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Structure, spectra and redox studies of nickel(II) bis(benzimidazole-2-ylmethyl)amines with coenzyme M reductase

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Abstract—The 1 : 1 and 1 : 2 nickel(II) complexes with the tridentate ligand bis(benzimidazol-2-ylmethyl)amine (bbma) and its amine (bbmma) and benzimidazole (bmbma) *N*-methyl-substituted derivatives have been prepared and their spectroscopic and redox properties studied. While the 1 : 1 complexes are of the type $NiLX_2 \cdot nH_2O$ ($X = ClO_4^-$, Cl^- or NO_3^-), the 1 : 2 complexes are of the type $NiL_2(ClO_2) \cdot nH_2O$ (L = bbma, bbmma or bmbma, $n = 0$–4). The purple complex $Ni(bbma)_2(ClO_4)_2MeOH \cdot H_2O$ has been characterized by X ray crystallography. The Ni^{II} ion has an octahedral geometry with one nitrogen from the amine and one nitrogen atom of the benzimidazole in axial positions and the remaining three benzimidazole and amine nitrogen atoms coordinated in an equatorial fashion. A red shift was observed in the electronic spectra and an elevation of the redox potential was detected during the addition of the sodium salt of 2-mercaptoethanesulfonic acid (CoM) to the Ni^{II} complexes. The effects of methylation on the amine and also on the benzimidazole was observed in the electronic spectra and redox behaviour. © 1997 Elsevier Science Ltd

Keywords: benzimidazole; Ni(II) complexes; F_{430}; redox potentials.

Methyl coenzyme-M reductase [1,2] contains the nickel hydrocorphinoid complex F_{430} [3–5]; it is implicated in the final methane evolution step of methanogenic bacteria and has attracted considerable attention [6,7]. The essential role of F_{430} in methane formation was demonstrated by Ankel-Fuchs *et al.* [8]. Since F_{430} exists both in the Ni^I and the Ni^{II} states in *Methanobacterium thermoautotrophicum*, it is of interest to examine the role of the nickel ion oxidation state in methyl-CoM catalysis.

The presence of Ni^I in methyl-coenzyme M reductase, where $Ni^{II}F_{430}$ is first reduced to Ni^IF_{430}, causes the homolytic cleavage of methyl-CoM to produce methyl-Ni^IF_{430}, followed by the protonation of methyl-Ni^IF_{430} to yield CH_4 and $Ni^{II}F_{430}$ [9]. A mechanism has been proposed for the function of methyl coenzyme M reductase [10]. Nickel(I)-tetraazamacrocyclic complexes are somewhat more effective in producing methane from methyl CoM in aqueous solution [11]. It is clear that the ligand activates Ni^{II} toward methyl-CoM. The ligand in F_{430} might also play an important role in activating nickel toward methyl-CoM.

Synthesis of the active sites of various metalloproteins/enzymes has been used in elucidating the relationship between their structure and function [12–17]. To overcome the difficulties of synthesizing pyrrole rings around methyl-Coenzyme M reductase, synthetic accessable benzimidazole tridentate ligands were synthesized and complexed with nickel(II) ions. The Ni^{II} complex of bis(benzimidazol-2ylethyl)amine was crystallized in single crystal form and structurally characterized by X-ray crystallography. Generally, the red shift observed in the electronic spectra irrespective of inductive or steric effects, when CoM was added to Ni^{II} compounds, indicates that the coordination of CoM to Ni^{II} compounds leads to lower symmetry in the Ni^{II} structure. The electrochemical data illustrate the stabilization and destabilization by amine and benzimidazole *N*-methyl groups, respectively, in 1 : 1 nickel(II) perchlorates and the reverse order in 1 : 2 Ni^{II} complexes. Addition of 2-mercaptoethanesulfonic acid as coenzyme M reductase (CoM) to NiL compounds (L = bbma, bbmma, bmbma) generally raises the redox potential of the complexes, however, 1 : 1 nickel(II) complexes have more positive redox potential than 1 : 2 nickel compounds due to limited structural changes in 1 : 2 nickel compounds.

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The anaerobic reaction studies of Ni^{II} complexes with methyl-CoM to produce methane is under further investigation.

EXPERIMENTAL

Materials

The following reagents were used as received: $Ni(NO_3)_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, iminodiacetic acid, *N*-methyliminodiacetic acid (Aldrich), *N*-methylbenzene-1,2-diamine dihydrochloride (Kodak), 2-mercaptoethanesulfinic acid, sodium salt (coenzyme M reductase, Fluka). Tetra-*n*-hexylammonium perchlorate (G. F. Smith) was recrystallized twice from aqueous ethanol.

Physical measurements

Elemental analysis were performed at Central Drug Research Institute (CDRI), Lucknow, India. Nickel was determined volumetrically [18]. The diffuse refluctance and absorption spectra in methanol were measured on an Hitachi U-3400 double beam UV–vis–NIR spectrophotometer.

Cyclic voltammetry at a platinum sphere electrode was performed at 25±0.2°C. The temperature of the electrochemical cell was maintained by a cryocirculator (HAKKE D8 G) and solutions were deoxygenated by bubbling with research-grade nitrogen. The instrument utilized included a EG & G PAR 273 potentiostat interfaced with an IBM-2 computer along with EG & G M270 software employed to carry out the experiments and to acquire the data. A three-electrode cell configuration was used. The reference electrode was $Ag(s)/(AgNO_3)$ in methanol. Methanol for electrochemistry was distilled over magnesium turnings.

Synthesis of ligands

Bis(benzimidazol-2-ylmethyl)amine [19] (bbma), bis(benzimidazol-2-ylmethyl)methylamine [19] (bbmma) and bis(1-methylbenzimidazol-2-ylmethyl)amine [20] (bmbma) were synthesized as previously reported.

Synthesis of complexes

$Ni(bbma)(ClO_4)_2 \cdot MeOH$. The compound "bbma" (0.277 g, 1.0 mmol) was dissolved in methanol (10.0 cm^3) and a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1.0 mmol) in methanol (5.0 cm^3) was added. The blue crystals obtained were collected, washed with a small amount of methanol and dried over P_4O_{10} *in vacuo*.

$Ni(bbma)Cl_2 \cdot 2H_2O$. To the ligand "bbma" (0.277 g, 1.0 mmol) dissolved in methanol (10.0 cm^3) was added a solution of $NiCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol) in methanol (5.0 cm^3). The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} *in vacuo*.

$Ni(bbma)(NO_3)_2 \cdot MeOH$. A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) in methanol (5.0 cm^3) was added under stirring to bbma (0.277 g, 1.0 mmol) dissolved in methanol (10.0 cm^3). The blue crystals obtained were collected, washed with small amounts of methanol and dried over P_4O_{10} *in vacuo*.

$Ni(bbma)_2(ClO_4)_2 \cdot H_2O \cdot MeOH$. The compound "bbma" (0.554 g, 2.0 mmol) was dissolved in methanol (10.0 cm^3) and a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1.0 mmol) in methanol (5.0 cm^3) was added. The blue crystals obtained were collected, washed with a small amount of methanol and dried over P_4O_{10} *in vacuo*.

A solution of the complex (0.01 g) dissolved in methanol (10 cm^3) was allowed to evaporate. The fine blue single crystals obtained were suitable for X-ray diffraction. The crystals were unstable in the absence of the solvent.

$Ni(bbmma)(ClO_4)_2$, $Ni(bmbma)(ClO_4)_2 \cdot H_2O$, $Ni(bbmma)Cl_2 \cdot H_2O$, $Ni(bmbma)Cl_2 \cdot 2H_2O$, $Ni(bbmma)(NO_3)_2 \cdot MeOH$, $Ni(bmbma)(NO_3)_2$, $Ni(bbmma)_2(ClO_4)_2$ and $Ni(bmbma)(ClO_4)_2$ complexes were prepared by a similar procedure to that used for $Ni(bbma)(ClO_4)_2 \cdot MeOH$, $Ni(bbma)Cl_2 \cdot 2H_2O$, $Ni(bbma)(NO_3)_2 \cdot MeOH$ and $Ni(bbma)_2(ClO_4)_2 \cdot 4H_2O$, respectively. Elemental analyses of Ni(II) complexes are presented in Table 1.

The reaction of Ni^{II} compounds with CoM

The nickel compounds (0.1 mmol) was added to the sodium salt of 2-mercaptosulfonic acid (0.1 mmol) under anaerobic conditions (nitrogen atmosphere). The colour changes were observed from blue to yellow during the addition of CoM to the nickel solutions. The electronic spectra were recorded and the redox potentials were measured for the nickel(II) solution and also for the nickel(II) coenzymatic solution. The precipitation was noticed after keeping standing for a long time.

Crystallographic data collection and structure analysis of $[Ni(bbma)_2](ClO_4)_2 \cdot H_2O \cdot MeOH$

The recrystallization of the compound $Ni(bbma)_2(ClO_4)_2 \cdot H_2O \cdot MeOH$ gave air-sensitive purple crystals. Details of the data collection and processing are presented in Table 2. A single crystal was mounted in a glass capillary tube with the mother solution. The diffraction data were collected at 298 K on a Siemens P4/PC automatic diffractometer using graphite monochromatized Mo-K_α radiation and the $\theta/2\theta$-scan mode at variable scan speed in ω (3–60° min^{-1}) in the 2θ range 3–42°. The measured intensities were corrected for variation of three check reflections monitored periodically (min: 0.97, max: 1.24) and *Lp*

Table 1. Elemental analyses of Ni^{II} complexes; calculated values in parentheses

Compounds	C%	H%	N%	Ni%
$Ni(bbma)(ClO_4)_2 \cdot MeOH$	36.0	3.3	12.0	9.9
	(36.0)	(3.4)	(12.3)	(10.3)
$Ni(bbma)Cl_2 \cdot 2H_2O$	42.1	4.0	15.5	12.9
	(43.4)	(4.3)	(15.8)	13.2
$Ni(bbma)(NO_3)_2 \cdot MeOH$	41.2	(3.6)	19.6	(11.5)
	(41.5)	3.9	(19.9)	11.9
$Ni(bbma)_2(ClO_4)_2 \cdot H_2O \cdot MeOH$	45.5	4.0	15.9	6.5
	(46.0)	(4.2)	(16.2)	(6.81)
$Ni(bbmma)(ClO_4)_2$	38.8	3.0	12.5	10.1
	(37.2)	(3.1)	(12.8)	(10.7)
$Ni(bbmma)Cl_2 \cdot H_2O$	46.2	4.0	15.7	12.9
	(46.5)	(4.4)	(16.0)	(13.4)
$Ni(bbmma)(NO_3)_2 \cdot MeOH$	42.4	3.8	19.0	11.1
	(42.7)	(4.2)	(19.4)	(11.6)
$Ni(bbmma)_2(ClO_4)_2$	48.2	3.8	16.3	6.5
	(48.6)	(4.1)	(16.4)	(7.0)
$Ni(bmbma)(ClO_4)_2$	38.0	3.0	12.0	10.3
	(38.4)	(3.4)	(12.4)	(10.4)
$Ni(bmbma)Cl_2 \cdot 2H_2O$	47.7	4.2	14.5	12.2
	(46.1)	(4.5)	(14.9)	(12.5)
$Ni(bmbma)(NO_3)_2$	43.7	3.5	19.9	(11.8)
	(44.3)	(3.9)	20.1	12.0
$Ni(bmbma)_2(ClO_4)_2 \cdot H_2O$	48.5	4.3	15.5	6.4
	(48.8)	(4.6)	(15.8)	(6.6)

effects, and were reduced to F_0^2. An absorption correction was applied using 14 ψ-scans with χ close to 90°. Computations were performed with the SHELXTL [21] package on a PC and the scattering factors were taken from International Tables of Crystallography [22]. The centrosymmetric character of the space group was confirmed by the Wilson's statistics yielding $\langle |E^2-1| \rangle = 0.936$. The structure was solved by direct methods, followed by subsequent difference Fourier maps, and refined by full-matrix least squares, minimizing the quantity $\Sigma[w(F_0-F_c)^2]$, without restraints nor constraints. An ORTEP [23] view of the complex cation $[Ni(bbma)_2]^{2+}$, also showing the atomic numbering scheme, is depicted in Fig. 1.

RESULTS AND DISCUSSION

The nickel(II) is surrounded by two ligands, each acting in a tridentate manner. The nitrogen atom of the secondary amine and two nitrogen atoms of benzimidazole groups are involved in the coordination. Relevant bond distances and angles are given in Tables 3 and 4, respectively. The geometry of the complex is *fac*-octahedral and the equatorial plane is formed by a amine and three benzimidazole nitrogen atoms. It should be noted that one benzimidazole and an amine nitrogen are located at the axial positions. The bond distances of equatorial $Ni—N_{bzim}$ in the present complex fall in the range of those reported for nickel(II) complexes of benzimidazole-containing ligands [24]. The equatorial distance for N(3), N(7) and N(8) nitrogens with metal ion are 2.062 (5), 2.069 (6), 2.074 (5) Å, respectively, and the equatorial distance between $Ni—N(1)_{amine}$ is 2.196 (7) Å. The axial $Ni—N(2)_{bzim}$ and $Ni—N(6)_{amine}$ distances are 2.066(5) and 2.192(5) Å, respectively. The benzimidazole nitrogens bonds have a shorter distance than amine, which is due to the lone-pair electron of nitrogen involved in the resonance in benzimidazole rings. The maximum angle deviations from ideal octahedral geometry are displayed by N(2)—Ni—N(7), N(3)—Ni(1)—N(8) and N(3)—Ni—N(7), with deviations of 14.1, 13.7 and 11.9°, respectively. The remaining 12 angles subtended at the metal centre by adjacent donor atoms range from 79.7(2) to 100.8(2)° for donor atoms in a *cis* position and 175.3(2) to 175.7(2)° for donor atoms in a *trans* position. The packing of the structure is stabilized by strong hydrogen bonds between two oxygen atoms of one perchlorate anion and hydrogen atoms attached to C(9), C(1) and C(10) (see Tables S3, supplementary material).

IR spectra

All the perchlorate complexes exhibit bands at 600 and 1100 cm^{-1}, which corresponds to v_3 and v_4 vibrations, respectively, of the perchlorate anions. In all the other complexes the v_3, v_4 vibrations of ClO_4 are split into three and two bands, respectively, indicating that the anion is coordinated or forms hydrogen bonds with an amine [25]. The N—H stretching vibration of the benzimidazole moiety or amine is not discernible. The broad band observed around 3300 cm^{-1} in a few complexes is due to coordinated or lattice water.

Electronic spectra

The reflectance spectra of the nickel(II) compounds display a broad band in the visible region. On dissolution in methanol, relatively sharp well separated bands were obtained, indicating the probable involvement of the solvent in the coordination sphere. The spectral data and band assignment are presented in Table 5. The bands in the visible region are asymmetric, indicating the presence of more than one transition [26]. Assignments of the bands position are $^3A_{2g} \rightarrow {}^3T_{2g}$ (9.0–12.0 kK), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (14.0–18.0 kK) and $^3A_{2g} \rightarrow {}^3T_{1g}(p)$ (20.0–23.0 kK) [27]. The *N*-methylation at the secondary amine nitrogen as in $Ni(bbma)(ClO_4)_2$ leads to a red shift (1.1 kK) without changes in the intensity of the bands. However, benzimidazole methylation effects only a very small change in the band position. This illustrates the importance of the steric demand of N—Me, which would change the orientation of the lone-pair orbital towards the nickel(II) orbital and leads to a distorted square geometry [19,28] rather than that of its inductive

Table 2. Crystal structure determination summary for $Ni(bbma)_2(ClO_4)_2 \cdot CH_3OH \cdot H_2O$

Empirical formula	$C_{32}H_{30}Cl_2N_{10}NiO_8 \cdot CH_3OH \cdot H_2O$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 10.011(1)$, $b = 13.087(2)$, $c = 15.112(2)$ Å $\alpha = 86.19(1)$, $\beta = 83.88(1)$, $\gamma = 72.40(1)°$
Volume (Å^3)	1875.3(4)
Z	2
Formula weight	862.33
Density (calc.) (g cm^{-3})	1.527
Absorption coefficeint (mm^{-1})	0.73
$F(000)$	892
Data collection	
2θ range (°)	3–42
Scan type	$\theta/2\theta$
Index ranges	$-1 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 14$
Reflections collected	4954
Independent reflections^a	4007 ($R_{int} = 8.37\%$)
Observed reflections	2675 [$F > 4\sigma(F)$]
Transmission factors	min : 0.464, max : 0.505
Solution and refinement	
Extinction correction	$\chi = 0.00049(11)$, where $F^* = F[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U, except for hydrogen atoms of water and methanol molecules, which were omitted.
Weighting scheme	$w^{-1} = \sigma^2(F)+0.0005F^2$
Parameters refined	506
Final R indices (observed data)^b (%)	$R = 4.58$, $wR = 5.05$
Final R indices (all data)^b (%)	$R = 8.23$, $wR = 5.88$
Goodness-of-fit^c	1.26
Largest and mean Δ/σ	0.020, 0.004
Largest difference peak (e Å^{-3})	0.40
Largest difference hole (e Å^{-3})	-0.28

$$^a R_{int} = \sqrt{\frac{\Sigma N \Sigma w(\langle F \rangle - F)^2}{\Sigma(N-1)\Sigma w F^2}}.$$

$$^b R = \frac{\Sigma |F_0 - F_c|}{\Sigma |F_0|} \quad wR = \frac{\Sigma \sqrt{w}|F_0 - F_c|}{\Sigma \sqrt{w}|F_0|}.$$

$$^c S = \sqrt{\frac{\Sigma w |F_0 - F_c|^2}{m-n}}.$$

effect. Generally the red shift was also observed in the electronic spectra when CoM was added to Ni^{II} compounds, irrespective of inductive or steric effects, showing that coordination of CoM to Ni^{II} compounds leads to lower symmetry in the Ni^{II} structure (Fig. 2). The charge-transfer band with low ε coefficients illustrates the partial interaction of the π-orbital of ligand with the nickel ion [13].

Electrochemical properties

The redox behaviour of the present Ni^{II} complexes were investigated using cyclic voltammetry (CV) on a stationary platinum electrode. Electrochemical experiments were carried out in methanol and tetra-*n*-hexylammonium perchlorate was used as a supporting electrolyte. All the 1 : 1 nickel(II) complexes reveal irreversible redox behaviours, however, the 1 : 2 complexes exhibit quasi-reversible Ni^I/Ni^{II} redox behaviours. The electrochemical data of the complexes are presented in Table 6. The non-Nernstian behaviour may be ascribed to heterogenous electron-transfer kinetics and a coupled chemical reaction. The latter is evident from the cathodic shift of the reduction peak and the anodic shift of oxidation wave that increase with the scan rate [29].

The electrochemical data shows the stabilization and destabilization by amine *N*-methyl and benzimidazole *N*-methyl groups, respectively, in 1 : 1 nickel(II) perchlorates and the reverse order in 1 : 2 Ni^{II} complexes. The Ni^{II}/Ni^I reduction potentials of the 1 : 1 perchlorate complexes follow the order $Ni(bbmma)^{2+}$ < $Ni(bbma)^{2+}$ < $Ni(bmbma)^{2+}$,

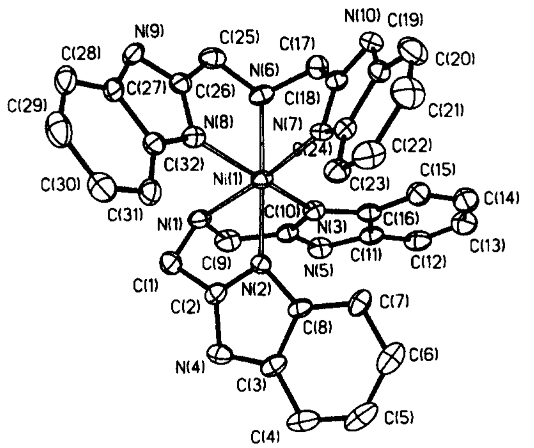

Fig. 1. An ORTEP drawing of the $Ni(bbma)_2^{2+}$ cation showing the atom numbering and the thermal motion ellipsoids (30% probability level). Hydrogen atoms are omitted for clarity.

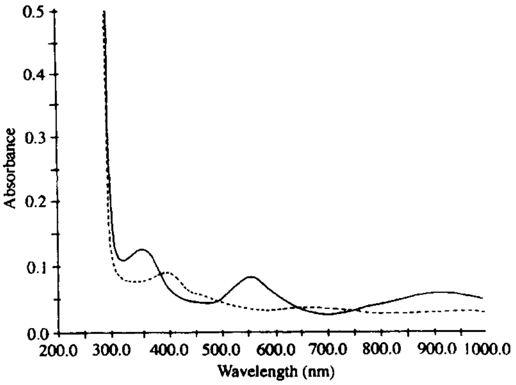

Fig. 2. Electronic absorption spectra of $Ni(bbma)_2(ClO_4)_2 \cdot 4H_2O$ (–) and with coenzyme M reductase (...) in methanol.

Table 3. Selected bond lengths (Å) for $Ni(bbma)_2(ClO_4)_2 \cdot CH_3OH \cdot H_2O$

Ni(1)—N(1)	2.196(7)	Ni(1)—N(2)	2.066(5)
Ni(1)—N(3)	2.062(5)	Ni(1)—N(6)	2.192(5)
Ni(1)—N(7)	2.069(6)	Ni(1)—N(8)	2.074(5)
N(1)—C(1)	1.468(9)	N(1)—C(9)	1.488(9)
N(6)—C(17)	1.491(9)	N(6)—C(25)	1.480(8)
C(1)—C(2)	1.495(11)	C(9)—C(10)	1.493(10)
C(17)—C(18)	1.496(11)	C(25)—C(26)	1.491(10)

which reflects the stabilization of Ni^{II} towards reduction by the electron-donating *N*-methyl group of benzimidazole and destabilization of steric effects of the amine *N*-methyl group. Interestingly, a reverse order $Ni(bmbma)_2^{2+} < Ni(bbma)_2^{2+} <$ Ni $(bbmma)_2^{2+}$ was observed for 1 : 2 perchlorates complexes, indicating the stabilization of nickel(II) by amine *N*-methylation and destabilization by steric hindrance of benzimidazole methyl group.

Addition of the CoM to NiL compounds (L = bbma, bbmma, bmbma) generally elevates the redox potential of the complexes, irrespective of amine

Table 4. Selected bond angles (°) for $Ni(bbma)_2(ClO_4)_2 \cdot CH_3OH \cdot H_2O$

N(1)—Ni(1)—N(2)	79.7(2)	N(1)—Ni(1)—N(3)	80.8(2)
N(2)—Ni(1)—N(3)	87.5(2)	N(1)—Ni(1)—N(6)	96.5(2)
N(2)—Ni(1)—N(6)	175.7(2)	N(3)—Ni(1)—N(6)	90.0(2)
N(1)—Ni(1)—N(7)	175.3(2)	N(2)—Ni(1)—N(7)	104.1(2)
N(3)—Ni(1)—N(7)	101.9(2)	N(6)—Ni(1)—N(7)	79.8(2)
N(1)—Ni(1)—N(8)	89.9(2)	N(2)—Ni(1)—N(8)	100.8(2)
N(3)—Ni(1)—N(8)	166.3(3)	N(6)—Ni(1)—N(8)	81.0(2)
N(7)—Ni(1)—N(8)	86.7(2)		
Ni(1)—N(1)—C(1)	104.6(5)	Ni(1)—N(1)—C(9)	110.7(4)
C(1)—N(1)—C(9)	113.6(5)	Ni(1)—N(2)—C(2)	111.9(5)
Ni(1)—N(2)—C(8)	139.7(4)	C(2)—N(2)—C(8)	105.5(5)
Ni(1)—N(3)—C(10)	114.4(4)	Ni(1)—N(3)—C(16)	140.0(6)
C(10)—N(3)—C(16)	105.6(6)	Ni(1)—N(6)—C(17)	106.5(4)
Ni(1)—N(6)—C(25)	110.4(4)	C(17)—N(6)—C(25)	112.4(5)
Ni(1)—N(7)—C(18)	112.7(5)	Ni(1)—N(7)—C(24)	140.0(4)
C(18)—N(7)—C(24)	105.7(6)	Ni(1)—N(8)—C(26)	113.1(4)
Ni(1)—N(8)—C(32)	141.6(5)	C(26)—N(8)—C(32)	105.1(5)

Table 5. Electronic absorption spectral data (ν_{max}/cm^{-1} with ε/dm^3 mol^{-1} cm^{-1} in parentheses)

Compounds	Medium	Ligand field[a]	Charge transfer[a]
Ni(bbma)$(ClO_4)_2\cdot MeOH$	Solid	22.8, 18.2, 11.4	26.4
	MeOH	22.2(72) (17.9(10) 10.9(21)	26.8(111)
Ni(bbma)$Cl_2\cdot 2H_2O$	Solid	22.6, 18.4, 11.6	25.8
	MeOH	22.3(65) 17.8(9) 10.8(16)	28.2(126)
Ni(bbma$(NO_3)_2\cdot MeOH$	Solid	22.6, 18.2, 11.8	25.6
	MeOH	22.2(63) 17.9(9) 10.9(17)	25.2(120)
$Ni(bbma)_2(ClO_4)_2\cdot H_2O\cdot MeOH$	Solid		26.6
	MeOH	22.3(43) 15.8(11) 11.1(20)	28.3(130)
Ni(bbmma)$(ClO_4)_2$	Solid	21.4, 17.2, 9.9	26.7
	MeOH	20.8(74) 16.8(12) 09.8(19)	30.9(144)
Ni(bbmma)$Cl_2\cdot H_2O$	Solid	21.5, 17.2, 9.9	25.1
	MeOH	20.9(67) 16.7(10) 09.5(17)	27.6(134)
Ni(bbmma)$(NO_3)_2\cdot MeOH$	Solid	21.4, 17.2, 9.9	26.0
	MeOH	20.9(78) 16.8(8) 09.6(17)	28.2(138)
$Ni(bbmma)_2(ClO_4)_2$	Solid	21.4, 17.2, 9.9	26.8
	MeOH	22.3(94) 15.9(10) 10.9(22)	27.6(135)
Ni(bmbma)$(ClO_4)_2$	Solid		26.6
	MeOH	22.2(110) 17.8(25)	31.3(220)
Ni(bmbma)$Cl_2\cdot 2H_2O$	Solid		26.3
	MeOH	22.3(114) 17.9(22)	29.7(206)
Ni(bmbma)$(NO_3)_2$	Solid		26.4
	MeOH	22.1(103) 17.9(19)	29.8(231)
$Ni(bmbma)_2(ClO_4)_2\cdot H_2O$	Solid		26.6
	MeOH	22.0(98) 17.9(18) 11.8(9)	32.1(254)
Ni(bbma)$(ClO_4)_2$+CoM	MeOH	15.1(9) 10.5(6)	25.4(117)
$Ni(bbma)_2(ClO_4)_2$+CoM	MeOH	21.1(23) 14.7(15) 10.5(11)	25.1(98)
Ni^{II}(bbmma)$(ClO_4)_2\cdot$CoM	+MeOH	14.4(19) 9.6(12)	24.8(112)
$Ni^{II}(bbmma)_2(ClO_4)_2\cdot$CoM	+MeOH	14.8(18) 9.6(12)	24.9(120)
Ni^{II}(bmbma)$(ClO_4)_2\cdot$CoM	+MeOH	14.4(21) 9.9(8)	25.1(105)
$Ni^{II}(bmbma)_2(ClO_4)_2\cdot$CoM	+MeOH	14.9(17) 10.1(10)	25.1(107)

[a] Concentration ≈ 5×10^{-2}.

$^3A_{2g}\rightarrow{}^3T_{2g}$ (9.0–12.0), $^3A_{2g}\rightarrow{}^3T_{1g}$(F) (14.0–18.0), $^3A_{2g}\rightarrow{}^3T_{1g}$(p) (20.0–23.0).

Table 6. Electrochemical data^{a} for Ni^{II} compounds at 25°C

Compound	E_{pc} (V)	E_{pa} (V)	ΔF_p (mV)	$E_{1/2}$ (V)	$E_{1/2}$ (V)^{b}
$Ni(bbma)(ClO_4)_2 \cdot MeOH$	−0.460	—	—	—	−0.468
	—	0.268^{c}			
$Ni(bbma)Cl_2 \cdot 2H_2O$	−0.568	—	—	—	−0.597
	—	0.078^{c}			
$Ni(bbma)(NO_3)_2 \cdot MeOH$	−0.462	—	—	—	−0.456
		−0.079^{c}			
$Ni(bbma)_2(ClO_4)_2 \cdot H_2O \cdot MeOH$	−0.590	−0.432	158	−0.511	−0.471
		−0.052^{c}			
$Ni(bbmma)(ClO_4)$	−0.511	—	—	—	−0.555
		−0.088^{c}			
$Ni(bbmma)_2(ClO_4)$	−0.484	−0.332	152	−0.408	−0.411
		−0.082^{c}			
$Ni(bmbma)(ClO_4)_2$	−0.470	−0.298	172	−0.384	−0.391
		0.106^{c}			
$Ni(bmbma)_2(ClO_4)_2 \cdot H_2O$	−0.510	−0.342	168	−0.426	−0.482
		0.062^{c}			
$Ni(bbma)(ClO_4)_2$+CoM	−0.365	—	—	—	−0.361
$Ni(bbma)_2(ClO_4)_2$+CoM	−0.460	−0.328	—	—	−0.418
	—	0.093^{c}			
$Ni(bbmma)(ClO_4)_2$+CoM	−0.360	—	—	—	−0.337
$Ni(bbmma)_2(ClO_4)_2$+CoM	−0.470	—	—	—	−0.468
$Ni(bmbma)(ClO_4)_2$+CoM	−0.386	—	—	—	−0.377
$Ni(bmbma)_2(ClO_4)_2$+CoM	−0.444	−0.318	—	—	−0.440

^{a}Measured *vs* non-aqueous silver reference electrode; add 544 mV to convert into normal hydrogen electrode (NHE); scan rate 50 mV s^{-1}, supplying electrolyte tetra-*n*-hexylammonium perchlorate (0.1 mol dm^{-3}); complex concentration 1.0 mmol dm^{-3}.

^{b}Differential pulse voltammetry, scan rate 1.0 mV s^{-1}, pulse height 50 mV.

^{c}Additional anodic peak.

N-methyl or benzimidazole *N*-methyl group effects (Fig. 3), this may be ascribed to the geometrical changes in the complexes during the addition of CoM. However, 1 : 1 nickel(II) complexes have more positive redox potential than 1 : 2 nickel compounds due to limited structural changes in 1 : 2 nickel compounds.

Supporting information available. Full details of the X-ray structure of complex II including the complete table of crystal data (Table S1), atomic parameters (Table S2), bond lengths (Table S3) and angles (Table S4), anisotropic displacement coefficients (Table S5), calculated hydrogen parameters (Table S6) and observed and calculated structure factors (Table S7) have been deposited as supplementary material (19 pages) and are available on request to S.B.

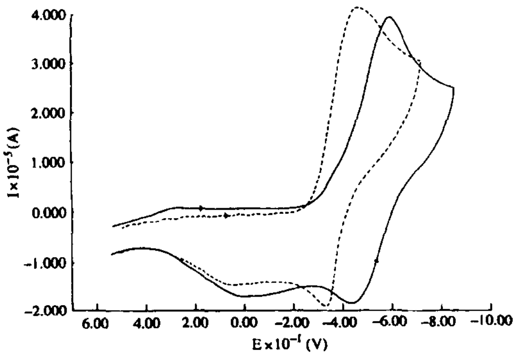

Fig. 3. Cyclic voltammograms of 1.0 mM $Ni(bbma)_2(ClO_4)_2 \cdot 4H_2O$(—) and with coenzyme M reductase (. . .) in methanol at 25°C. Supporting electrolyte: Tetra-*n*-hexylammonium perchlorate (0.1 M). Scan rate 0.05 V s^{-1}.

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REFERENCES

1. Rouviere, P. E. and Wolfe, R. S., *J. Biol. Chem.*, 1988, **263**, 7913.
2. Friedmann, H. C., Klein, A. and Thauer, R. K., *FEMS Microbiol. Rev.*, 1990, **87**, 339.
3. Pfaltz, A., Jaun, B., Faessler, A., Eschenmoser, A., Jaenchen, R., Gilles, H. H., Diekert, G. and Thauer, R. K., *Helv. Chim. Acta*, 1982, **65**, 828.
4. Livingston, D. A., Pfaltz, A., Schreiber, J., Esch-

enmoser, A., Ankel-Fuchs, D., Moll, J., Jaenchen, R. and Thauer, R. K., *Helv. Chim. Acta*, 1984, **67,** 334.

5. Faerber, G., Keller, W., Kratky, C., Jaun, B., Pfaltz, A., Spinner, C., Kobelt, A. and Eschenmoser, A., *Helv. Chim. Acta*, 1991, **74,** 697.
6. Fassler, A., Pfaltz, A., Krautler, B. and Eschenmoser, A., *J. Chem. Soc., Chem. Commun.*, 1984, 1365.
7. Hausinger, R. P., Orme-Johnson, W. H. and Walsh, C., *Biochemistry*, 1984, **23,** 801.
8. Ankel-Fuchs, D., Huester, R., Moeschel, E., Albracht, S. P. J. and Thauer, R. K., *Syst. Appl. Microbiol.*, 1986, **7,** 383.
9. (a) Bakae, A. and Espenson, J. H., *J. Am. Chem. Soc.*, 1986, **108,** 5353; (b) Ram, M. S., Bakae, A. and Espenson, J. H., *Inorg. Chem.*, 1986, **25,** 3267; (c) Stoltzenberg, A. and Stershic, M. T., *Inorg. Chem.*, 1987, **26,** 3082.
10. Walsh, C. and Orme-Johnson, W. H., *Biochemistry*, 1987, **26,** 4901.
11. Zilbermann, Y., Golub, G., Cohen, H. and Meyerstein, D., *Inorg. Chim. Acta*, 1994, **227,** 1.
12. Thompson, J. S., Marks, T. J. and Ibers, J. A., *J. Am. Chem. Soc.*, 1979, **101,** 4180.
13. Pandiyan, T., Palaniandavar, M., Lakshiminarayanan, M. and Manohar, H., *J. Chem. Soc., Dalton Trans.*, 1992, 3377.
14. Pandiyan, T., Murali, M. and Palaniandavar, M., *Trans. Met. Chem.*, 1995, **20,** 440.
15. Palaniandavar, M., Pandiyan, T., Lakshiminarayanan, M. and Manohar, H., *J. Chem. Soc., Dalton Trans.*, 1995, 445.
16. Murali, M., Palaniandavar, M. and Pandiyan, T., *Inorg. Chim. Acta*, 1994, **224,** 19.
17. Pandiyan, T., Durán de Bazua, C. and Soriano-Garcia, M., *Fresenius J. Anal. Chem.*, 1996, **354,** 636.
18. Reilley, C. N., Schmid, R. W. and Sadek, F. A., *J. Chem. Educ.*, 1959, **36,** 555.
19. Nishida, Y. and Takahashi, K., *J. Chem. Soc., Dalton Trans.*, 1988, 691.
20. Usha, S., Pandiyan, T. and Palaniandavar, M., *Indian J. Chem., Sect. B.*, 1993, **32,** 572.
21. Sheldrick, G.M., SHELXTL 4.2/360. Crystallographic Computing System, Siemens Analytical X-Ray Instruments, Madison, WI, U.S.A., 1990.
22. International Tables for X-ray Crystallography, Vol. IV. Kynoch Press, Birmingham, U.K., 1974.
23. Johnson, C. K., *ORTEP II. A Program for Thermal Ellipsoid Plotting.* Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A., 1976.
24. Soriano-Garcia, M., Pandiyan, T. and Duràn de Bazúa, C., *Acta Cryst.*, 1995, **C51,** 1107.
25. Rosenthal, M. R., *J. Chem. Educ.*, 1973, **56,** 337.
26. Deeth, R. J. and Kemp, C. M., *J. Chem. Soc., Dalton Trans.*, 1992, 2013.
27. Stranger, R., Wallis, S. C., Gahan, L. R., Kennard, C. H. L. and Byriel, K. A., *J. Chem. Soc., Dalton Trans.*, 1992, 2971.
28. West, D. X. and Palaniandavar, M., *Inorg. Chim.*, 1983, **77,** L97.
29. Bard, A. J. and Faulkner, L. R., *Electrochemical Methods: Fundamental Applications*, p.218, Wiley, New York, U.S.A., 1990.