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A New Macrocyclic Ligand Combining Two Different Coordination Sites: Macrocyclic Biquinazoline (Mabiq$^-$). Synthesis and Structure of the Free Ligand and of a Cobalt(III) Complex

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The synthesis of the new macrocyclic ligand 2–4:6–8-bis(3,3,4,4-tetramethyldihydropyrrolo)-10–15-(2,2′-biquinazolino)-[15]-1,3,5,8,10,14-hexaene-1,3,7,9,11,14-N_6^{22} (HMabiq = macrocyclic biquinazoline, $C_{33}H_{34}N_8$), combining a corrin type macrocyclic environment with an additional diimine type coordination site, is described. The yellow compound crystallizes in the orthorhombic system ($P2_12_12_1$) with a = 10.831 (2) Å, b = 12.201 (2) Å, c = 21.978 (4) Å, $\alpha = \beta = \gamma = 90°$, and Z = 4. Its dicyano–Co^{III} complex ($[Co(Mabiq)(CN)_2]$, $C_{35}H_{33}N_{10}Co$) crystallizes in the triclinic system ($P\bar{1}$) with a = 10.211 (1) Å, b = 18.785 (3) Å, c = 19.262 (3) Å, α = 107.80 (1)°, β = 100.14 (2)°, γ = 98.96 (2)°, and Z = 4. This compound is a model for dicyanocobalamine, as seen from its narrow UV/vis absorption peak at 536 nm (ϵ = 19 000) and the reversible Co^{II}/Co^{I} reduction–oxidation wave at –0.41 V (NHE).

Introduction

There is currently much interest in understanding and imitating the photosynthetic processes that take place in green plants and some microorganisms, in order to develop artificial systems capable of converting solar energy directly into chemical energy.[1] Much work has been devoted to the ruthenium(II)–diimine complexes (especially the tris(bipyridyl)ruthenium(II) cation), because they show a long-lived metal-to-ligand charge-transfer excited state (MLCT), which can participate in subsequent chemical reactions and transfer some of its excitation energy onto an appropriate substrate.[2]

A necessary condition for an efficient photoenergy conversion is, however, a good coupling of the primary photoexcitation to the secondary chemical processes. This can be achieved through the design of larger molecular systems that contain both a photosensitizer and a catalyst, able to take over the excitation energy (available either as oxidizing or as reducing power) and to incorporate it immediately into a chemical product.[3]

In this goal, we designed the new macrocyclic ligand IV (HMabiq, Scheme I), able to combine a cobalt ion in a corrin type environment—a system that is already known for its catalytic properties in the reduction of organic substrates[4]—with a diimine site, allowing coordination to Ru(II) or Cu(I) ions and thus the photoactivation of the catalyst by a metal-to-ligand or a metal-to-metal charge-transfer excitation. The sterically hindered diimine site in our system is especially suited for the study of Cu(I) ions, which, in such environments, show short-lived MLCT excited states.[5] These states, however, have to be exploited via an intramolecular follow-up mechanism, because they would not have sufficient time to encounter a substrate molecule in solution during their lives.[6]

In the following, we report on the synthesis, properties, and structures of the metal-free ligand HMabiq (IV) and of its dicyano–Co(III) complex (V), an analogue of dicyanocobalamin.

Experimental Section

All chemicals were purchased from Fluka (Buchs, Switzerland), unless indicated otherwise. The bis(amidine) X was synthesized from commercial α,α'-azoisobutyronitrile by the method of Scheffold et al.[7] The 4,4′-substituted 2,2′-biquinazoline part of the molecule is described for the first time.

Oxalylbis(anthranilamide) (I). To a suspension of 54.6 g (0.4 mol) of anthranilamide in 500 mL of dichloromethane and 41 g (0.4 mol) of triethylamine, contained in a 3-L reaction vessel equipped with an efficient mechanical stirrer and a reflux condenser, was slowly added a solution of 25.4 g of oxalyl chloride in 100 mL of dichloromethane at reflux temperature over a period of about 30 min. The reaction is very exothermic, and the addition has to be performed carefully. After the addition was completed, the white precipitate of I was filtered, washed with CH_2Cl_2, and dried; 60 g of crude material was obtained. Its IR spectrum showed absorptions in the region of 2500–3000 cm^{-1}, characteristic of triethylammonium salts, and the material was therefore purified as follows: A 30-g portion of the crude product was suspended in 250 mL of absolute ethanol, and the mixture was heated to reflux with efficient mechanical stirring for about 5 min. Filtering, washing with ethanol, and drying gave 23.2 g of a purer product, which showed no more IR absorptions between 2500 and 3000 cm^{-1}. The product is a white, microcrystalline solid, insoluble in the usual solvents, which does not melt below 250 °C.

Anal. Calcd for $C_{16}H_{14}O_4N_4$ (M_r = 326.312): C, 58.89; H, 4.32; N, 17.17. Found: C, 59.53; H, 4.35; N, 17.58. IR spectrum (cm^{-1}, KBr): 3400 s, 3300 w, 3200 s, 3060 vw, 1690 s, 1650 vs, 1610 s, 1590 s, 1580 sh, 1510 vs, 1450 s, 1395 s, 1300 m, 1230 w, 1170 w, 1150 vw, 1125 vw, 1085 vw, 1045 w, 950 vw, 870 m, 820 m, 755 s, 730 w, 630 m, 560 w, 530 m, 490 m, 390 w, 350 w.

4,4′-Dihydroxy-2,2′-biquinazoline (II, *Dione* Form). A 10-g portion of I was placed into the bottom part of a sublimation apparatus and heated in air to about 350 °C on a ceramic heating calotte (air bath), when vapors of steam escaped and the product finally melted to a dark, mobile liquid. (Heating under vacuum at this point resulted in considerably lower yields of the title compound; the product obtained in this way was contaminated by an intermediate of the double cyclization.) After it was cooled, the sublimation apparatus was fitted with its top (cold finger and vacuum connection) and the solidified product was sublimed in vacuo. At the end of the sublimation, some carbonaceous

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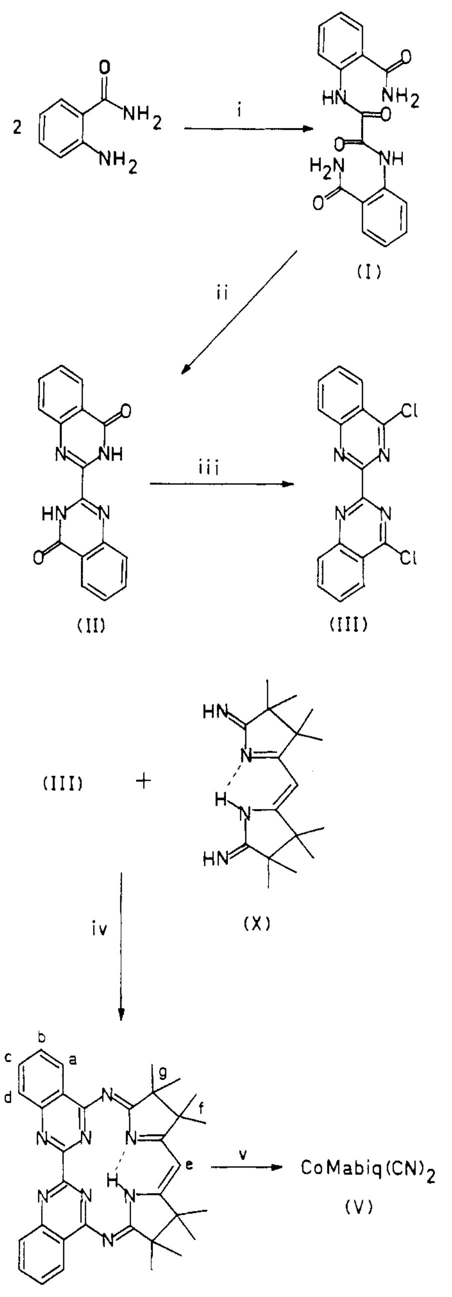
Scheme I. Synthesis of HMabiq (IV) and of CoMabiq(CN)$_2$ (V)[a]



[a] Legend: (i) (COCl)$_2$/2 NEt$_3$/CH$_2$Cl$_2$, reflux; (ii) heat to fusion (350 °C; -2 H$_2$O); (iii) 2 PCl$_5$/POCl$_3$, reflux; (iv) 2 NEt$_3$/DMF, reflux; (v) CoCl$_2$/H$_2$O$_2$/2 NaCN/EtOH–CH$_2$Cl$_2$.

material remained at the bottom. The yellowish product was scraped from the cold finger and directly used in the subsequent step; yield 6.53 g (73.5%). A purer product may be obtained by resublimation or recrystallization from dimethylformamide (DMF).

Anal. Calcd. for $C_{16}H_{10}N_4O_2$ (M_r = 290.284): C, 66.20; H, 3.47; N, 19.30. Found: C, 66.28; H, 3.51; N, 19.48. IR spectrum (cm^{-1}, KBr): 3120 m (broad), 1660 vs, 1600 s, 1565 m (sh), 1465 s, 1425 s, 1380 m (sh), 1330 s, 1310 m (sh), 1240 s, 1225 m (sh), 1140 m, 1100 m, 1090 w (sh), 1020 m, 960 w, 955 w, 920 s, 880 w (sh), 860 s, 820 m, 800 w, 775 s (sh), 770 s, 730 w (sh), 685 m, 670 w (sh), 630 w, 595 w, 580 w, 510 m, 490 s, 445 w, 310 m. As shown by the strong absorption at 1660 cm^{-1}, the compound is mainly in the *dione* form.

4,4′-Dichloro-2,2′-biquinazoline (III). A 10-g portion of the finely powdered dione II and 20 g of phosphorus pentachloride (PCl$_5$) were heated to reflux in 50 mL of phosphorus oxychloride (POCl$_3$). At about 90 °C, a vigorous evolution of HCl gas began and heating was continued with care. After 3 h of reflux, the reaction mixture was allowed to cool to ambient temperature and the resulting precipitate was isolated on a sintered-glass filter, washed with a small amount of POCl$_3$ followed by several portions of dry ether (to remove phosphorus chlorides), and dried in vacuo; yield 8.95 g. A further crop of 0.51 g of less pure material was obtained from the mother liquor after evaporation of the POCl$_3$ and destruction of the remaining PCl$_5$ with ethanol. (*Caution*! This is a vigorous reaction; cooling on ice is necessary.) The total yield was 9.46 g (84%). The product was directly used in the subsequent step. A small part was further purified by sublimation in vacuo. The compound is sensitive to moisture and should be kept in a tightly closed bottle or in a desiccator.

Anal. Calcd for $C_{16}H_8N_4Cl_2$ (M_r = 327.174): C, 58.74; H, 2.46; N, 17.12. Found: C, 58.40; H, 2.55; N, 17.14. IR spectrum (cm^{-1}, KBr): 3090 vw, 3060 vw, 3040 vw, 1605 s, 1545 vs, 1470 vs, 1445 m, 1370 s, 1330 vs, 1290 s, 1245 s, 1170 m, 1145 w, 1125 vw, 1100 m, 1015 w, 985 s, 905 w, 875 w, 840 s, 820 s, 790 m, 775 m (sh), 765 vs, 730 w (sh), 680 s, 670 m, 595 w, 550 m, 535 w, 500 m, 475 m, 400 w.

Macrocyclic Biquinazoline (IV, HMabiq). A 3.27-g (10-mmol) portion of the dichloride III and 2.88 g (10 mmol) of the bis(amidine) X were slowly heated with stirring to 150 °C in a mixture of 25 mL of dry dimethylformamide (DMF) and 2.5 g (25 mmol) of triethylamine in a 100-mL flask equipped with a reflux condenser. The initial suspension of III dissolved slowly above 120 °C, and the solution turned to an intense yellow. After about 45 min, the reaction mixture was almost homogeneous. It was allowed to cool to room temperature, when some of the yellow product crystallized, together with white triethylammonium chloride. The product was isolated by addition of 200 mL of water and 200 mL of CH$_2$Cl$_2$ and extraction of IV into the dichloromethane phase. Evaporation and recrystallization from DMF yielded 4.95 g of IV (90%) as yellow crystals, suitable for X-ray work. HMabiq is appreciably soluble in CH$_2$Cl$_2$ and CHCl$_3$, less soluble in DMF, sparingly soluble in alcohols, and completely insoluble in water and hydrocarbons. It does not melt below 300 °C.

Anal. Calcd for $C_{33}H_{34}N_8$ (M_r = 542.691): C, 73.04; H, 6.32; N, 20.65. Found: C, 72.88; H, 6.47; N, 20.49. IR spectrum (cm^{-1}, KBr): 3150 m, 3060 w, 2980 m, 2930 w, 2860 vw (sh), 1620 vs, 1595 vs, 1555 vs, 1490 s (sh), 1485 vs, 1460 s, 1395 s, 1380 s, 1355 s, 1295 m, 1275 m, 1265 m (sh), 1250 m, 1225 m, 1175 m, 1160 m, 1135 s, 1125 m (sh), 1100 s, 1060 m, 1015 w, 990 w, 960 w, 930 w, 925 w (sh), 895 w, 865 m, 845 vw, 835 w, 825 w (sh), 815 m, 790 m (sh), 780 m, 760 w, 745 vw, 735 vw, 690 m, 680 w (sh), 625 w, 610 m, 570 vw, 520 vw, 510 vw. ^{1}H NMR (ppm, 100 MHz, CDCl$_3$; signals relative to TMS): aromatic part, 8.823 (2 H, pseudodoublet a), 8.395 (2 H, pseudodoublet d), 7.911 (2 H, pseudotriplet c), 7.659 (2 H, pseudotriplet b); aliphatic part, 5.664 (1 H, singlet e), 1.375 (12 H, singlet g), 1.282 (12 H, singlet f), broad absorption at 13.5 (1 H, acidic proton in the center of the macrocycle). ^{13}C NMR (ppm, 100.394 MHz, CDCl$_3$; signals relative to TMS): 15 signals were found at 184.82, 179.15, 165.18, 159.02, 152.79, 133.50*, 129.43*, 127.56*, 125.89*, 122.39, 91.55*, 49.52, 48.94, 23.59*, and 23.20*. The starred signals belong to carbon atoms carrying hydrogen substituents (NOE enhancement). UV/vis spectrum (nm, in CH$_2$Cl$_2$; Figure 2): maxima at 260 (ϵ = 62000), 336 (ϵ = 30200), and 580 (sh; ϵ = 11000).

[Co^{III}(Mabiq)(CN)$_2$] (V). A 543-mg portion of HMabiq (IV, 1 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$ (clear yellow solution), and a solution of 238 mg (1 mmol) of [Co(H$_2$O)$_6$]Cl$_2$ in 15 mL of ethanol was added with stirring, followed by 0.25 g of triethylamine in 5 mL of ethanol. The resulting dark green solution was oxidized by addition of a few drops of H$_2$O$_2$ (30% in H$_2$O), when it became brown and evolution of oxygen gas was noted. A solution of 200 mg of KCN in 1 mL of water was now added with stirring drop by drop to the reaction mixture, until it turned to a clear, translucent red. Some excess of cyanide had to be used, as there are CN$^-$-consuming side reactions; however, too much cyanide lowered the yield again considerably. The reaction mixture was then filtered to remove any suspended solids; these were rinsed with CH$_2$Cl$_2$ until the washings were colorless. The resulting clear orange-red filtrate was evaporated slowly at room temperature on a rotary evaporator until all of the dichloromethane had gone, leading to a precipitation of the product in the remaining ethanol. The red-orange crystals of V were filtered, washed with methanol, and dried in vacuo; yield 370 mg. Suitable crystals for X-ray work were grown from chlorobenzene by slowly cooling a hot, saturated solution of V.

Mass spectrum (*m*/*e*; Figure 1): intense peaks at 600 (molecular cation without the two axial cyano groups), 570 and 540 (subsequent aromatization of the two dihydropyrrole subunits by loss of two CH$_3$• radicals each time). No signal corresponding to the molecular cation M$^+$ (*m*/*e* = 652) was detected. IR spectrum (cm^{-1}, KBr): 3070 vw, 3060 vw, 3030 vw, 2975 m, 2925 w, 2125 vw (CN groups), 1600 s, 1570 s, 1555 s, 1510 vs, 1490 s (sh), 1460 vs, 1410 s, 1370 s, 1330 w (sh), 1325 w, 1300 w, 1265 m, 1255 m (sh), 1230 m, 1200 w, 1185 w, 1165 s, 1135 w (sh), 1120 m, 1090 s, 1060 vs, 1025 w (sh), 1015 w (sh), 960 w, 945 vw (sh), 895 m, 885 vw (sh), 865 w, 855 vw (sh), 825 w, 810 w, 785 m,

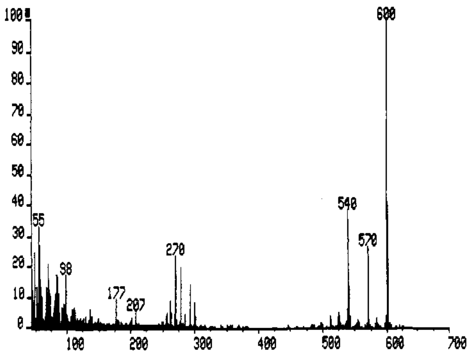


Figure 1. Mass spectrum of CoMabiq(CN)$_2$ (V).

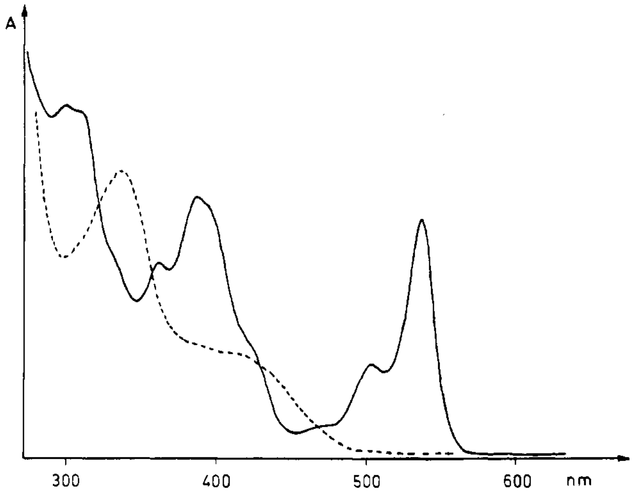


Figure 2. Electronic absorption spectra of (---) HMabiq (IV) and (—) CoMabiq(CN)$_2$ (V) (solutions 5×10^{-5} M in CH_2Cl_2).

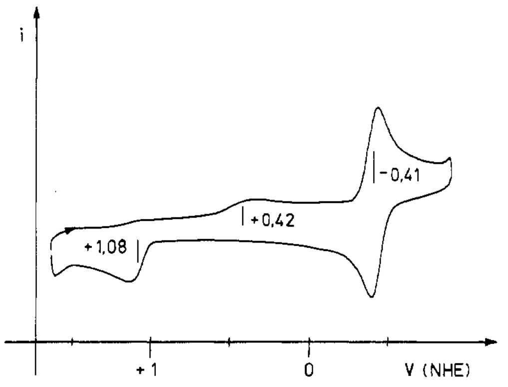


Figure 3. Cyclic voltammogram of CoMabiq(CN)$_2$ (V) (solution 10^{-3} M in propylene carbonate; 0.1 M TBAP; glassy-carbon working electrode; scan rate 0.1 V/s).

760 w, 730 m, 720 vw (sh), 700 w, 695 w, 660 vw, 630 m, 610 m, 580 w, 555 w, 520 vw, 480 vw, 445 vw, 340 w, 325 w, 320 vw (sh). ^{1}H NMR (ppm, 200 MHz, $CDCl_3$; signals relative to TMS): aromatic part, 9.01 (2 H, pseudodoublet a), 8.45 (2 H, pseudodoublet d), 8.12 (2 H, pseudotriplet c), 7.88 (2 H, pseudotriplet b); aliphatic part, 6.10 (1 H, singlet e), 1.45 (12 H, singlet g), 1.40 ppm (12 H, singlet f). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$; signals relative to TMS): 14 signals were found at 187.29, 177.51, 158.68, 154.28, 150.96, 136.06*, 129.95*, 129.04*, 126.16*, 123.57, 93.71*, 51.67 (2 signals superposed), 23.86*, and 23.00*. The starred signals have been assigned to the carbon atoms with hydrogen substituents via an APT pulse sequence. The signal of the CN carbon atoms could not be located in the spectrum. UV/vis spectrum (nm; Figure 2): maximum at 536 (ϵ = 19 000) with a vibrational progression at 502 (ϵ = 7200) and at 465 nm; further maximum at 386 (ϵ = 21 000) with shoulders at 395 (ϵ = 20 000) and at 420 (ϵ = 9000) and a vibrational progression at 361 (ϵ = 15 600); further features at higher energies.

Spectroscopic Measurements. Electronic spectra in solution were obtained with a Perkin-Elmer Lambda 5 spectrometer; IR spectra were recorded on a Perkin-Elmer 597 instrument. NMR spectra were taken on a Varian XL 200 spectrometer, and the mass spectrum was obtained on a WG 7000 E instrument.

Table I. Summary of Crystal Data, Intensity Measurement, and Structure Refinement^a

	HMabiq (IV)	CoMabiq (V)
formula	$C_{33}H_{34}N_8$	$C_{35}H_{33}N_{10}Co(C_2H_6O)_{0.5}(H_2O)_{0.5}$
mol wt	542.7	684.7
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	10.831 (2)	10.211 (1)
b, Å	12.201 (2)	18.785 (3)
c, Å	21.978 (4)	19.262 (3)
α, deg	90	107.80 (1)
β, deg	90	100.14 (2)
γ, deg	90	98.96 (2)
V, Å^3	2904.4	3375.1
Z	4	4
ρ_c, g·cm^{-3}	1.24	1.35
μ, cm^{-1}	0.72	5.49
λ, Å	0.710 69	0.710 69
temp, °C	20	20
R, %	7.8	8.4

^{a} Esd's are given in parentheses in terms of the least significant digit.

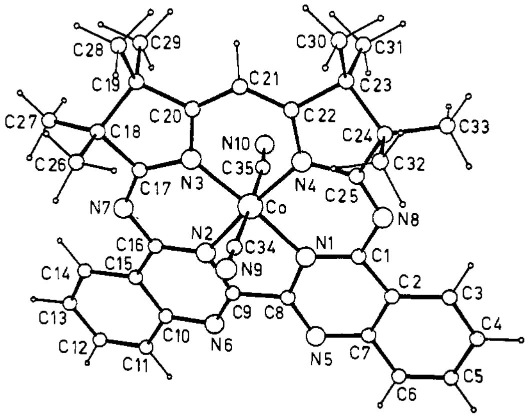


Figure 4. Atom-labeling scheme of the non-hydrogen atoms of HMabiq (IV) and CoMabiq(CN)$_2$ (V). In V, labels 1–35 are for the first molecule and 101–135 are for the second molecule.

Electrochemical Measurements. Cyclic voltammograms were recorded with a Tacussel PRGE-DEC potentiostat, connected to a function generator and an XY plotter. A three-electrode system, consisting of a glassy-carbon working electrode, a platinum counter electrode, and a nonaqueous Ag/Ag$^+$ reference electrode, was used. Tetrabutylammonium perchlorate (TBAP 0.1 M) served as inert electrolyte. The potential of the reference electrode was determined against the known $[Ru(bpy)_3](ClO_4)_2$ system.[8] The scan speed was 0.1 V/s. The voltammograms were analyzed according to established procedures.[8] The solutions were degassed with a current of nitrogen prior to scanning.

Crystal Structures. Experimental data and structure refinement are summarized in Table I. Diffracted intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation, $\Omega/2\theta$ scans, Lorentz and polarization correction, and no absorption correction; the structures were solved with MULTAN80.[9] Atomic scattering factors and anomalous dispersion terms were from ref 10, no secondary extinction correction was used, and all calculations were performed with a local version of the XRAY76[11] and

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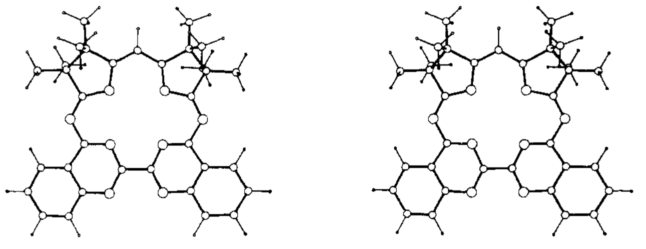

Figure 5. Stereo diagram of HMabiq (IV).

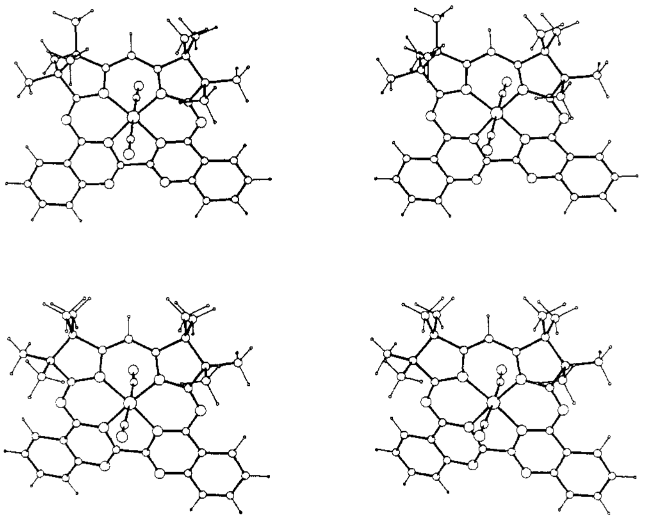

Figure 6. Stereo diagrams of the two independent molecules of CoMabiq(CN)$_2$ (V).

ORTEP II[12] programs. For compound V, the intensities of two reference reflections measured every 90 min during the data collection decreased by about 2.5%; all the intensities were corrected for this drift. For both molecules of the asymmetric unit, all the carbon atoms were refined with isotropic atomic displacement. The refinements were applied alternatively to each molecule of the asymmetric unit. There are two well-localized guest molecules (ethanol and water) in this structure; the positional parameters of the corresponding non-hydrogen atoms were refined with a fixed value for the atomic displacement. A refinement of the corresponding population parameters showed that the guest sites are not fully occupied. These disorders are presumably responsible for the relatively high final R value.

Results and Discussion

The results of the X-ray structure determinations are reported in Tables II–IV and in Figures 4–7. Table IV contains a juxtaposition of the most important averaged geometric values of IV and V. The atom labeling is shown in Figure 4. There is little variation in the bond lengths and angles between the free ligand geometry and that of its Co(III) complex, so we discuss them together: The geometry of the substituted biquinazoline moiety shows a variety of different bond types. Whereas the mean C–C distance of 1.395 Å in the phenyl rings corresponds to the usual aromatic bond order of 1.5, the distance C1–C2 in the pyrimidine rings appears somewhat elongated (1.43 Å) compared to an aromatic bond. N1–C1 (1.30 Å) is clearly shorter than N1–C8 (1.36 Å) or N5–C8 (1.33 Å), which themselves are comparable with aromatic C–N bonds such as those found in pyridines or pyrimidines. N5–C7 (1.38 Å) is also elongated, as well as the exo distance N8–C1 (1.41 Å). The distance N8–C25 (1.30 Å) again corresponds more to a C–N double bond.

In contrast to this *alternating* behavior found in the biquinazoline part of the molecule, the dihydropyrrolic part of it is symmetric and is evenly delocalized, as judged from the observed bond lengths. These are comparable with the mean values observed in a similar compound prepared by Scheffold et al.,[13] although this latter compound shows also a localized *alternation* of single and double bonds throughout its framework.

Table II. Refined Positional Parameters of HMabiq (IV) and U_{eq} Values (Å^2 × 10^3)^a

	x	y	z	U_{eq}
N1	0.2428 (9)	0.3340 (8)	0.6607 (4)	38 (6)
N2	0.3194 (9)	0.4678 (9)	0.5737 (4)	45 (7)
N3	0.5419 (9)	0.3731 (8)	0.5730 (5)	47 (7)
N4	0.4640 (9)	0.2359 (9)	0.6658 (5)	45 (7)
N5	0.0688 (8)	0.4509 (8)	0.6802 (4)	36 (6)
N6	0.1172 (8)	0.5489 (8)	0.5704 (4)	36 (6)
N7	0.4711 (9)	0.5086 (9)	0.4993 (4)	47 (7)
N8	0.2878 (10)	0.1830 (9)	0.7243 (5)	52 (7)
C1	0.2131 (12)	0.2715 (10)	0.7069 (6)	42 (8)
C2	0.1084 (10)	0.2909 (9)	0.7436 (5)	27 (7)
C3	0.0683 (12)	0.2234 (11)	0.7925 (5)	43 (8)
C4	−0.0349 (13)	0.2498 (11)	0.8255 (6)	45 (9)
C5	−0.0980 (13)	0.3456 (12)	0.8113 (6)	51 (9)
C6	−0.0641 (12)	0.4122 (11)	0.7636 (6)	49 (9)
C7	0.0396 (10)	0.3845 (9)	0.7284 (5)	28 (7)
C8	0.1688 (11)	0.4180 (10)	0.6489 (5)	31 (7)
C9	0.2001 (11)	0.4842 (10)	0.5945 (5)	36 (7)
C10	0.1513 (11)	0.6040 (10)	0.5175 (5)	33 (7)
C11	0.0651 (13)	0.6717 (11)	0.4890 (6)	50 (10)
C12	0.0981 (13)	0.7257 (11)	0.4378 (6)	50 (9)
C13	0.2153 (14)	0.7147 (12)	0.4096 (6)	60 (10)
C14	0.2985 (12)	0.6479 (12)	0.4373 (6)	46 (8)
C15	0.2695 (12)	0.5911 (10)	0.4917 (5)	34 (8)
C16	0.3511 (12)	0.5198 (9)	0.5250 (5)	34 (7)
C17	0.5513 (12)	0.4434 (11)	0.5239 (6)	45 (9)
C18	0.6803 (12)	0.4325 (11)	0.4948 (6)	46 (9)
C19	0.7560 (13)	0.3867 (12)	0.5511 (7)	59 (10)
C20	0.6559 (12)	0.3295 (11)	0.5868 (7)	51 (9)
C21	0.6755 (14)	0.2489 (14)	0.6286 (9)	82 (13)
C22	0.5837 (13)	0.2046 (11)	0.6642 (7)	57 (10)
C23	0.6084 (13)	0.1135 (13)	0.7110 (8)	78 (12)
C24	0.4803 (13)	0.0731 (12)	0.7240 (6)	53 (10)
C25	0.4004 (12)	0.1695 (10)	0.7053 (5)	36 (7)
C26	0.7278 (13)	0.5398 (14)	0.4694 (7)	68 (11)
C27	0.6699 (15)	0.3479 (18)	0.4440 (8)	105 (14)
C28	0.8018 (12)	0.4838 (14)	0.5911 (7)	74 (11)
C29	0.8642 (13)	0.3151 (13)	0.5333 (9)	88 (13)
C30	0.7096 (14)	0.0365 (13)	0.6996 (8)	82 (12)
C31	0.6372 (25)	0.1708 (15)	0.7762 (9)	148 (19)
C32	0.4575 (18)	−0.0212 (13)	0.6727 (9)	100 (15)
C33	0.4400 (15)	0.0184 (16)	0.7830 (9)	102 (15)

^{a}Esd's are given in parentheses; U_{eq} is the average of the eigenvalues of U.

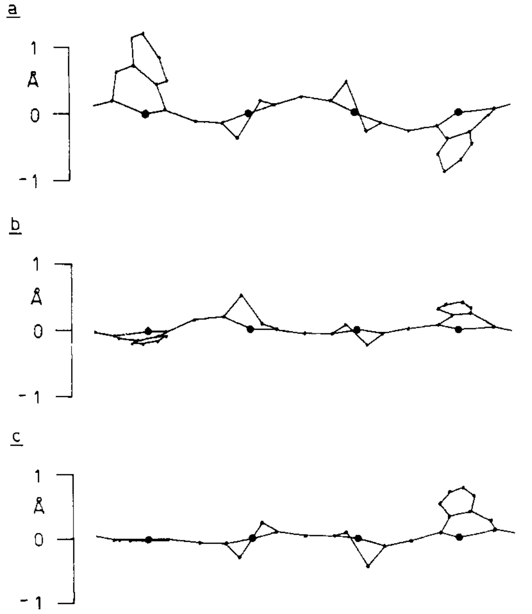

Figure 7. Cylinder projections of the macrocyclic 15-membered rings[14] of (a) HMabiq (IV), (b) CoMabiq(CN)$_2$ first molecule, and (c) CoMabiq(CN)$_2$ second molecule.

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Table III. Refined Positional Parameters of CoMabiq(CN)$_2$ (V) and U_{eq} (Å^2 × 10^3)[a]

	x	y	z	U/U_{eq}		x	y	z	U/U_{eq}	PP
Co1	0.30052 (21)	0.07512 (12)	0.75554 (12)	29.8 (9)	C27	−0.0984 (18)	−0.0005 (10)	0.8445 (10)	55 (5)	
N1	0.4422 (12)	0.0526 (7)	0.7037 (6)	33 (6)	C28	0.0520 (18)	0.2202 (10)	0.9236 (10)	57 (5)	
N2	0.3616 (12)	0.0090 (6)	0.8065 (7)	29 (6)	C29	−0.1609 (17)	0.1417 (10)	0.8305 (9)	49 (5)	
N3	0.1661 (11)	0.0926 (6)	0.8115 (6)	26 (5)	C30	0.120 (3)	0.3052 (15)	0.6956 (14)	107 (8)	
N4	0.2559 (12)	0.1435 (7)	0.7041 (7)	31 (6)	C31	0.0514 (25)	0.1850 (14)	0.5885 (14)	101 (8)	
N5	0.6060 (12)	−0.0263 (7)	0.6912 (7)	37 (6)	C32	0.4060 (23)	0.3034 (13)	0.7107 (13)	88 (7)	
N6	0.5303 (12)	−0.0661 (7)	0.8103 (7)	37 (6)	C33	0.3247 (22)	0.2483 (12)	0.5779 (12)	80 (7)	
N7	0.2082 (11)	0.0143 (6)	0.8868 (6)	25 (5)	C34	0.4331 (17)	0.1587 (9)	0.8316 (9)	43 (5)	
N8	0.4283 (14)	0.1373 (7)	0.6344 (7)	43 (7)	C35	0.1735 (17)	−0.0078 (9)	0.6800 (9)	44 (5)	
N9	0.5142 (14)	0.2062 (8)	0.8767 (8)	50 (7)	C101	0.6536 (14)	0.2978 (8)	0.2405 (8)	30 (4)	
N10	0.0938 (15)	−0.0583 (9)	0.6317 (8)	65 (7)	C102	0.7614 (14)	0.2641 (8)	0.2211 (8)	31 (4)	
Co101	0.48010 (20)	0.40832 (11)	0.22921 (11)	28,6 (9)	C103	0.8114 (14)	0.2109 (8)	0.2533 (8)	33 (4)	
N101	0.6186 (11)	0.3505 (6)	0.2111 (6)	32 (5)	C104	0.9151 (14)	0.1794 (8)	0.2291 (8)	35 (4)	
N102	0.5421 (11)	0.4537 (6)	0.1600 (6)	28 (5)	C105	0.9740 (16)	0.1986 (9)	0.1760 (9)	45 (4)	
N103	0.3461 (11)	0.4673 (6)	0.2409 (6)	29 (5)	C106	0.9340 (15)	0.2510 (8)	0.1472 (8)	41 (4)	
N104	0.4343 (11)	0.3604 (6)	0.2981 (7)	35 (6)	C107	0.8262 (14)	0.2843 (8)	0.1705 (8)	32 (4)	
N105	0.7887 (12)	0.3371 (6)	0.1387 (6)	36 (6)	C108	0.6879 (13)	0.3674 (7)	0.1615 (7)	25 (4)	
N106	0.7207 (11)	0.4568 (6)	0.0961 (6)	31 (5)	C109	0.6524 (13)	0.4299 (8)	0.1360 (7)	27 (4)	
N107	0.3856 (11)	0.5348 (7)	0.1563 (7)	36 (6)	C110	0.6829 (14)	0.5160 (8)	0.0772 (8)	32 (4)	
N108	0.5886 (11)	0.2750 (7)	0.2881 (6)	36 (6)	C111	0.7564 (15)	0.5485 (9)	0.0341 (8)	40 (4)	
N109	0.6716 (15)	0.5446 (8)	0.3544 (8)	72 (7)	C112	0.7224 (14)	0.6081 (8)	0.0149 (8)	36 (4)	
N110	0.2681 (14)	0.2779 (7)	0.1051 (7)	62 (7)	C113	0.6123 (14)	0.6356 (8)	0.0356 (7)	28 (4)	
C1	0.4765 (16)	0.0803 (9)	0.6520 (9)	40 (5)	C114	0.5360 (14)	0.6071 (8)	0.0777 (8)	35 (4)	
C2	0.5795 (16)	0.0532 (9)	0.6160 (9)	42 (5)	C115	0.5722 (14)	0.5441 (8)	0.0987 (8)	34 (4)	
C3	0.6240 (18)	0.0822 (10)	0.5609 (10)	50 (5)	C116	0.4971 (13)	0.5089 (7)	0.1389 (7)	22 (3)	
C4	0.7249 (19)	0.0526 (11)	0.5285 (10)	61 (5)	C117	0.3168 (14)	0.5133 (8)	0.2005 (8)	30 (4)	
C5	0.7873 (19)	0.0028 (11)	0.5501 (11)	63 (6)	C118	0.1830 (15)	0.5366 (8)	0.2082 (8)	36 (4)	
C6	0.7486 (18)	−0.0251 (10)	0.6075 (10)	52 (5)	C119	0.1759 (15)	0.5267 (8)	0.2841 (8)	38 (4)	
C7	0.6403 (16)	0.0011 (9)	0.6371 (9)	41 (4)	C120	0.2613 (13)	0.4690 (8)	0.2885 (7)	26 (4)	
C8	0.5088 (15)	−0.0010 (8)	0.7216 (8)	32 (4)	C121	0.2604 (14)	0.4256 (8)	0.3333 (8)	34 (4)	
C9	0.4695 (15)	−0.0222 (8)	0.7847 (8)	31 (4)	C122	0.3413 (14)	0.3764 (8)	0.3402 (8)	28 (4)	
C10	0.4925 (15)	−0.0837 (8)	0.8686 (8)	31 (4)	C123	0.3441 (15)	0.3335 (8)	0.3954 (8)	36 (4)	
C11	0.5614 (17)	−0.1307 (9)	0.8996 (9)	46 (5)	C124	0.4083 (15)	0.2670 (8)	0.3567 (8)	38 (4)	
C12	0.5150 (17)	−0.1476 (10)	0.9578 (9)	48 (5)	C125	0.4898 (14)	0.3019 (8)	0.3116 (8)	31 (4)	
C13	0.4076 (17)	−0.1231 (9)	0.9835 (9)	43 (5)	C126	0.1750 (19)	0.6142 (10)	0.2021 (10)	71 (5)	
C14	0.3404 (16)	−0.0754 (9)	0.9546 (9)	37 (4)	C127	0.0734 (18)	0.4743 (10)	0.1415 (10)	64 (5)	
C15	0.3838 (14)	−0.0558 (8)	0.8961 (8)	26 (4)	C128	0.2463 (16)	0.5997 (9)	0.3507 (9)	54 (5)	
C16	0.3165 (14)	−0.0094 (8)	0.8607 (8)	26 (4)	C129	0.0259 (17)	0.4994 (9)	0.2894 (9)	54 (5)	
C17	0.1414 (14)	0.0584 (8)	0.8628 (8)	29 (4)	C130	0.2027 (16)	0.3082 (9)	0.4077 (9)	50 (5)	
C18	0.0151 (15)	0.0733 (8)	0.8881 (8)	31 (4)	C131	0.4380 (17)	0.3897 (9)	0.4690 (9)	53 (5)	
C19	−0.0104 (16)	0.1420 (9)	0.8627 (9)	36 (4)	C132	0.3022 (16)	0.2004 (9)	0.2989 (9)	50 (5)	
C20	0.0746 (16)	0.1367 (9)	0.8051 (9)	36 (4)	C133	0.4980 (16)	0.2374 (9)	0.4090 (9)	48 (4)	
C21	0.0701 (17)	0.1790 (9)	0.7570 (9)	43 (5)	C134	0.6040 (15)	0.4905 (8)	0.3089 (8)	33 (4)	
C22	0.1580 (14)	0.1823 (8)	0.7110 (8)	29 (4)	C135	0.3463 (14)	0.3253 (8)	0.1479 (8)	26 (4)	
C23	0.1564 (16)	0.2334 (9)	0.6633 (9)	38 (4)	O1*	0.2078 (15)	0.6790 (8)	0.0365 (8)	80 (5)	0.910 (22)
C24	0.2964 (19)	0.2335 (10)	0.6458 (10)	59 (5)	O2*	0.8866 (20)	0.3689 (11)	0.4609 (11)	80 (6)	0.760 (22)
C25	0.3336 (15)	0.1630 (9)	0.6604 (9)	35 (4)	C201*	0.9219 (21)	0.5203 (12)	0.4682 (12)	80	0.96 (3)
C26	0.0356 (18)	0.0933 (10)	0.9744 (10)	58 (5)	C202*	0.8604 (24)	0.4268 (14)	0.4422 (13)	80	0.87 (3)

[a] Esd's are given in parentheses; for non-carbon atoms, U_{eq} is the average of the eigenvalues of U. For the two guest molecules ethanol and water (starred atoms), PP is the population parameter.

The sum of the five bond angles in the dihydropyrrole rings of our compounds is only 533–534° (instead of 540° as expected for a flat ring), indicating considerable puckering of these five-membered rings. The calculated puckering coordinates[20] are included in Table IV. The sum of the six angles in the pyrimidine rings is 720°, showing them to be essentially flat.

The length of the C–C bond joining the two quinazoline subunits (1.48 Å) is close to the value of a single bond, a feature that is also observed in 2,2′-bipyridyls. In the metal-free ligand, the two quinazoline subunits are twisted by 17° about this bond; in the Co(III) complex, the value of this twist angle is considerably lower.

The methyl groups of the dihydropyrrole subunits are in a staggered conformation (dihedral angles of 30–40°). In the metal-free ligand, these two subunits adopt a syn conformation, with a pseudo mirror plane relating the halves of the molecule, whereas in the complex V, which crystallizes with two independent molecules in the asymmetric unit, one of them adopts as well a syn conformation but the second is found in an anti conformation, where a pseudo-2-fold axis relates the halves of the molecule (Figures 5 and 6). This feature is reflected also by the signs of the corresponding dihedral angles between the methyl groups (Table IV).

The cobalt ion in the macrocyclic hole is slightly asymmetrically coordinated, as reflected by a longer bond (1.93 Å) to the quinazoline nitrogen atoms and a shorter one (1.90 Å) to the dihydropyrrole nitrogen atoms. This could be an effect due to the different bite angles of the biquinazoline and of the dipyrrolic part of the ligand, respectively, but we tend to interpret it more as a sign of a different donor strength (basicity) of the two types of nitrogen ligators.

"Ruffling" of the Corrinoid Ring System. A cylinder projection of the macrocyclic rings, by the method of Kratky et al.[14] (Figure 7), shows the free ligand to be considerably more "ruffled" than its Co(III) complex. In the former, the macrocycle adopts a saddle shape, with conformationally coupled dihydropyrrole subunits (alternative sense of puckering, paralleling the wave form of the saddle-shaped ligand periphery, as described by Eschenmoser et al.[15]). In the Co(III) complex V, the ligand periphery is essentially

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Table IV. Mean Geometric Values of HMabiq (IV) and CoMabiq$(CN)_2$ (V)^a

	HMabiq (IV)	CoMabiq$(CN)_2$ (V)		HMabiq (IV)	CoMabiq$(CN)_2$ (V)
		Bond Lengths and Angles in the Chromophore			
Co–N1		1.926 (3)	N1–Co–N4		91.3 (2)
Co–N4		1.898 (3)	Co–C34		1.918 (17)
N1–Co–N2		84.2 (1)	N9–C34		1.133 (15)
N3–Co–N4		93.3 (1)			
		Bond Lengths			
C8–C9	1.481 (16)	1.481 (7)	C23–C24	1.543 (43)	1.544 (6)
N1–C8	1.356 (29)	1.381 (6)	C22–C23	1.522 (14)	1.514 (3)
N1–C1	1.299 (9)	1.336 (4)	N5–C8	1.327 (19)	1.301 (14)
N8–C1	1.414 (9)	1.362 (4)	N5–C7	1.381 (11)	1.370 (5)
N8–C25	1.297 (2)	1.287 (9)	C2–C7	1.406 (2)	1.390 (11)
N4–C25	1.378 (4)	1.365 (8)	C1–C2	1.426 (14)	1.421 (9)
N4–C22	1.366 (13)	1.353 (8)	C–CH_3 (av)	1.540 (19)	1.538 (7)
C21–C22	1.369 (6)	1.367 (9)	C–C of Ph rings (av)	1.395 (6)	1.397 (5)
C24–C25	1.530 (12)	1.512 (7)			
		Bond Angles			
N1–C8–C9	114.9 (12)	113.3 (7)	C22–C23–C24*	101.5 (2)	101.4 (7)
C1–N1–C8$^{\dagger b}$	116.9 (1)	117.9 (5)	N4–C22–C23*	110.6 (1)	111.1 (5)
N1–C1–N8	121.4 (2)	123.6 (3)	N1–C1–C2†	123.3 (4)	119.0 (3)
C1–N8–C25	121.8 (14)	123.6 (5)	C1–C2–C7†	115.1 (1)	118.8 (2)
N4–C25–N8	128.7 (20)	129.3 (11)	N5–C7–C2†	122.3 (6)	121.2 (6)
C22–N4–C25*^{c}	109.8 (3)	109.8 (6)	C7–N5–C8†	115.2 (13)	116.6 (6)
N4–C22–C21	125.5 (10)	123.7 (3)	N1–C8–N5†	127.2 (8)	126.4 (6)
C20–C21–C22	123.6 (14)	126.2 (14)	pyrrole rings (sum)	533.1	534.1
N4–C25–C24*	109.9 (1)	110.2 (9)	pyrimidine rings (sum)	720.0	719.9
C23–C24–C25*	101.3 (13)	101.6 (10)			

		CoMabiq$(CN)_2$ (V)				CoMabiq$(CN)_2$ (V)	
	HMabiq (IV)	molecule 1	molecule 2		HMabiq (IV)	molecule 1	molecule 2
				Dihedral Angles			
N1–C8–C9–N2	−16.7 (15)	+7.4 (14)	−7.7 (13)	C26(27)–C18–C19–C28(29)	+36.4 (12)	+26.9 (3)	−36.0 (7)
N5–C8–C9–N6	−18.0 (16)	−0.3 (14)	−3.3 (16)	C30(31)–C23–C24–C32(33)	−44.4 (13)	+42.1 (46)	+35.5 (1)
				Puckering Coordinates of the Dihydropyrrole Rings[20]			
				N3,C17,C18,C19,C20			
q_2, Å	0.286	0.195	0.260	ϕ_2, deg	269.2	91.5	83.3
				N4,C22,C23,C24,C25			
q_2, Å	0.227	0.206	0.272	ϕ_2, deg	275.7	97.8	92.7
				Puckering Coordinates of the Macrocycle[20]			
				C21,C22,N4,C25,N8,C1,N1,C8,C9,N2,C16,N7,C17,N3,C20			
q_2, Å	0.540	0.218	0.224	q_5, Å	0.064	0.034	0.081
ϕ_2, deg	12.3	217.2	331.7	ϕ_5, deg	327.3	111.5	179.8
q_3, Å	0.053	0.103	0.092	q_6, Å	0.143	0.090	0.063
ϕ_3, deg	37.3	274.9	187.8	ϕ_6, deg	59.6	250.5	296.5
q_4, Å	0.021	0.053	0.032	q_7, Å	0.109	0.052	0.045
ϕ_4, deg	118.4	42.3	17.6	ϕ_7, deg	254.9	279.4	269.8

[a] Values were averaged over noncrystallographic symmetry elements and over both molecules in the case of V, with use of the formulas of Domenicano, Vaciago, Coulson.[19] Bond lengths are given in angstroms; bond angles and dihedral angles are given in degrees; esd's are in terms of the least significant digits. [b] Pyrimidine rings. [c] Pyrrole rings.

flat, and the dihydropyrrole subunits are conformationally decoupled, as shown by the existence of a syn and an anti isomer.

The mass spectrum of V (Figure 1) does not show a parent ion M^+ at $m/e = 652$. The highest peak is seen at $m/e = 600$, corresponding to $(M - 2\ CN)^+$. This is a general feature, observed also in other dicyano corrinoid compounds.[16] The unusual decay peaks at $m/e = 570$ and $m/e = 540$ are strong evidence for the ease of aromatization of the dihydropyrrole subunits, through the loss of two and four methyl radicals, respectively. The simultaneous loss of two methyl radicals from a fragment could not be well explained otherwise.

The low-energy features in the electronic spectrum of V (Figure 2) are quite similar to those of dicyanocobalamin;[16] the origin of these bands has been discussed previously[17] and assigned to π–π^* transitions of the conjugated system. The position of the lowest absorption band (α band) is very sensitive to the *net charge* of the coordinated central atom, moving to higher energies (lower wavelengths) if this charge increases.[17b] Our value of 536 nm is lower than the value found in dicyanocobalamin (583 nm),[16] and it is also lower than in most of the published corrin model compounds.[16]

The spectrum of the metal-free ligand does not show absorptions above 490 nm; this seems, however, to be consistent with the stronger charge effect of a proton (H^+) when compared to that of a Co(III) ion: NH_4^+ is known to be much more acidic than is $Co(NH_3)_6^{3+}$. That the acidic proton of IV is indeed chelated in the center of the macrocycle is also supported by its very high ^{1}H NMR shift of 13.5 ppm relative to TMS.

The cyclic voltammogram of V (Figure 3) at a glassy-carbon electrode in the weakly corrdinating solvent propylene carbonate shows an irreversible Co^{III}/Co^{II} reduction wave at +0.42 V (NHE), followed by a completely reversible Co^{II}/Co^{I} reduction–oxidation wave at −0.41 V (NHE). The reoxidation of Co^{II} to Co^{III} takes place at +1.08 V (NHE). These observations are consistent with the interpretation that V loses its two axial CN^- groups upon reduction to the Co^{II} state. The reoxidation to the Co^{III} state then has to take place at a much higher potential, due to the absence of the stabilizing cyanide ligands. The Co^{II}/Co^{I} potential of V is less negative then that of vitamin B_{12s}, which has

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been estimated to be –0.59 V (NHE).[18] This indicates that the cobalt ion in our ligand Mabiq$^-$ is somewhat less solvated than in the corrin system of vitamin B_{12}.

Conclusions

We have shown that a corrin type macrocyclic ligand, containing an additional diimine type coordination site, can be synthesized from commercially available materials in a few inexpensive steps. Its dicyano–cobalt(III) complex was shown to be comparable to dicyanocobalamin in its spectroscopic and electrochemical properties. Further investigation is needed to elucidate the behavior of the diimine coordination site of the new ligand HMabiq, as well as the photochemical and catalytic properties of the corresponding simple and mixed complexes, e.g. those of the [Cu^I(Mabiq)Co^{III}] type. It is felt that new and interesting "molecular machines" could be constructed upon this principle.

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Supplementary Material Available: A full table of crystal data, intensity measurement, and structure refinement parameters (Table V), full tables of bond distances and angles, and listings of atomic coordinates and displacement parameters for both structures (32 pages); tables of structure factors in the format of ref 21 (38 pages). Ordering information is given on any current masthead page.

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Syntheses and Characterization of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic Acid (HL^1) and Its Transition-Metal Complexes: Crystal Structures of HL^1·2HBr·H_2O, [NiL^1(H_2O)]Br, and [NiL^1(NCS)]H_2O[†]

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A simple stereospecific synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid (HL^1) is reported. The Ni^{2+}, Co^{3+}, and Cu^{2+} complexes of HL^1 have been prepared and characterized. HL^1·2HBr·H_2O (**1**) crystallizes in the orthorhombic space group *Pbca* with a = 16.079 (3) Å, b = 16.918 (3) Å, c = 17.837 (4) Å, and Z = 8. The structure was refined to R = 0.060 with 2001 reflections. [NiL^1(H_2O)]Br (**3**) crystallizes in the monoclinic space group $P2_1/n$ with a = 9.214 (2) Å, b = 19.972 (3) Å, c = 12.580 (4) Å, β = 106.34 (2)°, and Z = 4. The structure was refined to R = 0.041 with 2971 reflections. [NiL^1(NCS)]H_2O (**6**) crystallizes in the monoclinic space group $P2_1/a$ with a = 12.746 (3) Å, b = 11.809 (2) Å, c = 15.568 (2) Å, β = 102.29 (2)°, and Z = 4. The structure was refined to R = 0.044 with 2999 reflections. In both complexes **3** and **6**, the nickel ion coordination is approximately octahedral with the second ligand coordinated at axially on the octahedron, while the four nitrogen atoms of the macrocycle are essentially coplanar and the nickel ion shows +0.002 and –0.04 Å deviation from the least-squares plane, respectively. Complexes [NiL^1(H_2O)]X react with X_2 (X = Br, I) to yield the novel five-coordinated low-spin species containing trihalide counteranions, [NiL^1]X_3. The pH-dependent coordination geometry change of metal complex **3** accompanied by the change of its electrochemical behavior is also discussed.

The field of coordination chemistry of polyazamacrocycles has undergone spectacular growth after the early 1960s due to the pioneering independent contributions of Curtis[1] and Busch.[2] Since then a large number of synthetic polyazamacrocyclic ligands have been reported.[3] Their metal complexes often exhibit properties that are distinctly different from those of complexes with analogous open-chain ligands.

Recently, many efforts[4–9] have been made to introduce additional ligating groups into macrocycles in order to obtain new types of ligands that have the relatively rigid and kinetically stable structural element of the macrocycle as well as the more flexible and kinetically labile open-chain structural elements.

The synthesis of per-N-substituted tetraazamacrocycles is straightforward. The reaction of a macrocyclic tetraamine such as cyclam with an excess of chloroacetic acid or ethylene oxide usually gives the per-substituted product.[7] However, the synthesis of partial-N-substituted macrocycles is generally more complicated and necessitates several steps.[9] Recently Kaden and Studer[10] presented a one-step preparation method to obtain some mono-N-substituted polyazamacrocycles containing a carboxyalkyl or carboxyaryl side chain. We present here a simple stereospecific synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid (HL^1) and discuss its metal complexes.

HL^1 is a pentadentate ligand, in which the relative rigidity of the macrocyclic ring and the flexibility of the pendent carboxylate group should give rise to square-pyramidal or octahedral complexes. It forms metal complexes with Co^{3+} and Ni^{2+} of the type MLY, in which Y is the second monodentate ligand. Our interest in this paper is to study the influences of the second ligand on the structure of the complexes, and we report the novel five-coordinated low-spin nickel complexes containing trihalide counteranions [NiL^1]X_3 (X = Br, I) and the structures of HL^1·2HBr·H_2O, [NiL^1(H_2O)]Br, and [NiL^1(NCS)]H_2O. Preliminary accounts describing some of our results have been published.[11,12]

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