

have been produced. For all the complexes of the mixed-donor macrocycles the macrocyclic effect is much smaller than is the case for the all-nitrogen-donor analogues.

(5) For the tetradentate macrocycles, an increase in the number of atoms forming the macrocyclic ring is usually considered to lead to an increase in the size of the macrocyclic cavity. However, for both the all-nitrogen- and the nitrogen-oxygen mixed-donor macrocycles studied here, the results suggest that the ligands with smaller macrocyclic rings, e.g. 12-aneN₄ or 12-aneN₃O, complex larger metal ions such as Pb²⁺ more strongly than do those with larger macrocyclic rings, e.g. 13-aneN₄ or 13-aneN₃O. In contrast, small metal ions such as Cu²⁺ show a strong preference for the macrocycles with larger macrocyclic rings. This effect does not

appear to depend on the presence of a macrocyclic ring, but is rather related to the presence of five-membered vs. six-membered chelate rings in the complexes formed, since similar size-selectivity patterns are observed in the open-chain analogues.

Acknowledgment. We thank the Council Research Grants Committee of the University of the Witwatersrand and the Foundation for Research Development of the Council for Scientific and Industrial Research for generous financial support for this work.

Registry No. 9-aneN₂O, 80289-59-4; 13-aneN₃O, 88915-58-6; 13-aneN₂O₂, 60350-15-4; 12-aneN₃O, 53835-21-5; 12-ane(1,4)N₂O₂, 60350-13-2.

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Structure and Dynamic Behavior in Solution of Binuclear Nickel(II) Face-to-Face Complexes with Bis(cyclidene) Ligands

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A series of dinickel(II) complexes having macrotricyclic bis(cyclidene) ligands has been prepared and characterized. NMR studies revealed a dynamic molecular motion in solution, and electrochemical investigations showed that the difference in redox couples ($\Delta E_{1/2}$) for the two Ni-cyclidene units correlates well with the sequence of intermetallic distances.

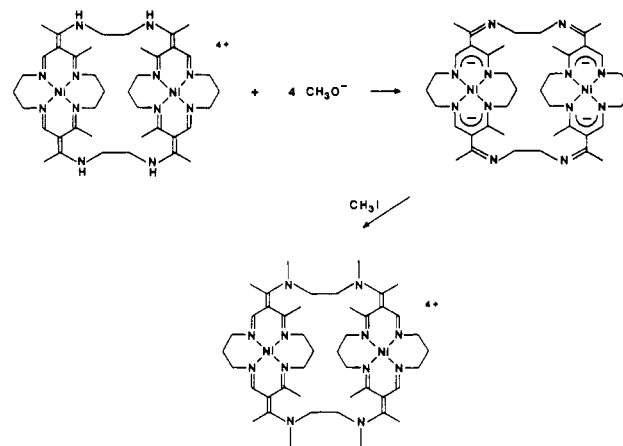
Introduction

The number of synthetic model compounds for metalloproteins having more than one metal center has continuously increased and the structure types have been diversified substantially since the first report on a side-by-side example in 1970.¹ One advantage for such bioinorganic models is that the coordination geometry around the metal center and its surroundings can be easily controlled by ligand design; e.g., bridging two macrocyclic units into a stacked pair leads to the "face-to-face" structure.^{2,3}

Face-to-face diporphyrins, whose electrochemical applications have been extensively investigated,^{4,5} exemplify stacked macrocyclic systems. Efforts in this area have focused on the relationships between electrocatalytic activity in the reduction of O₂ to H₂O and structural parameters of the cobalt-containing catalyst.

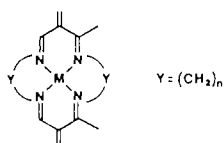
We have developed a distinct family of dinuclear transition-metal complexes in which two macrocyclic units, called *cyclidene* rings,⁶ are joined together in a macrotricyclic ligand. The cyclidene groups have approximately face-to-face orientations, but they may be displaced with respect to a common axis or tilted with respect to that same axis. Because of the saddle shape of the cyclidene

Scheme I



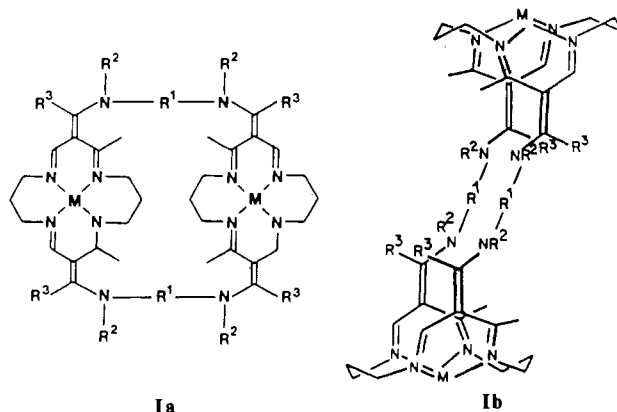
rings, many of these dinucleating ligands will maintain a constant separation between the two chelated metal ions. Structure Ia indicates the bonding in the complex while structure Ib shows the 3-dimensional array of atoms. These dinuclear complexes fall

- (1) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225-2236.
- (2) See for example: Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027-6036.
- (3) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177-3184 and references therein.
- (4) For example: Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710-2718.
- (5) Liu, H. Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 665-670.
- (6) The cyclidene notation is based on the tetraimine macrocycle



$n = 2$, [14]cyclidene

$n = 3$, [16]cyclidene



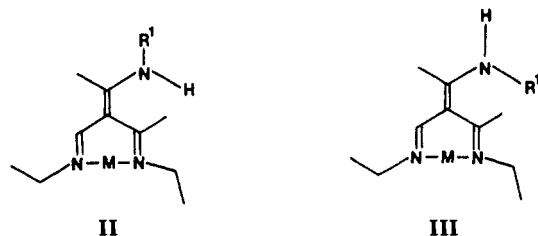
in a category of bimetallic species having large intermetallic separations, and studies on both the nickel(II) and iron(II) complexes have failed to reveal properties peculiar to metal-metal interaction.⁷⁻⁹

This report adds three new members to the family of bis(cyclidene) ligands and reports on the dynamic behavior of the nickel derivatives of ligands of this class in solution. Electrochemical studies show that despite the apparent large intermetallic distances, an electrostatic metal-metal interaction can be detected. In the compounds studied, the bridging groups R¹ (see structure Ia) are -N(CH₃)(CH₂)₂N(CH₃)-, -NH(CH₂)₂NH-, -NH(CH₂)₃NH-, -NH(CH₂)₅NH-, -N(CH₂CH₂)₂N-, and -NHCH₂C₆H₄CH₂NH-. The substituents are generally indicated by the listing R₂(NR²)₂R¹, and R³ is methyl in all cases.

Results and Discussion

Synthesis and Characterization. Synthetic procedures for the dinickel(II) bis(cyclidene) complexes have been reported previously.^{7,8} In those previous examples, the substituent on the bridging nitrogen atom R² is hydrogen, while other R² groups have been studied for the corresponding mononuclear lacunar cyclidene complexes.^{8,10} In this study, the possibility of N-alkylation has been examined, since the relatively acidic N-bonded protons are thought to confer undesirable properties on related complexes.¹¹ Scheme I illustrates an alkylation pathway as demonstrated by the N-methylation of [Ni₂[(Me₂(NH)₂CH₂CH₂)([16]cyclidene)₂](PF₆)₄. Deprotonation at the bridge nitrogens followed by reactions with methyl iodide led to formation of the Me₂(NMe)₂CH₂CH₂ bridged analogue. Loss of NH stretching absorptions in the infrared spectrum of the product confirms the complete substitution on the four nitrogen atoms of this kind.

Infrared spectral data suggest that a change in configuration at the bridge nitrogen(s) may accompany this N-methylation. A broad absorption band centered at 1580 cm⁻¹, assignable to a combination of the C=N and C=C vibrations, splits into two distinct, widely separated peaks (1618 and 1548 cm⁻¹) upon N-methylation. This change is tentatively assigned to isomerization from the lid-on form to the lid-off counterpart⁸ (structures II and III). On the basis of ¹³C NMR data, the lid-on structure



has been assigned to all of the previously reported bis(cyclidene) complexes having R² = H. In the lid-off configuration, the two cyclidene macrocycles are expected to approximate a side-by-side orientation. It is also possible that reaction at the four nitrogen sites led to formation of mixed lid-on/lid-off configurations. The suggestion of at least a partially lid-off configuration is supported

Scheme II

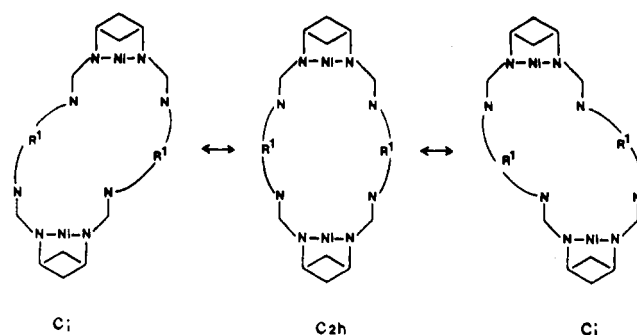


Table I. ¹³C NMR Data for [Ni₂[(Me₂(NH)₂mxylyl)₂][16]cyclidene)₂](PF₆)₄ in Various Solvents

carbon ^a	chemical shifts/ppm ^b			
	Me ₂ SO-d ₆	CDNO ₂ ^c	CD ₃ CN ^c	CD ₃ CN
A	169.4	169.4, 168.8, 168.2	168.9, 168.4, 167.9	170.7, 170.1, 168.7
B	166.4	160.7	160.7	164.0
C	159.7	160.7	160.7	161.8, 160.7
W	138.0	139.5, 137.7	138.6, 137.4	140.2, 139.0
Y	129.9	131.4	131.0	131.1, 129.7, 129.2
Z	128.8	130.5	130.1	127.6, 127.1
X	126.6	127.8	128.0	123.8
D	109.3	113.2	118.3	114.1
K	54.4	57.1	56.4	56.3, 54.7
E	50.2	52.0	51.6	51.7, 50.5
F	48.7	50.2	49.6	47.4
I	29.1	31.0	30.5	31.6, 30.9
J	28.7	30.5	30.0	30.1, 29.7
M	21.0	20.8	21.1, 20.8	22.1, 21.4, 21.1
N	20.6	15.5	15.7	14.7

^aSee Figure 1 for signal assignment. ^bReferenced to solvents (C-D₃)₂SO, CD₃NO₂, and CD₃CN. ^cSample contained ethanol of crystallization. ^dIndistinguishable.

by ¹³C NMR results for the N-methylated dimer (vide infra).

Laser desorption-ionization (DI) and fast atom bombardment (FAB) mass spectroscopies have proven useful in establishing the dinuclear formulations of the new compounds. Reasonable mass spectra were obtained despite the highly nonvolatile nature of the tetrapositive cationic species. Under laser desorption-ionization conditions, the complexes appear to lose protons from the ligand and accept a potassium ion from the KBr matrix material used in sample preparation. Thus, a positive pseudomolecular ion of *m/z* 1018, for the Me₂(NH)₂mxylyl-bridged (mxylyl = *m*-xylylene) complex, [Ni₂[(Me₂(NH)₂mxylyl)₂][16]cyclidene)₂]⁴⁺, was found to be consistent with the formulation [complex - H + K]⁺. Similarly, a major peak at *m/z* 865 for the Me₂(NH)₂CH₂CH₂-bridged bis([16]cyclidene) complex corresponds to [complex - 2H + K]⁺. The FAB technique gave useful results only for the latter complex as the tetrachloride salt. Three positive molecular ions were formulated as [complex - H]⁺ (827), [complex - 4H + H₂O]⁺ (842), and [complex - 2H + Cl]⁺ (861). The water molecule and the chloride ion in the heavier species may be involved in intercavity multiple hydrogen bonding to the N-H (R²) groups, an interaction that might facilitate their vaporization as part of the complex cation.

Dynamic Behavior in Solution. Both ¹H and ¹³C NMR spectroscopy were used to probe the overall conformations of the bis(cyclidene) ligands of the diamagnetic nickel(II) complexes in solution. Selected examples are given to demonstrate the flexibility of the ligand and the fluxional behavior due to some of the protons in the structure.

The interpretation of the ¹³C spectra is relatively straightforward. Figure 1 shows both the broadband, proton-decoupled spectrum (a) and the DEPT spectra (labeled b) of [Ni₂[(Me₂(NH)₂mxylyl)₂][16]cyclidene)₂]⁴⁺ obtained in Me₂SO-d₆ at room temperature. The DEPT (distortion enhancement by polarization

- Busch, D. H.; Jackels, S. C.; Callahan, R. W.; Grzybowski, J. J.; Zimmer, L. L.; Kojima, M.; Olszanski, D. J.; Schammel, W. P.; Stevens, J. C.; Holter, K. A.; Mocak, J. *Inorg. Chem.* **1981**, *20*, 2834-2844.
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- For example, the cobalt(II) lacunar complexes with R² = H are known to have more rapid rates of autoxidation than the analogous N-methylated complexes.¹² Also, oxidized cyclidene complexes are unstable with regard to deprotonation in aqueous solutions.¹³
- Nosco, D. L.; Jackson, P. J.; Stevens, J. C.; Busch, D. H., unpublished results.
- Goldsby, K. A.; Busch, D. H., work in progress.

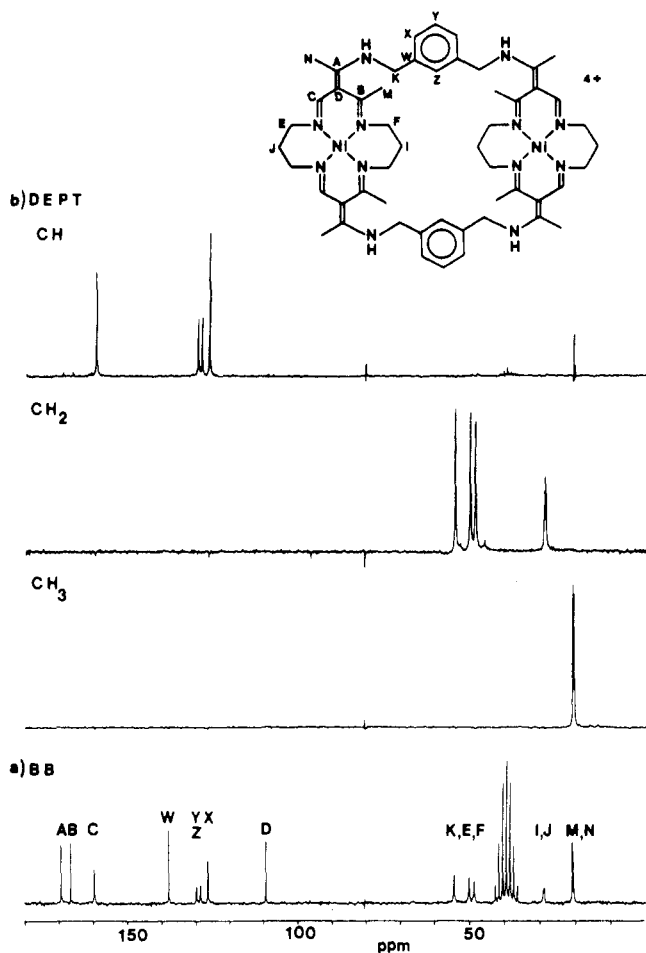


Figure 1. Broad-band proton-decoupled and DEPT ^{13}C NMR spectra of $[\text{Ni}_2\{\text{Me}_2(\text{NH})_2\text{mxy}\}_2\{[16]\text{cyclidene}\}_2](\text{PF}_6)_4$ in $\text{Me}_2\text{SO}-d_6$ at room temperature.

transfer) technique allows one to identify the methyl, methylene, and methine carbons, as shown in Figure 1b.

The number of carbon signals in the proton-decoupled spectrum is consistent with the presence of two symmetry elements. On the basis of the crystal structure of this complex,⁸ one of these symmetry elements must be an inversion center. The other element is probably a mirror plane through both cyclidene macrocycles containing the nickel atoms and carbon atoms I and J. The latter symmetry element is absent from the species in the crystal structure because of a horizontal displacement of the two macrocycles with respect to each other. In solution, the molecular motions allowed by the linking groups are fast on the NMR time scale, resulting in overall mirror symmetry. These relationships are illustrated in Scheme II. It should be pointed out that the molecular motions depicted here involve simple single bond rotations within the linking groups ($\text{N}-\text{R}^1-\text{N}$) and *not* lid-on/lid-off conversions.

The ^{13}C chemical shifts for this complex are given in Table I for different solvents. The most striking solvent effect is seen in the signals due to the two methyl carbons labeled M and N. They occur at almost the same location (ca. 20 ppm) in $\text{Me}_2\text{SO}-d_6$, while the corresponding peaks occur with a separation of about 5 ppm in acetonitrile- d_3 and nitromethane- d_3 . Previous studies on the related lacunar complex¹⁴ attributed the first pattern to the lid-off configuration while the latter was assigned to the lid-on structure. Apparently this criterion does not apply to the dinuclear species. Since the $\text{Me}_2(\text{NH})_2\text{mxy}$ -bridged complex was shown to exist in the lid-on configuration by an X-ray structure determination and because the structure is not likely to convert to the lid-off

form under mild conditions, the variation in the spectral behavior is attributed to a solvent effect involving hydrogen bonding in the present case. It is suggested that a molecule of the solvent Me_2SO hydrogen bonds strongly to the R^2 proton and that while in that position it influences the environment of methyl carbon N in the same way the bridging group R^1 does in the lid-off species. In Me_2SO the separation between the resonances due to the imine carbon atoms B and C is also unusually large, being about 7 ppm (see Table I).

Two lines of evidence suggest that ethanol may enter into a hydrogen bonding interaction similar to that inferred above. Ethanol of solvation is retained in samples of the $\text{Me}_2(\text{NH})_2\text{R}^1$ -bridged dimers when they are recrystallized from acetonitrile/ethanol. Further, the last two columns of Table I compare the NMR signals of the ethanol-solvated complex and the identical ethanol-free complex in acetonitrile- d_3 solvent. The ethanol-free system gives a number of carbon signals, agreeing roughly with that for a structure having only one symmetry element, probably the inversion center. This provides the additional result that the complex assumes a lower symmetry, probably a *slipped* or off-set conformation (see Scheme II), in the absence of hydrogen-bonding solvent. In previous studies, the multiplicity of bands observed for the ^{13}C NMR spectrum of this complex in ethanol-free acetonitrile was attributed to the coexistence of isomers,⁸ however, the fact that the same chromatographically pure sample shows the solvent-dependent spectra reported here argues for the suggested fluxional relationships.

A particularly interesting consequence of the explanation given above is the requirement that hydrogen bonding to small molecules must promote the interconversion among the different conformers as indicated, for example, in Scheme II. It is reasonable to suppose that such an interaction favors rapid motion around the linking groups by preventing the structure from collapsing the two cyclidene units toward each other. These two opposing phenomena may be considered to be examples of factors tending to minimize the vacant volume in the permanent voids of these unusual complexes. The involvement of particular carbon atoms in such motions is demonstrated by comparing ^{13}C signals for dimers having linking groups of different size. Figure 2 compares the ^{13}C NMR spectra in acetonitrile- d_3 of a series of dinickel(II) bis([16]cyclidene) species containing di-, tri-, and pentamethylene bridges. Some of the signals are broadened most extensively in the spectrum (Figure 2a) of the dimethylene-bridged complex. The broadened signals are assignable to carbons A (imine), D (γ -carbon), K (methylene next to the bridge nitrogen), and N (vinylic methyl). In contrast, the sharper signals all arise from the cyclidene moiety. This pattern suggests that the source of the broadening is the restricted rotational motion about the entire alkylbis(aminoethylidene) linking group. As the R^1 groups are lengthened, first to trimethylene and then to pentamethylene linkages, the carbon signals A, D, K, and N progressively sharpen up, indicating that the longer polymethylene chain can rotate more freely.

The extreme opposite behavior might be expected for the dinickel(II) bis(cyclidene) complex having the piperazine bridge. In this case, the simple R^2 groups are replaced by a second bridging dimethylene group and conformational motion about the linking groups is expected to be severely restricted. The ^{13}C NMR spectrum of this complex is given in Figure 3. The expected rigidity of the double dimethylene links and, perhaps, the higher molecular symmetry are reflected in the extreme sharpness of all of the signals in this spectrum. The number of signals corresponds to the C_{2h} point group for this molecule. In sharp contrast, in the case of the $\text{Me}_2(\text{NMe})_2\text{CH}_2\text{CH}_2$ -bridged complex, most of the signals are split, suggesting that this molecule may be locked into the lid-off (off-set) configuration, as indicated earlier.

Additional support for the molecular dynamic interpretation of the NMR data presented here is found in the observation of fluxional behavior for certain of the protons. The proton spectra of these dinuclear bis(cyclidene) complexes are complicated and symmetry changes may produce numerous unresolved signals. The proton signals that are easiest to assign are those of the vinyl

(14) Herron, N.; Nosco, D. L.; Busch, D. H. *Inorg. Chem.* **1983**, *22*, 2970-2971.

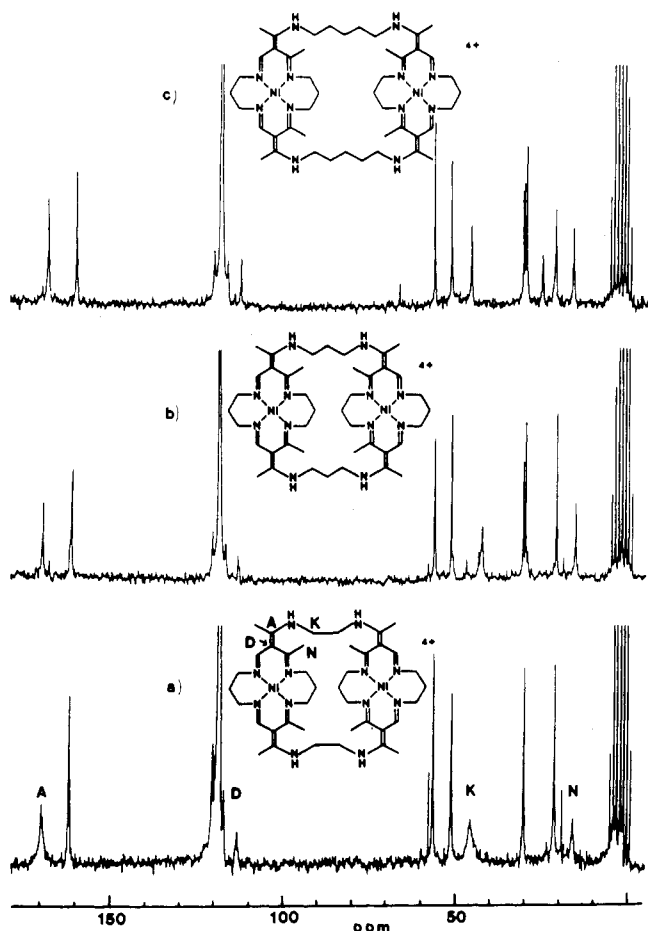


Figure 2. ^{13}C NMR spectra of a series of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{R}^1)_2\}(\text{[16]cyclidene})_2](\text{PF}_6)_4$ complexes in acetonitrile- d_3 at room temperature: (a) $\text{R}^1 = (\text{CH}_2)_5$; (b) $\text{R}^1 = (\text{CH}_2)_3$; (c) $\text{R}^1 = (\text{CH}_2)_2$.

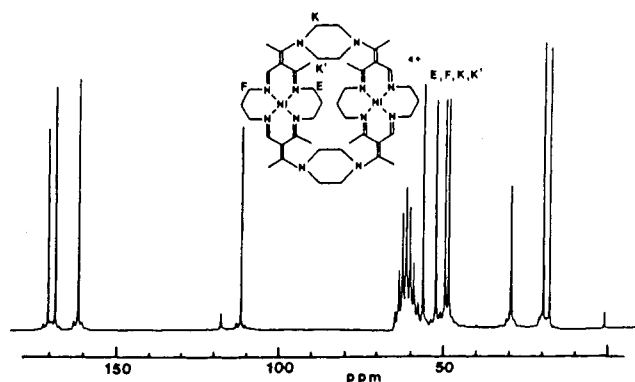


Figure 3. ^{13}C NMR spectrum of $[\text{Ni}_2\{(\text{Me}_2(\text{pip}))_2\}(\text{[16]cyclidene})_2](\text{PF}_6)_4$ in nitromethane- d_3 at room temperature.

protons (7.4–7.9 ppm) and those of the R^2 methyl groups (6.3–6.8 ppm). Also, symmetry permitting, two sharp singlets attributable to the two methyl groups may be identified in the region 2.0–2.5 ppm.

The ^1H NMR spectrum of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2\}(\text{[16]cyclidene})_2]^{4+}$, in acetonitrile- d_3 , provides an example of this complicated behavior, as shown in Figure 4a. The signals due to the protons on both the vinyl and the R^2 position are resolved into three separate peaks, one of which appears to be twice as intense as the other two. One possible explanation is that there is a single molecular form and that it has neither symmetry elements nor fluxional motions that render the four protons of each kind equivalent. Alternatively, the apparent asymmetry could arise from the presence of different conformers. The temperature dependence of the NMR spectrum was studied in order to explore this question further (note Figure 4b). At lower temperatures,

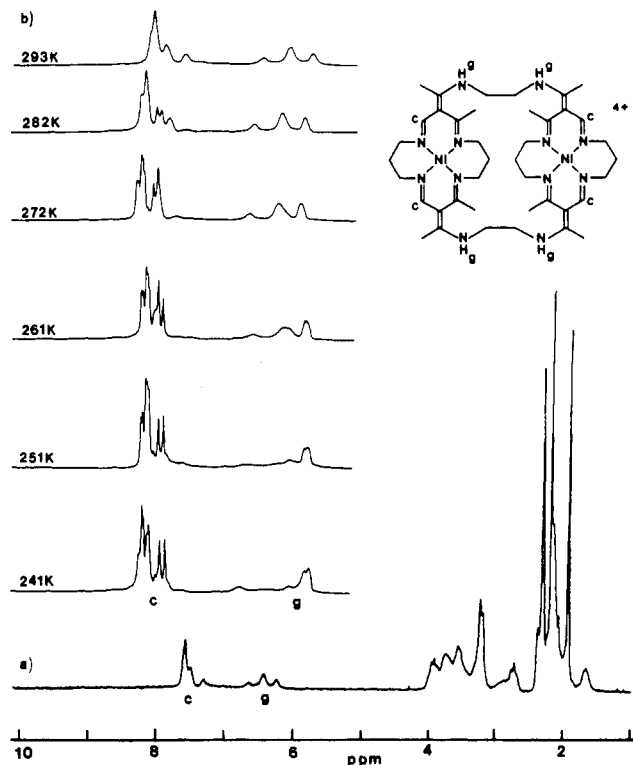


Figure 4. ^1H NMR spectra of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2\}(\text{[16]cyclidene})_2](\text{PF}_6)_4$ in acetonitrile- d_3 : (a) spectrum at 299 K, and (b) spectra in the region 6–8 ppm upon cooling.

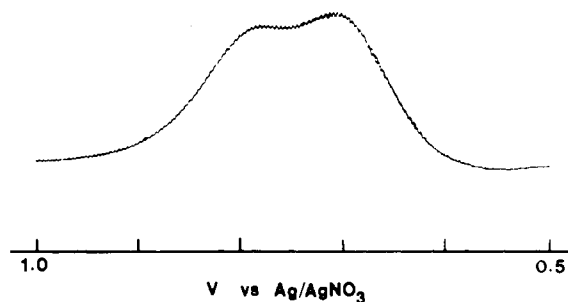


Figure 5. Differential-pulse polarogram of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2\}(\text{[14]cyclidene})_2]^{4+}$ (in acetonitrile containing 0.1 M TBAT, at room temperature; scan rate = 2 mV/s, “drop time” = 0.5 s).

this region of the spectrum becomes sharper, and at 241 K, four separate sharp peaks are observed. This suggests that the broadening observed at higher temperature is due to interconversion between different conformations and that at still higher temperatures the four peaks would eventually coalesce. Indeed in $\text{Me}_2\text{SO}-d_6$ the proton signals due to R^2 were observed to coalesce at 339 K.

Electrochemistry. The oxidation–reduction behavior of the dinickel(II) bis(cyclidene) complexes was studied by cyclic voltammetry and by differential-pulse polarography in acetonitrile solutions. The partial solution of the crystal structure of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2\}(\text{[16]cyclidene})_2](\text{PF}_6)_4$ ¹⁵ indicated an intermetallic distance of about 10 Å in this molecule, and even in those new members of the family of bis(cyclidene) complexes that are expected to have shorter metal–metal distances, the two metals are still too far apart to allow significant orbital overlap. However, the NMR results show that the complexes are very flexible, and this raises the possibility that the average metal–metal distance in solution may differ greatly from that in the solid state or from that estimated from models.

(15) Hoshino, N.; Jircitano, A. J.; Alcock, N. W.; Busch, D. H., unpublished work.

Table II. Differential-Pulse Polarographic Data for a Series of Dinickel(II) Complexes $[\text{Ni}_2\{(\text{Me}_2(\text{NR}^2)_2\text{R}^1)_2\}(\text{Q}[\text{cyclidene}])_2]^{4+}$ in Acetonitrile^a

R ¹	R ²	Q	width/ mV	$\Delta E_{1/2}/$ mV ^b	E_c/V	$E_{1/2}^1/V$	$E_{1/2}^2/V$
mxyI	H	16	108	50	0.899	0.879	0.929
(CH ₂) ₃	H	16	126	61	0.888	0.863	0.924
(CH ₂) ₂	H	16	168	87	0.929	0.891	0.978
pip		16	176	92	0.880	0.839	0.931
(CH ₂) ₂	H	14	191	105	0.755	0.708	0.812
(CH ₃) ₂ ^c		16	108	50			
$[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$			99	43			

^a Differential-pulse polarograms obtained in 0.1 M TBAT/CH₃CN vs. Ag/0.1 M AgNO₃/CH₃CN at room temperature. See Experimental Section for instrumental conditions. ^b Table I, p 1280 in ref 13. ^c Mononuclear unbridged complex, $[\text{Ni}\{\text{Me}_2(\text{NMe}_2)_2[16]\text{cyclidene}\}]^{2+}$.

The cyclic voltammograms of the dinickel complexes generally display reversible to quasireversible oxidation waves at 0.7–1.0 V vs. Ag/0.1 M AgNO₃/CH₃CN. The Ni(III/II) waves show a small but perceptible splitting—a feature that is readily measured using differential pulse polarography. This is illustrated in Figure 5 for the Me₂(NH)₂CH₂CH₂-bridged bis([14]cyclidene) species; the separation of the two $E_{1/2}$ values is most visible for this case. The values for $\Delta E_{1/2}$ were calculated from the half-widths of the polarograms by using the technique of Richardson and Taube.¹⁶ The contributing $E_{1/2}$ values were calculated from

$$E_{1/2}^2 = E_c + (\Delta E_{1/2} + E_{\text{pul}})/2$$

where E_{pul} is the pulse amplitude (10 mV in this study) and E_c is the center of symmetry of the polarogram.

Although the $\Delta E_{1/2}$ values are all small and represent weakly coupled systems, the steady increase from 50 mV for the Me₂(NH)₂mxyI-bridged bis([16]cyclidene) species to 105 mV for the Me₂(NH)₂CH₂CH₂-bridged bis([14]cyclidene) complex correlates well with the expected decreases in metal–metal separation. Two structural factors were used in controlling the metal–metal separation, the length of the bridging group and the size of the cyclidene ring. The double CH₂CH₂ link in the piperazine-bridged species is expected to bring two metal sites closer together than the stretched lid-on NHCH₂CH₂NH bridge in the dimethylene-linked complexes. [16]cyclidene macrocyclic complexes invariably have deep saddle shapes while [14]cyclidene macrocycles are expected to be more nearly planar. Therefore, the [14]cyclidene derivative with the dimethylene bridge should produce a considerably shortened metal–metal separation. It follows that a relatively good correlation exists between the values of $\Delta E_{1/2}$ and the approximate metal–metal distances.

For electronically symmetrical dimetallic complexes, nonzero values of $\Delta E_{1/2}$ may arise from any or all of the following five factors:^{17,18} (1) statistical contributions (36 mV); (2) electrostatic interactions; (3) solvation energy effects; (4) changes in coordination number; (5) electron delocalization. In the present case, the last factor should be negligibly small due to the absence of reasonable delocalization pathways. Also, other studies suggest that the redox potentials of the nickel(II) cyclidene complexes will be insensitive to changes in coordination number.¹⁹ It therefore follows that $\Delta E_{1/2}$ values greater than 36 mV arise because of electrostatic interactions within the binuclear molecules and/or solvation effects. The effect of electrostatics is to increase $\Delta E_{1/2}$ as the distance between metal sites is decreased, while the contribution from solvation energy varies in the opposite sense.¹⁷ As such, the observed increase in $\Delta E_{1/2}$ as the distance between cyclidene units is decreased suggests that the principal factor

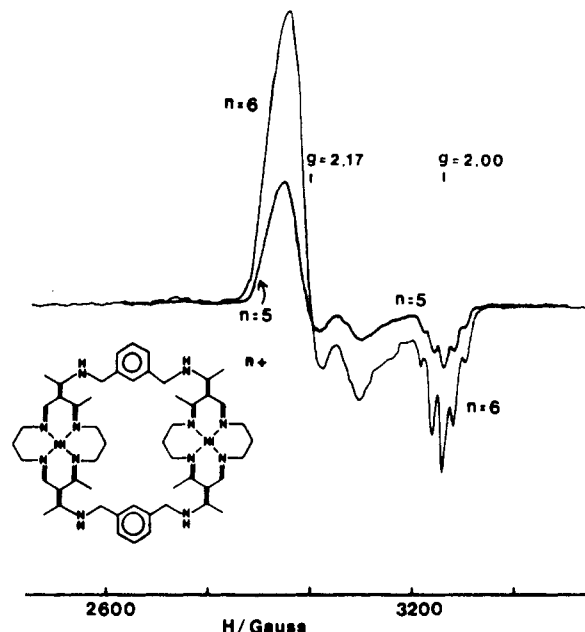


Figure 6. EPR spectra of $[\text{Ni}_2\{(\text{Me}_2(\text{NH})_2\text{mxyI})_2\}(\text{[16]cyclidene})_2]^{n+}$ obtained by controlled-potential electrolysis ($n = 5, 6$) (electrolyzed at 1.0 V; EPR recorded at 77 K).

determining $\Delta E_{1/2}$ is electrostatic.

The last two entries in Table II are mononuclear complexes. Assuming reversible redox chemistry, the mononuclear complexes represent systems that, if subjected to the same analysis as carried out for the differential-pulse polarograms of the dinuclear complexes, should yield $\Delta E_{1/2}$ values of 36 mV.^{16,20} The value obtained for $[\text{Ru}(\text{NH}_3)_5(\text{py})]^{2+}$, 43 mV, serves as a calibration, representing the deviation between experiment and theory due, in part, to cell configuration and the use of a nonaqueous electrolyte solution. In view of the extreme separation between the two metal ions, it is not surprising that the Me₂(NH)₂mxyI-bridged species behave in much the same way as the unbridged mononuclear cyclidene complexes ($\Delta E_{1/2} = 50$ mV in both cases), but the results demonstrate that electrostatic interactions operate and are detectable even in the Me₂(NH)₂CH₂CH₂-bridged species where the two nickel centers are some 10 Å apart.

Controlled-potential electrolysis experiments yielded information on the structure of the nickel(III) complexes. Figure 6 shows the EPR spectra of one-electron- and two-electron-oxidation products of the Me₂(NH)₂mxyI-bridged complex. The two spectra are identical, except for intensity, which doubles upon removal of the second electron. The parallel component of the axial spectrum is well resolved into a quintet, showing coupling to two axially coordinated acetonitrile molecules ($A_{\parallel}^{\text{N}} = 20.0$ G) and a 6-coordinate structure for the two nickel(III) centers. The identical shape of the two signals establishes the independence of the two sites and shows that each metal can be oxidized to a 6-coordinate, disolvated species without affecting the other metal.

The corresponding experiments with the shorter Me₂(NH)₂CH₂CH₂-bridged species exhibit EPR spectra indicating significant interactions between the two metal atom sites (Figure 7). The general pattern of the spectra, $g_{\parallel} > g_{\perp}$, is characteristic of low-spin d^7 species having reduced coordination numbers (4 or 5). This suggests that both sides of a metal atom cannot be fully coordinated in even the one-electron-oxidation product. The absence of superhyperfine splitting due to axial ligands is also consistent with such structures. The variation in behavior as a function of metal–metal separation is remarkable.

Experimental Section

Measurements. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Laser DI FT mass spectra were obtained by Dr.

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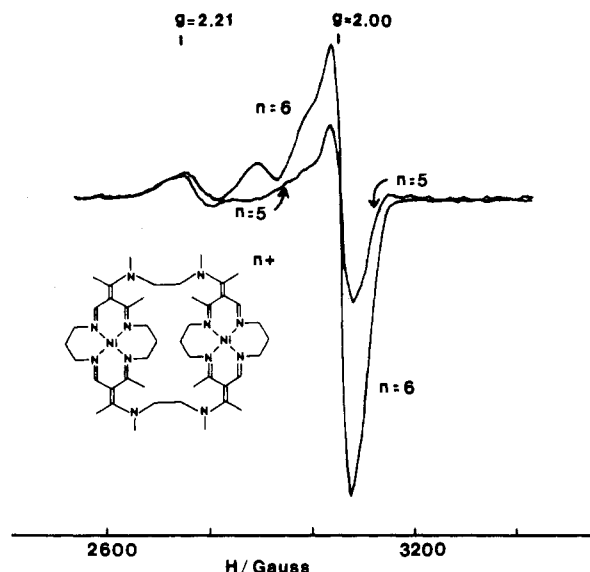


Figure 7. EPR spectra of $[\text{Ni}_2(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2([\text{16}]\text{cyclidene})_2]^{n+}$ obtained by controlled-potential electrolysis ($n = 5, 6$) (electrolyzed at 0.95 V; EPR recorded at 77 K).

C. Cody on a Nicolet FTMS-1000 instrument, equipped with a Tachisto Model 215G pulsed CO_2 laser, at Nicolet Analytical Instruments, Madison, WI. The FAB mass spectrum was recorded on a Kratos MS-30 mass spectrometer using xenon bombardment gas; an Ion-Tek gun operating at 6 kV was used to produce and accelerate the bombardment gas. High-resolution ^1H NMR spectra were recorded on Bruker WP200 or a Bruker WM300 spectrometer. The ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer operating in the FT mode at 20 MHz.

Electrochemical measurements were carried out with a Princeton Applied Research Corp. potentiostat-galvanostat Model 173, equipped with a Model 175 linear programmer and a Model 179 digital coulometer and also with a PAR Model 174A polarographic analyzer. Cyclic voltammetric and polarographic curves were recorded on a Houston Instruments Model 2000 X-Y recorder. A conventional H-cell was used, and the working electrode for cyclic voltammetry was a platinum disk with potentials measured vs. a silver wire immersed in 0.1 M silver nitrate in acetonitrile as the reference. Differential-pulse polarographic data were obtained by using a platinum bead electrode and are also referenced to $\text{Ag}/0.1 \text{ M AgNO}_3/\text{CH}_3\text{CN}$. A pulse amplitude of 10 mV was used in all pulse experiments with a scan rate of 2 mV/s and a "drop time" of 0.5 s. All measurements were carried out in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (TBAT) as supporting electrolyte in a dry box under an atmosphere of dry oxygen-free nitrogen.

Syntheses. The preparations of some of the dinickel(II) bis(cyclidene) complexes included in this paper have been described earlier.⁹ Slight modifications were made, when necessary, and CM-Sephadex ion-exchange chromatography with aqueous Na_2SO_4 as eluant was employed in the purification of all of the compounds used in this work. The syntheses of new members of the family are described below.

(2,3,6,7,9,15,17,18,21,22,24,30-Dodecamethyl-3,6,10,14,18,21,25,29,32,36,39,43-dodecaazatricyclo[21.7.7.8¹⁶]tetratetraconta-1,7,9,14,16,22,24,29,31,36,38,43-dodecane- $\kappa^8\text{N}$)dinickel(II) Hexafluorophosphate ($[\text{Ni}_2(\text{Me}_2(\text{NMe})_2\text{CH}_2\text{CH}_2)([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$). To 100 mL of an acetonitrile solution of $[\text{Ni}_2(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$ (1.63 g, 1.09 mmol) was added a methanolic solution of sodium metal (0.10 g, 4.4 mmol, in 7 mL), upon which the color of the solution turned immediately from yellow-orange to deep red. After the mixture was stirred for 1 h, the solvent was evaporated to dryness and the residue was extracted with 50 mL of dichloromethane and filtered through Celite. Solvent was added to the filtrate to produce a volume of 100 mL, and 3.2 mL (51 mmol) of methyl iodide was added under nitrogen. After being stirred overnight, the solution was concentrated on a rotovap and 1.6 g (9.5 mmol) of NH_4PF_6 dissolved in 100 mL of methanol was added. The resulting dark yellow-orange precipitate was collected by filtration. This solid was redissolved in acetonitrile and passed through a neutral alumina column, eluting with acetonitrile. A yellow solution was collected, leaving a brown band on the top of the column. Rotary evaporation followed by addition of ethanol resulted in the formation of a yellow solid.

The above product was metathesized to the chloride with $(n\text{-Bu})_4\text{NCl}$ and its aqueous solution was loaded on a CM-Sephadex column. Only

one orange band resulted from elution with 0.4 M aqueous Na_2SO_4 . The hexafluorophosphate salt of the complex was recovered from this effluent by adding excess NH_4PF_6 . The solid obtained in this way was recrystallized from acetonitrile/ethanol. Yield: 0.92 g (58%). Anal. Calcd for $\text{Ni}_2\text{C}_{44}\text{H}_{72}\text{N}_{12}\text{P}_4\text{F}_{24}$: Ni, 8.01; C, 36.04; H, 4.95; N, 11.46. Found: Ni, 7.94; C, 35.96; H, 4.90; N, 11.68.

(2,7,9,15,17,22,24,29-Octamethyl-3,6,10,14,18,21,25,29,32,36,41,45-dodecaazapentacyclo[21.7.7.7^{8,16}.2^{3,6}.2^{18,21}]octatetraconta-1,7,9,14,16,22,24,29,31,36,40,45-dodecaene- $\kappa^8\text{N}$)dinickel(II) Hexafluorophosphate ($[\text{Ni}_2(\text{Me}_2(\text{pip}))_2([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$). This complex was prepared by the method of Takeuchi.²¹ Two solutions, one containing 3.65 g (4.47 mmol) of $[\text{Ni}(\text{Me}_2(\text{pip}))_2([\text{16}]\text{cyclidene})](\text{PF}_6)_2$ in 200 mL of acetonitrile and the other containing 3.17 g (4.47 mmol) of $[\text{Ni}(\text{Me}_2(\text{OME})_2([\text{16}]\text{cyclidene})](\text{PF}_6)_2$ in 200 mL of acetonitrile, were simultaneously dripped into a reservoir of 300 mL of continuously stirred acetonitrile over a period of 3 h. After the mixture was stirred for an additional 3 h, the volume of the resulting deep red solution was reduced, upon which some yellow precipitate started to form. The solid was redissolved by adding 200 mL of acetone, and the solution was diluted to about 2 L with water and then loaded on a Sephadex column. Undesired species were washed away with 0.3 M Na_2SO_4 by eluting them until the eluate was almost colorless. The concentration of Na_2SO_4 was then raised to 0.4 M, and a broad brown band was collected. A 6-g quantity of NH_4PF_6 in water was added to this solution to precipitate the hexafluorophosphate salt. The resulting dark orange powder was isolated by vacuum filtration and quickly washed with 50 mL of acetonitrile, leaving a bright yellow solid. This material was dissolved in a minimum amount of 1:1 acetonitrile/nitromethane, and ethanol was added to induce recrystallization. Yield: 0.51 g (7.6%). Anal. Calcd for $\text{Ni}_2\text{C}_{44}\text{H}_{68}\text{N}_{12}\text{P}_4\text{F}_{24}$: Ni, 8.03; C, 36.14; H, 4.69; N, 11.49. Found: Ni, 7.91; C, 36.17; H, 4.92; N, 11.65.

(2,7,9,14,16,21,23,28-Octamethyl-3,6,10,13,17,20,24,27,29,33,35,39-dodecaazatricyclo[20.6.6.6^{8,15}]tetraconta-1,7,9,13,15,21,23,27,29,33,35,39-dodecaene- $\kappa^8\text{N}$)dinickel(II) Hexafluorophosphate ($[\text{Ni}_2(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)([\text{14}]\text{cyclidene})_2](\text{PF}_6)_4$). Two acetonitrile solutions (200 mL each), one containing 2.51 g (3.60 mmol) of $[\text{Ni}(\text{Me}_2(\text{OME})_2([\text{14}]\text{cyclidene})](\text{PF}_6)_2 \cdot 0.5\text{CH}_3\text{OH}$ and the other containing 0.22 g (3.66 mmol) of ethylenediamine, were simultaneously added dropwise to a vigorously stirred reservoir of the solvent (200 mL). The volume of the resulting red solution was reduced to a small amount and applied on a neutral alumina column. However, the elution with acetonitrile did not yield a clear separation into bands; therefore, the solution that was collected was subjected to Sephadex chromatography in a manner similar to that in the preceding synthesis. Elution with 0.4 M Na_2SO_4 resulted in three bands, the first two of which yielded no solid upon addition of excess NH_4PF_6 . An orange powdery solid was recovered from the last moving band. Yield: 0.18 g (3.2%). Anal. Calcd for $\text{Ni}_2\text{C}_{36}\text{H}_{56}\text{N}_{12}\text{P}_4\text{F}_{24} \cdot \text{C}_2\text{H}_5\text{OH} \cdot 2\text{Na}_2\text{SO}_4$: Ni, 7.04; C 27.35; H, 3.74; N, 10.07. Found: Ni, 7.24; C, 28.09; H, 3.78; N, 9.95.

The complexes $[\text{Ni}(\text{Me}_2(\text{NMe})_2([\text{16}]\text{cyclidene})](\text{PF}_6)_2$ ²⁵ and $[\text{Ru}(\text{NH}_3)_3(\text{py})](\text{PF}_6)_2$ ²⁶ were synthesized according to literature preparations.

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Registry No. $[\text{Ni}_2(\text{Me}_2(\text{NMe})_2\text{CH}_2\text{CH}_2)([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$, 102920-25-2; $[\text{Ni}_2(\text{Me}_2(\text{pip}))_2([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$, 102920-27-4; $[\text{Ni}_2(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)([\text{14}]\text{cyclidene})_2](\text{PF}_6)_4$, 102920-29-6; $[\text{Ni}_2(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)([\text{16}]\text{cyclidene})_2](\text{PF}_6)_4$, 77875-34-4; $[\text{Ni}$

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Multifrequency ESR of Cu(II)-(His)_n (His = Histidine). 1. Immobile Phase¹

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ESR studies of Cu(histidine)_n in the presence of excess histidine at two microwave frequencies were undertaken to support either the glycine-like or histamine-like complexes. Low-frequency, S-band data are well-resolved for the $M_I = -1/2$ line in the g_{\parallel} region, and the number of lines is attributed to four approximately equivalent nitrogen donor atoms. When the pH is increased from 6.8 to 7.3, a second form is detected from the $M_I = -1/2$ line in the g_{\parallel} region but not in other portions of the spectrum. The change in ESR parameters does not appear to be large enough to account for a change from four nitrogen donor atoms to three nitrogen donor atoms in the square-planar configuration. This small change is more consistent with a change in axial coordination or a change from four nitrogen donor atoms to an altered set of four nitrogen donor atoms. Further ESR analysis of frozen copper-histidine complexes in the presence of excess histidine where the ¹⁴N isotope in the imidazole ring is substituted with ¹⁵N is consistent with a structure for which four equivalent ¹⁵N nitrogen donor atoms are bound to cupric ion.

Introduction

Histidine is a tridentate ligand that acts like a bidentate ligand for cupric square-planar complexes due to steric constraints.² Histamine-like, glycine-like, and a mixture of histamine-like and glycine-like Cu(His)₂ (His = histidine) complexes are possible. Additional speciation occurs in the pH range of 5-7 because formation of a Cu(H-His,His) complex has a pK of 5.63.² In this report, these structures, which appear to be the major species present in solution, have been studied in the presence of excess histidine in the frozen state by utilizing the ESR method.

After comparison of the ESR parameters, g_{\parallel} and A_{\parallel} , Rotilio and Calabrese inferred that the Cu^{II}(His)₂ complex has the mixed histidine-like and glycine-like ligand.³ The ESR parameters for this complex in frozen solution are between the parameters for complexes with four nitrogen donor atoms and those for complexes with two nitrogen donor atoms and similar to those for a mixed glycine-histamine-Cu(II) complex that has three nitrogen donor atoms and a single oxygen donor atom. Detection of two species from the second-derivative hyperfine structure on the high-field line for the ESR spectra of ⁶³Cu(His)₂ complexes in D₂O recorded at room temperature suggests that equal concentrations of two species could exist at physiological pH.⁴ It is suggested that one of these species has three nitrogen donor atoms and the other four nitrogen donor atoms bound to cupric ion in a square-planar configuration.

Other techniques have been used to suggest the configuration of Cu^{II}(his)₂. Among these, a crystal structure determination of (L-histidinato)(D-histidinato)diaquocopper(II) tetrahydrate has been used to support a plausible structure for Cu(His)₂ in which bidentate amino and imidazole nitrogens from each ligand bind in a cis configuration to form the square plane.⁵ For crystallographic data combined with nuclear relaxation rate analysis, it is suggested that 76% of a complex with one imidazole coordinated in the histamine-like way is in equilibrium with 24% of a complex with two imidazoles bound.⁶ Multifrequency ESR analysis used in correlation with computer simulation of spectra can also be a

very useful tool in determining chemical structure and molecular dynamics of copper in biological systems⁷ mainly due to the existence of an optimal microwave frequency at which the super-hyperfine structure is best resolved.^{8,9} This work uses multifrequency ESR spectroscopy to determine whether low-frequency (S-band) ESR is consistent with or adds to the present understanding of frozen copper complexes in the presence of excess histidine.

Experimental Section

L-His from Merck and DL-His-1,3-¹⁵N₂ from MSD Isotopes were used without further purification. The solutions were made in 99.75% D₂O, from Merck, and the uncorrected pD was adjusted with either DCl or NaOD. Isotopically pure ⁶³Cu (from Oak Ridge National Laboratory, Oak Ridge, TN) was used for these ESR experiments.

X-Band ESR spectra ($\nu = 9.1$ GHz) were obtained with a Varian E-109 Century Series X-band spectrometer, and S-band spectra were obtained with a microwave bridge equipped with a loop-gap resonator operating at 3.4 GHz.¹¹ (The ESR facilities are located at the NIH-sponsored National Biomedical ESR Center at the Medical College of Wisconsin.) Microwave frequencies were measured with an EIP Model 331 counter, and the magnetic field was calibrated with a Radiospan MJ-110R NMR magnetometer.

Computer programs for simulation of frozen spectra of cupric complexes were obtained from Dr. J. Pilbrow, Monash University, Clayton, Victoria, Australia. The line width is determined from the quadratic equation $W_n' = [W_n'^2 + B_n M_I]^{1/2}$, where $M_I = +3/2, +1/2, -1/2, \text{ or } -3/2$,

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