*Inorg. Chem.* **1988**, *27*, 4219–4224

removed on a Schlenk line to give a red-black oil (0.218 g, 0.58 mmol, 51.3% based on carborane reagent employed).

**Synthesis of $Et_4C_4B_8H_6Et_2$ (13).** The iron complex **11** prepared in the preceding synthesis was opened to the air, 5 mL of dry THF was added, the solution was pipetted into an open flask, and 0.1 g of $FeCl_3$ was added. Dioxygen was bubbled into the solution, producing no detectable color change after 1 h. The $O_2$ treatment was continued for 12 h, which gave a brown suspension, from which solvent was removed by evaporation to give a brown sludge, which was extracted with *n*-hexane. The resultant solution was placed on a 5-cm silica column and eluted with 200 mL of 50:50 *n*-hexane/dichloromethane. The colorless eluent was rotary-evaporated to give 0.411 g of a viscous, colorless liquid. Thin-layer chromatography on silica in *n*-hexane gave one band, $R_f$ 0.68, which was extracted with dichloromethane and rotary-evaporated to give 0.125 g (0.40 mmol, 68% yield) of **13**. Exact mass: calcd for $^{12}C_{16}{}^{11}B_8{}^{1}H_{36}{}^{+}$, 316.3562; found, 316.3579. Visible–UV absorptions (nm): 234 (68%), 258 (76%), 296 (88%).

**Synthesis of $(PhCH_2)_4C_4B_8H_6(CH_2Ph)_2$ (14).** Following the procedure employed in the preceding two syntheses, 0.119 g (0.34 mmol) of the tribenzylcarborane **8** was deprotonated with 0.38 mmol of NaH in THF, and 0.34 mmol of $FeCl_2$ was added. The red iron complex **12** was not isolated in this case, but its solution was warmed to room temperature and stirred overnight. Workup identical with that used for **13** above gave a colorless liquid, which was thin-layer chromatographed on silica to give four bands. Band 1 ($R_f$ 0.03) was **14**, 0.070 g (62% yield). Bands 2 and 3 ($R_f$ 0.11 and 0.19) were unidentified non-boron-containing materials, and band 4 ($R_f$ 0.32) was the starting carborane **8**. Crystals of **14** were grown in 4:1 *n*-hexane/dichloromethane solution. Visible–UV absorptions (nm): 254 (60%), 284 (58%), 300 (59%).

**Acknowledgment.** Support of this work by the U.S. Army Research Office and the National Science Foundation (Grant No. 87-21657) is gratefully acknowledged. We thank Kathleen Fonda for assistance with the NMR spectroscopy and Professor Jack Steehler for discussions on the NMR studies.

**Registry No.** **1**, 80583-48-8; **2**, 105472-14-8; **3a**, 116910-63-5; **4a**, 116910-64-6; **5a**, 116910-65-7; **6**, 116910-66-8; **7**, 116910-67-9; **8**, 116910-68-0; **9**, 116910-69-1; **10**, 116910-70-4; **11**, 116926-52-4; **12**, 116926-53-5; **13**, 116910-71-5; **14**, 116910-72-6; $Na^+(PhCH_2)_2C_2B_4H_5{}^-$, 116926-51-3; $FeCl_2$, 7758-94-3; benzyl chloride, 100-44-7; xylyl chloride, 104-82-5; xylyl bromide, 104-81-4; 1-bromo-3-phenylpropane, 637-59-2; methyl iodide, 74-88-4; benzyl bromide, 100-39-0; ethyl bromide, 74-96-4.

---

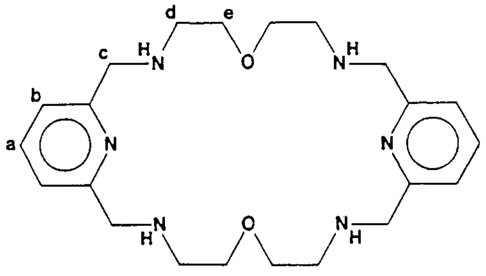
Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843-3255

# New Multidentate Ligands. 29. Stabilities of Metal Complexes of the Binucleating Macrocyclic Ligand BISBAMP and Dioxygen Affinity of Its Dinuclear Cobalt(II) Complex

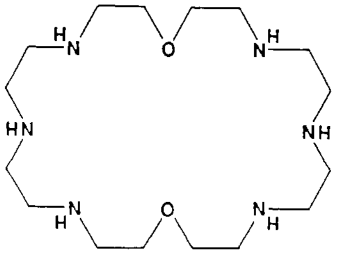
Manuel Garcia Basallote† and Arthur E. Martell*

*Received May 6, 1988*

The macrocyclic ligand 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1$^{11,15}$]triaconta-1(28),11,13,15(30),25,26-hexaene, BISBAMP, has been prepared and isolated as the hexahydrochloride. The protonation constants of BISBAMP are determined from potentiometric measurements at 25.0 °C and $\mu$ = 0.100 M ($KNO_3$). The stability constants of the mononuclear and binuclear Co(II), Ni(II), Cu(II), and Zn(II) complexes are reported. The formation of monoprotonated binuclear BISBAMP complexes with the metal ions is observed, as well as several protonated and hydroxo species. The dinuclear complexes show a strong tendency toward hydroxide ion bridging between the metal ions. The stability of the Co(II) dioxygen complex has been determined, and the potentiometric data reveal that dioxygen complex formation occurs in basic solution and that the ($\mu$-hydroxo)($\mu$-peroxo)dicobalt(III) complex forms several hydroxo species.



**1**, BISBAMP



**2**, BISDIEN

## Introduction

Metal complexes of binucleating macrocyclic ligands may serve as models for certain metalloproteins that require the presence of two metal centers. Thus, it has been proposed that type III copper proteins contain two Cu(II) ions with a hydroxo bridge.[1] In oxyhemocyanin two Cu(II) ions are doubly bridged by a peroxo and an oxygen-donor ligand.[2] In bovine superoxide dismutase an imidazolate ion acts as a bridge between Cu(II) and Zn(II).[3] In order to mimic the structure of these proteins, a large number of synthetic ligands have been prepared. For ligands with an appropriate disposition of donor atoms, it has been possible to show the presence of hydroxo,[4] imidazolato,[5] azido,[6,7] and thiocyanato[7-9] bridges between metal ions. Although these results show an increasing understanding of the synthetic and structural aspects of the problem, there are still few reports dealing with solution studies in which the interaction between the macrocycle and the metal ions is analyzed over a wide range of conditions[10-14] in order to determine the complex species formed and the corresponding equilibrium constants for their formation.

In this paper, the synthesis of the macrocyclic compound 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1$^{11,15}$]triaconta-1(28),11,13,15(30),25,26-hexaene, BISBAMP (**1**), is reported. It has been isolated as the hexahydrochloride with the purity required for potentiometric equilibrium determinations. This compound is structurally related to BISDIEN (**2**, 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane),[11,15] BIS-

---

† On leave from the Departamento de Quimica Inorganica, Universidad de Cadiz, Cadiz, Spain.

(1) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. J.; Spiro, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 86.

0020-1669/88/1327-4219$01.50/0

TREN (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo-[11.11.11]pentatriacontane),[10,15] and some of the Schiff-base-type compounds prepared by Nelson et al.[4,16,17] BISBAMP can be considered to contain two subunits of 2,6-bis(aminomethyl)pyridine capable of coordinating two metal ions. The 24-membered macrocyclic ring should enclose two metal ions at a distance suitable for cascade-type complex formation with small donor substrates such as hydroxide ion and dioxygen. The potentiometric studies of the formation of BISBAMP complexes with Co(II), Ni(II), Cu(II), and Zn(II) are reported in this paper, together with the formation constants of the dicobalt dioxygen complexes.

## Experimental Section

**Materials.** 1,5-Diphthalimido-3-oxapentane was prepared by adding a mixture of 23.4 mL of 1,5-dichloro-3-oxapentane and 20.0 mL of dimethylformamide (DMF) to a suspension of 88.8 g of potassium phthalimide in 220 mL of DMF. After stirring at 95-100 °C for 22 hrs the mixture was poured into ice. Precipitation was complete after 1 h, and the solid was filtered off and washed with water until no chloride was detected in the filtrate. The compound was dried at 60 °C for 16 h; yield 66 g (94%).

1,5-Diamino-3-oxapentane was prepared[18] by refluxing for 16 h a mixture of 14.4 mL of hydrazine and 55 g of 1,5-diphthalimido-3-oxapentane in 380 mL of absolute ethanol. HCl (6 N, 100 mL) was added to the cooled mixture before refluxing for 1 h more. A precipitate of phthaloylhydrazine was filtered off after 6 h and washed with water until neutral. Ethanol and water were then removed by vacuum evaporation, and the residue of phthaloylhydrazine was filtered off and washed with water. The filtrate was then evaporated to almost dryness. After addition of 35 g of KOH, the paste was extracted with 4 × 100 mL of $CH_2Cl_2$. The organic phase was filtered and dried with anhydrous $MgSO_4$ for 30 min. The clear $CH_2Cl_2$ solution was then vacuum-evaporated, and 16.4 g of yellow oily 1,5-diamino-3-oxapentane was obtained; yield 79%.

$Pb(SCN)_2$ was prepared from $Pb(NO_3)_2$ and KSCN. All the other chemicals used in synthetic work were used as obtained from Aldrich Chemical Co.

**Preparation of BISBAMP.** A mixture of 1.000 g of 2,6-pyridinedicarboxaldehyde, 0.81 g of 1,5-diamino-3-oxapentane, and 2.45 g of $Pb(SCN)_2$ in 380 mL of methanol was stirred at 40 °C for 1 h under an argon atmosphere. Under these conditions the binuclear lead(II) complex of the macrocyclic Schiff base of BISBAMP is formed. After the addition of 2.2 g of $NaBH_4$ the solution was stirred for 15 min at 42 °C and was then cooled at room temperature. A precipitate of metallic lead was separated, and the filtrate was vacuum-evaporated to dryness. Thus, 20 mL of 1.0 M EDTA (pH = 9.7) was added to remove lead(II) and 80 mL of $CHCl_3$ was also added to extract the ligand. The resulting organic phase was washed twice with 20 mL of saturated NaCl solution and dried with anhydrous $Na_2SO_4$. After it stood for 1 h, the solution was filtered and vacuum evaporated to give 1.36 g of oily BISBAMP free base, yield 90%.

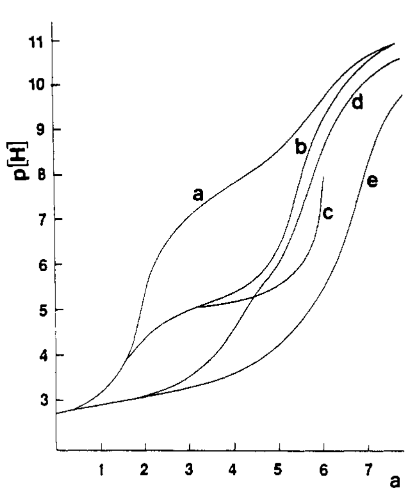


Figure 1. Equilibrium p[H] profiles for solutions containing: BISBAMP (**1**) (a), Ni(II) and BISBAMP in 1:1 (b) and 2:1 (c) molar ratios, and Cu(II) and BISBAMP in 1:1 (d) and 2:1 (e) molar ratios ($t$ = 25.0 °C; $\mu$ = 0.100 M ($KNO_3$); [BISBAMP] = $1.00 \times 10^{-3}$ M). $a$ = moles of base added per mole of ligand present.

In order to obtain a crystalline sample, the oily material was dissolved in 20 mL of 1:1 ethanol–ether mixed solvent and the solution was saturated with dry HCl gas. The precipitate that formed was filtered off and washed with ether. It was then dissolved in a small amount of methanol and vacuum-evaporated to dryness. The resulting solid was dissolved in a small amount of water and vacuum-evaporated to dryness to remove any excess HCl. The final product was dried for 5 h at 60 °C under vacuum, and 1.70 g of BISBAMP·6HCl was obtained; yield 85%. The HCl content was determined by potentiometric titration, and the purity of the sample was checked by recording the $^1H$ NMR spectrum in $D_2O$. Chemical shifts are reported in ppm from TMS, and protons are designated in accordance with **1**: a, 7.80 ppm (t, $J$ = 7.7 Hz); b, 7.34 ppm (d, $J$ = 7.7 Hz); c, 4.37 ppm (s); d, 3.31 ppm (t, $J$ = 4.9 Hz); e, 3.82 ppm (t, $J$ = 4.9 Hz). Anal. Calcd for $C_{22}H_{34}N_6O_2{\cdot}3H_2O$: C, 45.60; H, 7.36; N, 12.27. Found: C, 45.25; H, 7.33; N, 12.00.

Elemental analyses were made by Galbraith Laboratories. NMR spectra were recorded with a Varian XL200 spectrometer, and UV-visible spectra were measured with a Perkin-Elmer Model 553 Fast Scan UV–vis spectrophotometer.

Stock solutions of Co(II), Ni(II), Cu(II), and Zn(II) nitrates for potentiometric work were prepared in 0.100 M $KNO_3$, and their concentrations were determined by titration with EDTA (ethylenediaminetetraacetic acid) with the appropriate indicators.[19] The concentration of metal ion was close to 0.0050 M in all cases. A carbonate-free 0.0993 M KOH solution was prepared from a Dilut-it ampule and standardized with potassium acid phthalate. Reagent grade potassium nitrate was used as supporting electrolyte for all the experiments.

**Potentiometric Equilibrium Measurements and Computations.** The potentiometric determinations of stability constants were carried out with a Corning Model 250 ion analyzer fitted with glass and calomel reference electrodes. The system was calibrated to read $-\log [H^+]$ (p[H]) directly. Hydrogen ion activities (pH) were not employed in this research. All the experiments were made at 25.00 ± 0.05 °C with the ionic strength adjusted to 0.100 M by the addition of $KNO_3$. A stock solution of the ligand was prepared because of the hygroscopic nature of the solid sample, and it was standardized with 0.0993 M KOH. Aliquots containing 0.050 mmol of BISBAMP were used for every experiment. After the determination of the protonation constants of the ligand, equilibrium measurements were made on solutions containing 1:1 or 2:1 molar ratios of metal ion to BISBAMP. In order to obtain data at low p[H] values, the required amount of 0.100 M $HNO_3$ was added to the reaction mixtures. Oxygen and carbon dioxide were excluded from the solutions by maintaining an atmosphere of purified nitrogen over them. Oxygen was used instead of nitrogen for the determination of oxygenation constants.

The protonation constants of BISBAMP and the stability constants of metal complexes were determined form potentiometric data with program BEST.[20] In all cases, the model describing the equilibrium was kept as simple as possible by avoiding the inclusion of "invented" additional species. The species distribution diagrams were obtained with the program SPE, written by Dr. R. J. Motekaitis.

---

(2) Brown, J. M.; Powers, L.; Kincaid, B.; Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210.

(3) Tanier, J. A.; Getzoff, E. D.; Beem, K. M.; Richardson, J. S.; Richardson, D. C. *J. Mol. Biol.* **1982**, *106*, 181.

(4) Drew, M. G. B.; Nelson, J.; Esko, F.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1837.

(5) Coughlin, P. K.; Martin, A. E.; Dewan, J. C.; Watanabe, E. I.; Bulkowski, J. E.; Lehn, J. M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1004.

(6) Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381.

(7) Drew, M. G. B.; Esho, F. S.; Lavery, A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1984**, 545.

(8) Drew, M. G. B.; Nelson, S. M.; Esho, F. S. *J. Chem. Soc., Chem. Commun.* **1981**, 388.

(9) Drew, M. G. B.; Murphy, B. P.; Nelson, J.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1987**, 873.

(10) Motekaitis, R. J.; Martell, A. E.; Lehn, J. M.; Watanabe, E. J. *Inorg. Chem.* **1982**, *21*, 4253.

(11) Motekaitis, R. J.; Martell, A. E.; Lecomte, J. P.; Lehn, J. M. *Inorg. Chem.* **1983**, *22*, 609.

(12) Bencini, A.; Bianchi, A.; Garcia-España, E.; Giusti, M.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 681.

(13) Bencini, A.; Bianchi, A.; Garcia-España, E.; Giusti, M.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 1243.

(14) Motekaitis, R. J.; Martell, A. E.; Murase, I. *Inorg. Chem.* **1986**, *25*, 938.

(15) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441.

(16) Nelson, S. M. *Pure Appl. Chem.* **1980**, *52*, 2461.

(17) Nelson, S. M.; Knox, C. V.; McCann, M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1981**, 1669.

(18) Bogatskii, A. V.; Lukyanenko, N. G. *Zh. Org. Khim.* **1980**, *16*, 1301.

(19) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, 2nd Engl. ed.; Methuen: London, 1969.

(20) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

**Table I.** Logarithms of the Successive Protonation Constants $(K^{H}{}_{i})^{a}$ of BISBAMP and BISDIEN$^{b}$ ($\mu$ = 0.10 M, $t$ = 25.0 °C)

| | log $K^H_i$ | | | log $K^H_i$ | |
|---|---|---|---|---|---|
| *i* | BISBAMP | BISDIEN | *i* | BISBAMP | BISDIEN |
| 1 | 8.75 | 9.65 | 4 | 6.79 | 7.64 |
| 2 | 7.94 | 8.92 | 5 | | 3.81 |
| 3 | 7.36 | 8.30 | 6 | | 3.26 |

[a] $K^H_i = [H_iL^{i+}]/[H^+][H_{i-1}L^{(i-1)+}]$. [b] Reference 11.

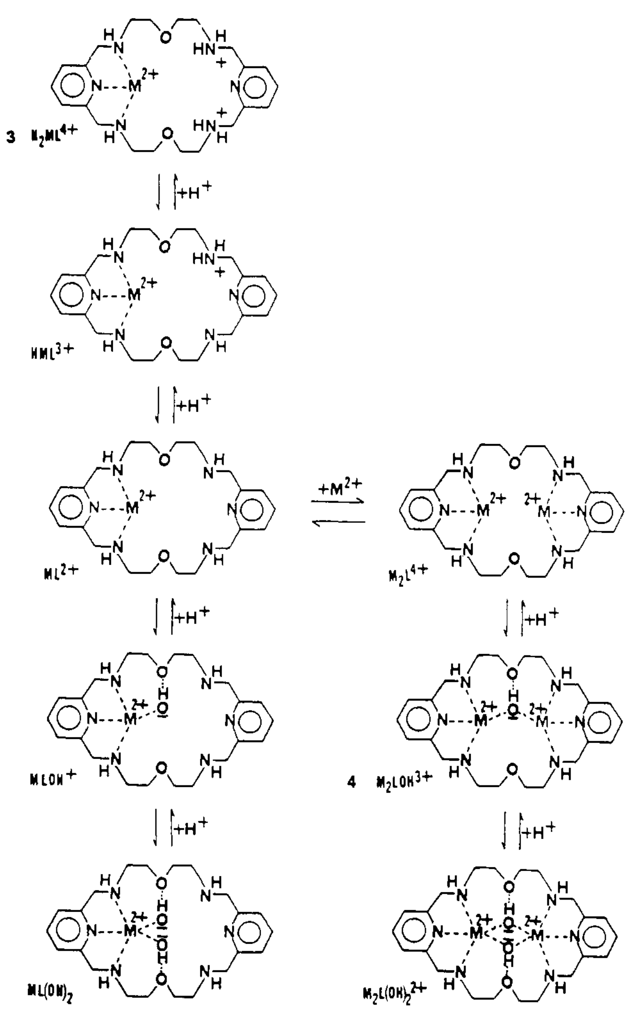
## Results and Discussion

**Protonation Constants of BISBAMP.** The titration curve of BISBAMP (Figure 1a) shows two inflections at 2 and 6 mol of base/mol of ligand. Processing of the data with the aid of the program BEST[20] led to the values in Table I for the protonation constants corresponding to the four aliphatic nitrogen atoms. No values could be obtained for the constants corresponding to the protonation of the pyridine nitrogens. Literature values for BISDIEN[11] are also included in Table I for comparison, and they are always over 0.9 log unit higher than those of BISBAMP. As the only difference between both molecules is the presence of the pyridine rings, the latter must be the reason for the lower basicity of BISBAMP. Similar differences can be found in the literature[21] for related ligands, and so it can be assumed that the protonation sequence for the new ligand is similar to that previously proposed for BISDIEN,[11] with successive protonation of aliphatic nitrogen atoms in such a way that Coulombic interactions between protonated nitrogens are minimized.

Since the BISBAMP molecule can be considered to consist of two 2,6-bis(aminomethyl)pyridine (BAMP) units, it is interesting to compare the protonation constants of both compounds. Unfortunately, literature data for BAMP[21-23] have been obtained under conditions (20 °C and 1 M $NaNO_3$) different from those employed in this work and direct comparison is not possible. However, the reported values of 9.53 and 9.15 are almost 1 order of magnitude higher than those of BISBAMP, indicating higher basicity. This decrease in the protonation constants when the macrocycle is formed has been observed previously for BISDIEN[11] and BISTREN.[10] A reliable value could not be obtained[22,23] for the logarithm of the third protonation constant of BAMP. The values corresponding to the protonation of the aromatic nitrogens in BISBAMP are expected to be even lower, and so they cannot be determined from potentiometric data.

**Metal Complexes of BISBAMP.** The molecule of BISBAMP (**1**) contains six nitrogens able to act as donor atoms in coordination complexes, but they are arranged in two separate subunits, and it is expected that mononuclear complexes ML will be formed by coordination of the metal ion to one of the tridentate subunits (Scheme I). In spite of the low flexibility of the molecule, a possible increase in the number of donor atoms cannot be discarded and mononuclear complexes of tetradentate BISBAMP can be formed in certain cases. Scheme I illustrates the complex species that can be formed from an ML complex. Thus, protonation of nitrogen atoms in the uncoordinated subunit will lead to the formation of HML and $H_2ML$. Mononuclear hydroxo complexes may also result from deprotonation of water molecules occupying the additional coordination sites on the metal ion. The addition of a second metal ion will result in the formation of $M_2L$, which can hydrolyze to form binuclear hydroxo complexes. All the species in Scheme I represent the basis of the model used in the determination of stability constants of BISBAMP complexes with Co(II), Ni(II), Cu(II), and Zn(II). Depending on their relative stabilities, they will be present in different concentrations at equilibrium and even some of them may not be formed in the case of some metal ions. However, no additional species were included in the calculations with the only purpose of improving the fit of the data.

**Scheme I.** Metal Complexes Formed by BISBAMP



The potentiometric data obtained for solutions containing BISBAMP and metal ions are illustrated in Figure 1. The titration curves of Cu(II)–BISBAMP solutions are very different from those corresponding to the other metal ions, and they indicate higher stability of the copper(II) complexes. The 1:1 curve reveals that $H_2ML$ (**3**) is formed at a very low p[H] and it deprotonates to form other mononuclear species at higher p[H]. The 2:1 curve shows the formation of a stable $M_2L$ complex that hydrolyzes to form a hydroxo complex, **4**. The potentiometric curves obtained for Co(II) and Zn(II) are very similar to those shown in Figure 1 for Ni(II). BISBAMP complexes with these metal ions are less stable than those of Cu(II), and they only begin to form at p[H] close to 4.5. Precipitation of metal hydroxides occurring between p[H] 7 and 8 in 2:1 solutions also renders the study of these systems more difficult.

The stability constants of BISBAMP complexes with the four metal ions studied in this work are included in Table II and compared with the values previously reported for BISDIEN.[11] ML complexes of BISBAMP in all cases are less stable than the analogous BISDIEN compounds, probably because of the lower basicity of the new ligand. Protonation of ML to form HML occurs for all the metal complexes with log $Q$ values ranging from 7.12 to 7.45. However, the formation of $H_2ML$ species is observed only for the cases of Ni(II) and Cu(II) probably because mononuclear complexes of Co(II) and Zn(II) are less stable and they begin to form at higher p[H]. Moreover, the log $Q$ values obtained for the formation of $H_2ML$ complexes of Ni(II) and Cu(II) are significantly lower than the analogous values for BISDIEN complexes. This decrease in the affinity for protons may be the result of the stronger Coulombic repulsions between the metal ion and the protonated amino groups, resulting from the lower flexibility of BISBAMP, as well as intrinsic lower basicities of the nitrogen donor groups of BISBAMP.

---

(21) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5.

(22) Couturier, Y.; Petitfaux, C. *Bull. Soc. Chim. Fr.* **1975**, 1043.

(23) Couturier, Y.; Petitfaux, C. *Bull. Soc. Chim. Fr.* **1978**, I-435.

**Table II.** Logarithms of the Formation Constants of Metal Complexes of BISBAMP and BISDIEN[a] ($\mu$ = 0.10 M, $t$ = 25.0 °C)

| | log $Q$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Co(II) | | Ni(II) | | Cu(II) | | Zn(II) | |
| equil quotient, $Q$ | BISBAMP | BISDIEN | BISBAMP | BISDIEN | BISBAMP | BISDIEN | BISBAMP | BISDIEN |
| $[H_2ML]/[HML][H]$ | *b* | 5.97 | 4.65 | 5.03 | 5.24 | 7.46 | *b* | 5.63 |
| $[HML]/[ML][H]$ | 7.12 | 7.58 | 7.40 | 7.17 | 7.44 | 8.01 | 7.45 | 7.58 |
| $[ML]/[M][L]$ | 9.05 | 9.73 | 11.25 | 13.65 | 15.19 | 16.46 | 8.89 | 10.66 |
| $[MLOH][H]/[ML]$ | −9.97 | <−11.8 | −10.23 | *b* | −9.70 | −10.63 | −9.52 | −10.13 |
| $[ML(OH)_2][H]/[MLOH]$ | *b* | *b* | *b* | *b* | *b* | *b* | −11.00 | *b* |
| $[M_2L]/[ML][M]$ | 3.00 | 2.7 | 3.73 | *b* | 8.82 | 10.84 | 3.80 | 4.20 |
| $[M_2LOH][H]/[M_2L]$ | −7.90 | *b* | −5.11 | *b* | −6.51 | −6.51 | −7.07 | >−7 |
| $[M_2L(OH)_2][H]/[M_2LOH]$ | *b* | *b* | *b* | *b* | −9.12 | −10.40 | *b* | *b* |

[a] Reference 11. [b] Species not found.

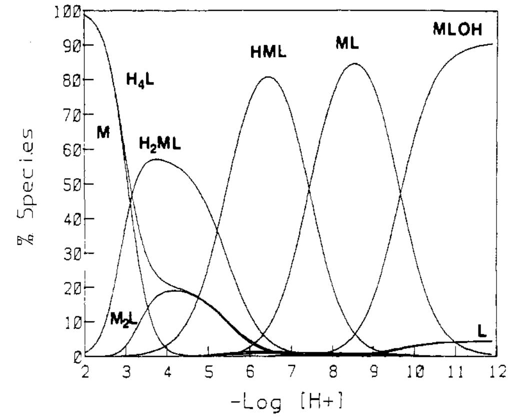


**Figure 2.** Species distribution diagram for the Cu(II)–BISBAMP system as a function of p[H] ($T_M$ = $T_L$ = 1.000 × $10^{-3}$ M).

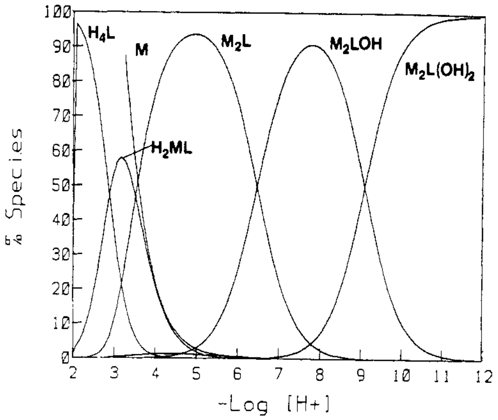


**Figure 3.** Species distribution diagram for the Cu(II)–BISBAMP system as a function of p[H] ($T_M$ = $2T_L$ = 2.000 × $10^{-3}$ M).

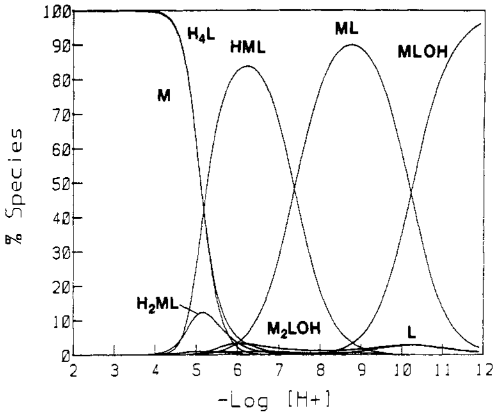


**Figure 4.** Species distribution diagram for the Ni(II)–BISBAMP system as a function of p[H] ($T_M$ = $T_L$ = 1.000 × $10^{-3}$ M).

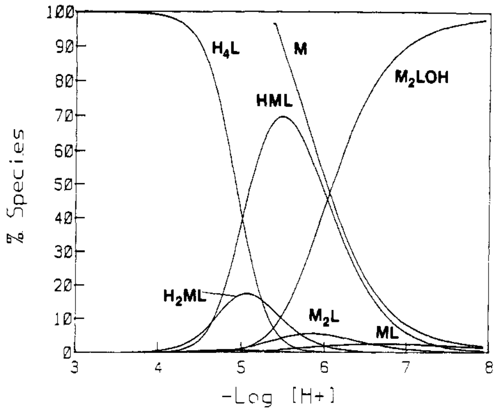


**Figure 5.** Species distribution diagram for the Ni(II)–BISBAMP system as a function of p[H] ($T_M$ = $2T_L$ = 2.000 × $10^{-3}$ M).

The hydrolysis of ML to form MLOH occurs in all the cases with a log $Q$ value close to −10, but the formation of $ML(OH)_2$ has been observed only for Zn(II). Addition of the second metal ion to ML to form $M_2L$ is characterized by a lower stability constant than the formation of ML because of the destabilization resulting from the Coulombic repulsions between the divalent metal ions in the macrocyclic cavity. The Coulombic repulsion between these ions can be reduced by the formation of hydroxo bridges, and in fact, the p$K_a$ values corresponding to the formation of $M_2LOH$ (**4**) are very low (Table II). The formation of this type of cascade-bridged species has been proposed by Lehn[15] to explain the behavior of some binuclear macrocyclic complexes. The p$K_a$ values obtained for these dinuclear BISBAMP complexes range from 5.1 to 7.90 for the metal ions listed in Table II and seem to be close to the values reported for the corresponding BISDIEN chelates, although the number of examples for comparison is restricted in the case of BISDIEN because of the tendencies to dissociate with precipitation of the metal hydroxides.

As has been previously pointed out, potentiometric studies of BAMP have been made under different experimental conditions and data are available only for Cu(II) complexes.[21] However, the log $Q$ value of 15.7 reported for the formation of Cu(II)–BAMP is close to the value obtained in this work for Cu(II)–BISBAMP, which seems to indicate that the decrease in stability caused by the lower basicity of the ligand is approximately compensated for by the stabilization due to the macrocyclic effect and by possible increase in the number of donor atoms used by BISBAMP when the mononuclear complex is formed.

The distribution of complex species in solutions containing 1:1 and 2:1 molar ratios of Cu(II) to BISBAMP are shown in Figures 2 and 3. The formation of mononuclear complexes begins at very low p[H] in the 1:1 solution, and they are the predominant species at p[H] values higher that 3.2. It is interesting to note that a significant amount of $M_2L$ is formed between p[H] 3 and 6. For the case of the 2:1 solution, dinuclear complexes are predominant at p[H] higher than 3.8, $H_2ML$ being the major species under more acidic conditions. The mononuclear complexes represent only a small percentage of the total amount of ligand at p[H] values higher than 5. $M_2L$, $M_2LOH$, and $M_2L(OH)_2$ are then the predominant species depending on the p[H] of the solutions. Figures 4 and 5 illustrate the species distributions for BISBAMP complexes with Ni(II), and similar results were obtained for the

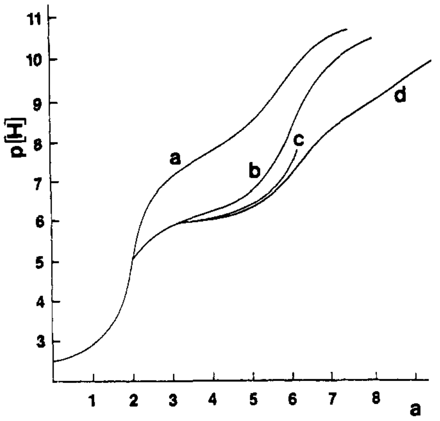
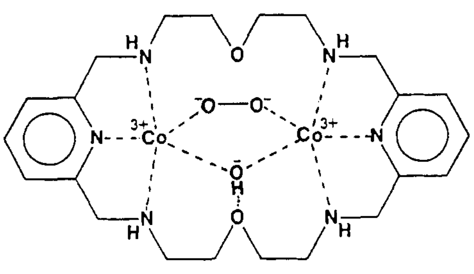


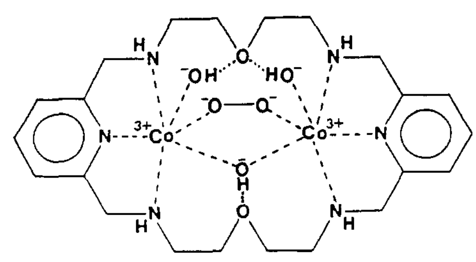
**Figure 6.** Equilibrium p[H] profiles for solutions containing BISBAMP (a), Co(II) and BISBAMP in 1:1 (b) and 2:1 (c) molar ratios under nitrogen, and Co(II) and BISBAMP in 2:1 molar ratio under oxygen (d) ($t = 25.0$ °C; $\mu = 0.100$ M ($KNO_3$); $P_{N_2} = P_{O_2} = 1.0$ atm; [BISBAMP] $= 1.00 \times 10^{-3}$ M).

behavior of Co(II) and Zn(II) complexes. As a consequence of the lower stabilities of these species, complex formation begins at higher p[H] and mononuclear complexes become the predominant species in 1:1 solution only at p[H] higher than 5. No significant formation of dinuclear complexes occurs in the 1:1 solution, with $M_2LOH$ representing only a maximum of 3.3% of the total amount of ligand. For the case of the 2:1 solution, binuclear complexes begin to form at p[H] 5, but whereas the concentration of $M_2LOH$ increases continuously as the p[H] is raised, $M_2L$ is only a minor species in solution, illustrating again the strong tendency to form the hydroxo-bridged binuclear complex.

**Formation of Dioxygen Complexes.** The p[H] profile obtained for a solution containing Co(II) and BISBAMP in 2:1 molar ratio under an oxygen atmosphere (Figure 6) indicates that dioxygen complexes are not very stable, but sufficiently so to prevent the precipitation of Co(II) hydroxide. The titration curves for 2:1 solutions in the presence and in the absence of oxygen are very similar for "*a*" values lower than 6, showing that dioxygen complexes are not formed in acidic solutions. However, under basic conditions a dioxygen complex is formed and it hydrolyzes to give soluble hydroxo species. The stability constants of dioxygen complexes included in Table III indicate that the $\mu$-hydroxy-$\mu$-peroxo complex **5** is less stable than the analogous BISDIEN complex, as expected because of the lower basicity of the ligand and probably also because of steric hindrance imparted by the rigidity of the pyridine rings. Di- and trihydroxo (**6**) dioxygen complexes result from hydrolysis of water molecules occupying the sixth coordination site on both metal ions. The stabilities of the BISBAMP dioxygen complexes are seen in Table III to be somewhat lower than that of the corresponding BISTREN dioxygen complex.



**5**, $Co_2LO_2(OH)^{3+}$



**6**, $Co_2LO_2(OH)_3^{+}$

**Table III.** Logarithms of the Oxygenation Constants of Co(II) Complexes with BISBAMP, BISDIEN,[a] and BISTREN[b] ($\mu = 0.10$ M, $t = 25.0$ °C, $P_{O_2} = 1.0$ atm)

| equil quotient, $Q$ | log $Q$ BISBAMP | log $Q$ BISDIEN | log $Q$ BISTREN |
|---|---|---|---|
| $[M_2LO_2(OH)][H]/[M_2L]P_{O_2}$ | -8.70 | -3.29 | -6.0 |
| $[M_2LO_2)(OH)_2][H]/[M_2LO_2(OH)]$ | -7.63 | -8.25 | |
| $[M_2LO_2(OH)_3][H]/[M_2LO_2(OH)_2]$ | -9.45 | -9.36 | |

[a] Reference 11. [b] Reference 10.

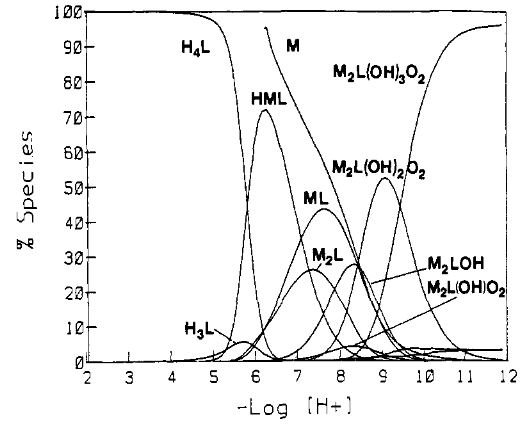


**Figure 7.** Species distribution diagram for the Co(II)-BISBAMP system in 2:1 molar radio under an oxygen atmosphere ($T_M = 2T_L = 2.000 \times 10^{-3}$ M; $P_{O_2} = 1.0$ atm).

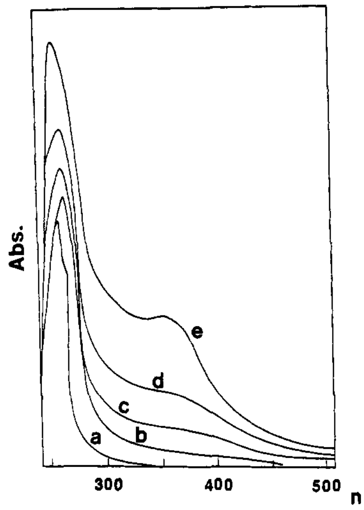


**Figure 8.** Electronic spectra of solutions containing Co(II) and BISBAMP under an oxygen atmosphere, with p[H] = 5.20 (a), 7.40 (b), 8.40 (c), 9.00 (d), and 10.90 (e) ($[Co^{2+}] = 4.2 \times 10^{-4}$ M; [BISBAMP] $= 2.1 \times 10^{-4}$ M; $t = 25.0$ °C; $P_{O_2} = 1.0$ atm).

The species distribution shown in Figure 7 illustrates the complicated mixture of complexes in equilibrium under an oxygen atmosphere. No complex is formed below p[H] 5, but as the p[H] increases, different amounts of mono- and dinuclear species are formed. Dioxygen complexes begin to form at p[H] close to 7, but they are the predominant species only at p[H] 8.5 and higher. The dibridged $M_2L(OH)O_2$ complex (**5**) is only a minor species because, when it is formed in a significant amount, the basic conditions favor its conversion to di- and trihydroxo complexes.

In order to confirm this description of dioxygen complex formation, electronic spectra of 2:1 solutions under an oxygen atmosphere were recorded as a function of p[H] (Figure 8). In acidic solutions there is no absorption band between 300 and 400 nm, and the intensity and position of the band close to 360 nm change only slightly with p[H]. Dioxygen complex formation is detected by the appearance of a band at 360 nm with a small shoulder close to 310 nm. This band appears only in the spectra corresponding to p[H] values higher than 7.4, and its shape and position are similar to those previously observed for other dibridged $\mu$-hydroxo–$\mu$-peroxo complexes.[24] However, at p[H] 10.5, where the degree of dioxygen complex formation is high, the absorbance values at 360 nm agree well with the values expected from Figure 6, showing that dioxygen complexes of Co(II) with BISBAMP have low stability and are formed only under basic conditions. Under the conditions employed for Figure 6, the concentrations of the dioxygen complexes (e.g., at p[H] values 9.0 and 11.0) indicated in Figure 7 may be employed to estimate their molar absorbances in solution. The values thus obtained for $Co_2LO_2(OH)_2$ and $Co_2LO_2(OH)_3$ are 4500 and 2800 $M^{-1}$ $cm^{-1}$, which correlate well with reported values for other $\mu$-hydroxo–$\mu$-peroxo complexes.[24] A corresponding value could not be obtained for $Co_2LO_2OH$ because of its low concentration.

**Acknowledgment.** This work was supported by The Robert A. Welch Foundation under Research Grant A-259 and the Commission for Educational Exchange between the United States and Spain for Fulbright/MEC (M.G.B.). Appreciation is expressed to D. Chen of this laboratory for synthesizing BISBAMP and supplying the procedure given in the Experimental Section.

---

(24) Fallab, S.; Mitchel, P. R. In *Advances in Inorganic and Bioinorganic Mechanisms*; Academic: New York, 1984; Vol. 3, p 311.

---

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

# Electron Transfer. 95. Reductions of Peroxide-Bound Chromium(IV)[1]

S. K. Ghosh, K. Laali, and E. S. Gould*

*Received April 12, 1988*

The peroxochromium(IV) derivative of diethylenetriamine $Cr^{IV}(dien)(O_2)_2\cdot H_2O$ (chelate I) may be prepared with ease and forms aqueous solutions that, when suitably buffered, are stable for over 1 h. Aqueous solutions of this complex in glycine buffers react rapidly with vanadium(IV), hexacyanoferrate(II), and Ti(III). With $VO^{2+}$, the Cr(IV) center, but not the peroxo ligands, is reduced, but $Fe(CN)_6^{4-}$ and Ti(III) reduce both functions. The chromium(III) products contain bound diethylenetriamine, and in the course of the reactions with Ti(III), carboxylate groups from the supporting media also enter the coordination sphere of chromium, with the extent of such intrusion greatest at highest carboxylate concentrations. Rate laws for reductions by $Fe(CN)_6^{4-}$ and $VO^{2+}$ feature both acid-independent and $[H^+]$-proportional terms, the latter indicating involvement of a more reactive protonated form of the peroxo complex, for which the $pK_A$ is less than 0.5. Specific rates for these two reductants are remarkably similar despite the poorer oxidation potential and the slower self-exchange associated with $VO^{2+}$. Reductions with Ti(III) appear to proceed through a strongly absorbing intermediate ($\epsilon_{380} = 600$ $M^{-1}$ $s^{-1}$), which is generated at a rate proportional to $[Ti^{III}]$ but decays unimolecularly ($k = 0.20$ $s^{-1}$). The behavior of this species corresponds to that of a Cr(IV)–Ti(III) precursor complex, formed prior to the act of internal electron transfer. Attachment of external carboxylate to the chromium center does not occur before electron transfer nor does it take place after all redox processes are complete. We suggest rather that it is associated with homolytic reduction, by Ti(III), of an O–O bond in a Cr(III)–peroxy intermediate, yielding a $Cr^{III}$–$O^\bullet$ fragment, which is rapidly converted to a substitution-labile $Cr^{IV}$–OH species. Reductions by $VO^{2+}$, which leave the peroxide group intact, are not accompanied by incorporation of external donors.

We have been interested since 1981 in the redox chemistry of the atypical states of chromium and have reported evidence that a variety of reductions of carboxylato-bound chromium(V) proceed through species having properties corresponding to complexes of the still less usual state chromium(IV).[2] However, this state appears to exist only transiently in carboxylate systems, for it is consumed by a combination of ligand oxidation, disproportionation, and rapid reaction with the added reductant. In contrast, several chromium(IV) diperoxo ammines may be isolated by conventional procedures and form aqueous solutions that, when suitably buffered, are stable for several hours. Prototype members of this series, featuring ligated ammonia[3] and ethylenediamine,[4] were reported near the turn of the century and attracted relatively little subsequent attention, but more stable derivatives were more recently described by Garner and co-workers.[5] Such complexes are attractive candidates for redox studies,[6] despite (or perhaps because of) possible complications stemming from the presence of two different oxidizing functions in the same molecule. This report deals with the reactions of the most robust of these diperoxo complexes, chelate I,[7,8] with the inorganic reductants vanadium(IV), titanium(III), and hexacyanoferrate(II).

## Experimental Section

**Materials.** Diperoxo(diethylenetriamine)chromium(IV) monohydrate, $Cr(dien)(O_2)_2\cdot H_2O$ (I), was prepared by the method of House and Garner.[5a,b] The complex, which precipitated from aqueous solution, was washed with methanol at 0 °C and then dried over $P_2O_5$ for 10–12 h.

---

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) See, for example: (a) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66. (b) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737. (c) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 899.

(3) Weide, O. F. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2178.

(4) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181.

(5) (a) House, D. A.; Garner, C. S. *Nature (London)* **1965**, *208*, 776. (b) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840. (c) House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1077.

(6) For recent studies of the reactions of these complexes, see: (a) Sriram, M.; Ramasami, T.; Ramaswamy, D. *Inorg. Chim. Acta* **1979**, *36*, L433. (b) Ranganathan, C. K.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Inorg. Chem.* **1986**, *25*, 915.

(7) Structure I has been assigned by House and Garner[5a] in analogy to that determined[8a] for the ethylenediamine analogue, $Cr(en)(O_2)_2\cdot H_2O$.

(8) (a) Stomberg, R. *Ark. Kemi* **1965**, *24*, 47. For determinations of related structures, see: (b) Stomberg, R. *Ark. Kemi* **1964**, *22*, 29, 49. (c) Stomberg, R. *Ark. Kemi* **1965**, *23*, 401. (d) Stomberg, R. *Ark. Kemi* **1965**, *24*, 111. For an overview of these investigations, see: (e) Stomberg, R. *Ark. Kemi* **1965**, *24*, 282.

0020-1669/88/1327-4224$01.50/0