases with increasing donor power of the in-plane ligands. Stronger in-plane donors increase the charge density on cobalt and thus stabilize the Co–C bond. A comparison of the Co–C CT transition of complexes of the type $RCoL_4py$ with different in-plane ligands, L_4, such as the bis(dimethylglyoximato) dianion, 1,2-cyclohexanedione dioxime, and diphenylglyoxime indicates that the σ-donor ability of the ligand under study is comparable with that of $(DH)_2$.

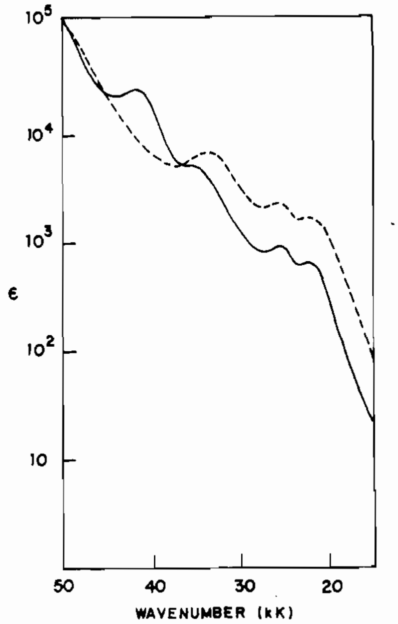

Figure 5. Electronic absorption spectra of $[CH_3Co(DODOHbzo)py]ClO_4$ (solid line) and $[C_2H_5Co(DODOHbzo)py]ClO_4$ (dashed line) in methanol at 25 °C.

The electronic spectra of $[CH_3Co(DODOHbzo)py]ClO_4$ in neutral and in acidic methanol (5 N $HClO_4$) are virtually the same with λ_{max} at 435 and 380 nm. In basic methanol (5 N NaOH) the absorption maxima are shifted to higher wavelengths at 445 and 390 nm, respectively. The identical nature of the spectra of $[CH_3Co(DODOHbzo)py]ClO_4$ both in neutral and in acidic methanol indicates that in solution the complex exists predominantly in the base-off form. Coenzyme B_{12} in acidic solution exists in the base-off form with the concomitant protonation of the base[52] whereas secondary alkylcobalamins exhibit absorption spectra similar to those of alkylcobinamides and exist predominantly in the base-off form even in neutral solution.[53] Even in 5 N $HClO_4$ and in 5 N NaOH the complex exhibits the Co–C CT transition, indicating that the Co–C bond is not cleaved.

Our model represents an improvement over Costa's model in that it does not appear to be readily dialkylated under reducing conditions. However, our model is more difficult to reduce to the Co(I) state, obviously because the ligand induces too high of a charge density on cobalt. While this reduces its value as a quantitative vitamin B_{12} model, it is still valuable for comparative studies, especially since cyclic voltammetric studies may be performed that provide rewarding insight into the role of the Co(I) nucleophile in mediating biochemical reactions of the corrin cofactors.[54]

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Registry No. $[Co(DODOHbzo)Br_2]$, 104544-51-6; $[Co(DODOHbzo)Cl_2]$, 109863-79-8; $[Co(DODOHbzo)I_2]$, 109863-80-1; [SCNCo(DODOHbzo)Br], 109863-78-7; $[N_3Co(DODOHbzo)Br]$, 109863-81-2; [CNCo(DODOHbzo)Br], 109863-82-3; [(py)Co(DODOHbzo)Br], 109889-29-4; $[IzCo(DODOHbzo)Br]PF_6$, 109863-83-4; [CNCo(DO-

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DOHbzo)py]Br, 109863-84-5; [CNCo(DODOHbzo)Iz]Br, 109863-85-6; [CH_3Co(DODOHbzo)py]ClO_4, 109889-31-8; [CH_3Co(DODOHbzo)-Iz]ClO_4, 109863-87-8; [CH_3Co(DODOHbzo)PPh_3]ClO_4, 109863-89-0; [CH_3Co(DODOHbzo)Me_2BIz]ClO_4, 109863-91-4; [C_2H_5Co(DODOHbzo)py]ClO_4, 109863-93-6; [C_2H_5Co(DODOHbzo)Iz]ClO_4, 109863-95-8; [*i*-PrCo(DODOHbzo)py]ClO_4, 109863-97-0; [$C_6H_4CH_2$Co(DODOHbzo)py]ClO_4, 109863-99-2; [C_6H_{11}Co(DODOHbzo)py]ClO_4, 109864-01-9; [Co{$(DO)_2$bzoBF_2}Br_2], 109864-02-0; $(DOH)_2$bzo, 75389-07-0; 2,3-butanedione monoxime, 57-71-6; *o*-phenylenediamine, 95-54-5; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; isopropyl bromide, 75-26-3; iodocyclohexane, 626-62-0; benzyl chloride, 100-44-7; vitamin B_{12}, 68-19-9; vitamin B_{12} coenzyme, 13870-90-1.

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Reaction of $[Ni(H_2O)_2(N,N'\text{-}Me_2\text{-}en)_2]^{2+}$ with Carbohydrates. Synthesis and Characterization of a Novel μ-Mannofuranoside Binuclear Nickel(II) Complex Containing *N*-Glycosides

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An unprecedented binuclear nickel(II) complex containing two types of *N*-glycosides formed from *N,N'*-dimethylethylenediamine (*N,N'*-Me_2-en) and D-mannose (D-Man) was synthesized, and its structure was determined by X-ray crystallography. The complex (μ-Man)[$Ni_2(CH_3OH)$(*N*-(D-Man)-*N,N'*-Me_2-en)(*N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en)]$Cl_2\cdot 2CH_3OH\cdot H_2O$ forms orthorhombic crystals with $a = 19.647\ (35)$ Å, $b = 17.169\ (8)$ Å, $c = 13.247\ (4)$ Å, $Z = 4$, in space group $P2_12_12_1$, where *N*-(D-Man)-*N,N'*-Me_2-en is 1-(*N*-methyl-D-mannosylamino)-2-(methylamino)ethane and *N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en is 1,2-bis(*N*-methyl-D-mannosylamino)ethane. The structure was solved by direct methods followed by least-squares and Fourier techniques. Refinement using 2199 reflections with $|F_o| > 3\sigma(|F_o|)$ gave $R = 0.077$ and $R' = 0.087$. The metal center is surprisingly a binuclear nickel complex with a bridging mannose residue. Both nickel atoms have distorted-octahedral geometry, and the Ni- - -Ni separation is 3.596 (4) Å, indicating that no appreciable metal–metal bonding is present. One of the nickel atoms is coordinated with a methanol and an *N*-glycoside, *N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en. The other nickel is coordinated with a tridentate *N*-glycoside, *N*-(D-Man)-*N,N'*-Me_2-en, and a part of the bridging sugar moiety of *N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en. The bridging sugar ring takes the unusual furanose ring, and the other two sugar rings adopt the usual β-$^4C_1$ chair conformation. When D-glucose was used as a starting sugar instead of D-mannose, a nickel(II) complex containing D-mannose was surprisingly obtained.

Introduction

The interactions of carbohydrates with metals have been of interest in recent years, above all in the field of industry and biochemistry in connection with metal-containing enzymes. In spite of the fact that it has been well-known that sugars can form complexes with various metal ions, those transition-metal complexes containing carbohydrates that were confirmed by their structural details are very few[3] and the field of sugar–metal complexes is still largely unexplored.

In order to elucidate the carbohydrate–transition-metal interaction, we have systematically studied the synthesis and characterization of transition-metal complexes containing *N*-glycosides derived from the reaction of sugars and diamines. During our investigations, the structures of [Ni(en)(D-Fru-en)]$Cl_2\cdot CH_3OH$[4] (**1**), [Ni(en)(L-Sor-en)]$Cl_2\cdot {}^1/_2CH_3OH$[5] (**2**), [Ni(D-GlcN-en)$_2$]$Br_2\cdot 4H_2O$[6] (**3**), and [Ni(L-Rha-tn)$_2$]$Br_2\cdot 2H_2O\cdot CH_3OH$[7] (**4**), and [Ni(*S*-ampr)(L-Sor-*S*-ampr)]$Cl_2\cdot CH_3OH\cdot H_2O$[8] (**5**) [Fru = fructose, Sor = sorbose, Glc = glucose, GlcN = 2-amino-2-deoxyglucose, Rha = 6-deoxymannose, en = ethylenediamine, tn = trimethylenediamine, and ampr = 2-aminomethylpyrrolidine) were determined by X-ray crystallography. The crystal structures of **3** and **4** revealed that an *N*-glycoside from an aldose and a diamine attaches to the nickel atom through the oxygen atom of the hydroxyl group on C-2 of the sugar moiety and through the two nitrogen atoms of the diamine residue, and the two tridentate *N*-glycoside ligands complete a distorted-octahedral coordination around the nickel atom in the meridional mode.[6,7] From these results, it is clear that diamines play an important role in anchoring sugars to metal. It is often observed that the *N*-alkyl groups on the coordinating nitrogen atoms influence the stereochemistry of metal complexes. Prompted by this knowledge, we have chosen *N,N'*-dimethylethylenediamine (*N,N'*-Me_2-N) as a diamine component with the hope of verifying the coordination behavior of *N*-glycoside ligands. Of many aldoses, only in the case using D-mannose, have we obtained the very unprecedented binuclear Ni(II) complex containing *N*-glucosides in moderate yield. To clarify the stereochemistry of this complex, we have undertaken an X-ray crystal structure determination. To elucidate further this specific formation of the binuclear complex, we examined other aldoses and their derivatives as starting sugars. A preliminary account of this work has already appeared.[9]

Experimental Section

Materials. All reagents were of the best commercial grade. [$Ni(H_2O)_2$(*N,N'*-Me_2-en)$_2$]X_2 (X = Cl, Br) complexes were prepared by the known method.[10] The following abbreviations are used: *N*-(D-Man)-*N,N'*-Me_2-en, 1-(*N*-methyl-D-mannosylamino)-2-(methylamino)ethane; *N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en, 1,2-bis(*N*-methyl-D-mannosylamino)ethane.

Preparation of the Complexes (μ-Man)[$Ni_2(CH_3OH)$(*N*-(D-Man)-*N,N'*-Me_2-en)(*N,N'*-(D-Man)$_2$-*N,N'*-Me_2-en)]$Cl_2\cdot 2CH_3OH\cdot H_2O$ (6) and (μ-Man)[$Ni_2(CH_3OH)$(*N*-(D-Man)-*N,N'*-Me_2-en)(*N,N'*-(D-Man)$_2$-*N,*

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