

understanding of the effects governing their reactivity.

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Registry No. $\text{SF}_3\text{NCF}_2\text{O}$, 73002-62-7; $\text{SF}_2\text{N}(\text{CF}_3)\text{C}(\text{O})\text{F}$, 73002-63-8; $\text{SF}_2\text{N}(\text{H})\text{CF}_2\text{OOCF}_3$, 73002-64-9; CF_3OOH , 16156-36-8; $\text{SF}_3\text{N}=\text{CF}_2$, 2375-32-8; COF_2 , 353-50-4; SF_6 , 2551-62-4; CF_3NO , 334-99-6; CF_3OF , 373-91-1; SF_2NCF_3 , 4101-60-4; KF , 7789-23-3; CsF , 13400-13-0; SF_4 , 7783-60-0.

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Adducts of Bis(N-substituted ethylenediamine)copper(II) Complexes with Hexacyanoferrate(III)

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The interactions between bis(N-R-ethylenediamine)copper(II), where R = H, C₂H₅, and C₃H₇, and hexacyanoferrate(III) have been studied by means of electronic spectra, magnetic resonance spectroscopies, and magnetic susceptibility measurements. Complexes with formulas $\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$, $[\text{Cu}(\text{N-Et-en})_2][\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$, and $[\text{Cu}(\text{N-Pr-en})_2][\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ have been obtained. Although the magnetic susceptibility data are essentially the sum of those of the parent complexes in the range 77–300 K, the electronic relaxation times of copper(II) in the mixed complexes are so much changed that the ESR signal disappears whereas the ¹H NMR signals of the R group sharpen, showing the existence of metal–metal interactions. The electronic spectroscopy data are consistent with such specific interactions. The analogous $\text{K}[\text{Cu}(\text{en})_2][\text{Co}(\text{CN})_6]$ compound has been prepared and characterized; ¹³C NMR data show evidence of a cyanide bridge between the two metals in solution, suggesting similar behavior in the other systems.

Introduction

It is well-known that the cyanide ion may coordinate through the carbon atom acting as a monodentate ligand or through both carbon and nitrogen atoms acting as a bridging ligand.² With respect to the latter type of coordination, studies have been performed on the hexacyanoferrate(III) of various metal ions where moieties $\text{M}-\text{N}\equiv\text{C}-\text{Fe}$ account for the physical properties of the compounds. In particular, magnetic exchange interactions between the two metal ions have been investigated as well as their role in heteronuclear intervalence transfer.^{3–5}

The hexacyanoferrate(III) ion is commonly used in biochemistry as a mild oxidizing agent especially to oxidize copper(I) to copper(II).⁶ The problem arises therefore to determine whether $[\text{Fe}(\text{CN})_6]^{3-}$ is capable of interacting with coordinatively unsaturated copper(II) complexes and, if so, to understand the physicochemical consequences of such interactions. With this in mind several adducts between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Cu}(\text{N-R-en})_2]^{2+}$ ions, where N-R-en represents an N-substituted ethylenediamine, have been prepared and characterized.

Experimental Section

Preparation of the Complexes. $\text{K}_3[\text{Fe}(\text{CN})_6]$ was analytical grade and was used without any further purification. $\text{K}_3[\text{Co}(\text{CN})_6]$ and $\text{K}_3[\text{Co}(\text{CN})_6]$ were prepared by reacting CoSO_4 with KCN or K^{13}CN in 1:2 ratio. The dicyanide cobalt salt was then dissolved in an excess of potassium cyanide solution. Solid potassium hexacyanocobaltates were obtained by concentration and twice recrystallized. The $[\text{Cu}(\text{N-R-en})_2](\text{ClO}_4)_2$ (R = H, C₂H₅) and $[\text{Cu}(\text{N-Pr-en})_2]\text{Cl}_2$ complexes were prepared as previously described.⁷ The adducts were obtained by mixing water solutions of the complexes in a 1:1 ratio (10^{-1} M in the case of N-substituted ethylenediamine and ca. 1 M in the case of $[\text{Cu}(\text{en})_2]^{2+}$) and allowing the solutions to evaporate in a desiccator.

Physical Measurements. The electronic spectra were recorded on a Cary 17 D, the ESR spectra on a Varian E 9, the ¹H NMR spectra on a Perkin-Elmer R 32, and the ¹³C NMR spectra on a Varian

Table I. Analytical Data (%) of the Complexes

	C	H	N	O	Cu	Fe
$\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$	calcd	27.6	3.70	32.2		
	found	27.4	3.66	32.2		
$\text{K}[\text{Cu}(\text{en})_2][\text{Co}(\text{CN})_6]$	calcd	27.4	3.68	32.0		
	found	27.0	3.73	31.8		
$[\text{Cu}(\text{N-Et-en})_2]_3 \cdot 4\text{H}_2\text{O}$	calcd	35.6	6.63	27.7	5.26	9.18
	found	35.5	6.49	28.4	5.40	8.90
$[\text{Cu}(\text{N-Pr-en})_2]_3 \cdot 5\text{H}_2\text{O}$	calcd	38.3	7.24	25.5	6.07	8.47
	found	37.8	7.04	25.9	6.40	8.73

Table II. Some Physical Data of the Complexes in Solution

	absorp max. 10^3 cm^{-1} ^a	Λ_M , S $\text{cm}^2 \text{ mol}^{-1}$ ^{c,d}	mol wt- (found)/ mol wt- (calcd) ^d
$[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$	18.4 (60)		
$\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$	18.1 (65) ^e	260 (w) ^f	0.57 (w)
$\text{K}[\text{Cu}(\text{en})_2][\text{Co}(\text{CN})_6]$	18.2 (65)		
$[\text{Cu}(\text{N-Et-en})_2](\text{ClO}_4)_2$	18.0 (90)		
$[\text{Cu}(\text{N-Et-en})_2]_3 \cdot 4\text{H}_2\text{O}$	17.5 (105) ^e	18 (D)	
$[\text{Cu}(\text{N-Pr-en})_2](\text{ClO}_4)_2$	18.1 (95)		
$[\text{Cu}(\text{N-Pr-en})_2]_3 \cdot 5\text{H}_2\text{O}$	17.5 (110) ^e	23 (D)	

^a In H₂O. ^b Calculated per mole of Cu(II) ions. ^c w = water; D = dimethyl sulfoxide. ^d 10^{-3} M solution at 25 °C. ^e The $[\text{Fe}(\text{CN})_6]^{3-}$ moiety shows an intense charge-transfer band at $24.0 \times 10^3 \text{ cm}^{-1}$, which does not change in the adducts. ^f $\Lambda_M = 137$ for a 10^{-2} M water solution.

CFT20. The Mössbauer spectra were obtained on a spectrometer which consisted of a linear velocity drive unit (MWE, Canberra), a

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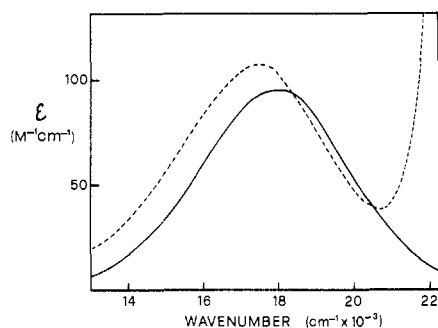


Figure 1. Electronic spectra of $[\text{Cu}(\text{N-Pr-en})_2](\text{ClO}_4)_2$ (—) and $[\text{Cu}(\text{N-Pr-en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ (---) in aqueous solutions. The molar absorptance is calculated per mole of Cu^{II} ions.

Xe-CO₂ proportional counter system, and a 1024-channel analyzer (Laben Model 8001). Cobalt-57 in Pd was used as the source. The velocity was calibrated with reference to an enriched metallic iron foil at room temperature. Molecular weight measurements were performed with an Hitachi Perkin-Elmer 115 osmometer and the conductivity measurements with a WTW Model LBR/B conductance bridge. The magnetic susceptibility measurements were performed on a Gouy balance with the procedure described elsewhere.⁸

Results

Depending on the particular diamine used, compounds with different formulas have been obtained: $\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$ (and $\text{K}[\text{Cu}(\text{en})_2][\text{Co}(\text{CN})_6]$), $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$, and $[\text{Cu}(\text{N-Pr-en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ (Table I). Whereas the first compound is soluble in water, the last two are only sparingly soluble in water and slightly in dimethyl sulfoxide; furthermore, $[\text{Cu}(\text{N-Pr-en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 5\text{H}_2\text{O}$ changes color upon heating, giving a product with a complex nonreproducible formula.

In the case of $\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$, molecular weight measurements on a 1.9×10^{-2} M solution in water gave a value which is about half of the reported formula weight (see Table II). Electric conductivity measurements of solutions at the same concentration are also consistent with a 1:1 electrolyte. Upon dilution of the solution the molar conductance (Table II) substantially increased, indicating further ion dissociation, although much less than expected for a 1:2:3 electrolyte. Although in the case of the *N-Et-en* and *N-Pr-en* adducts with hexacyanoferrate(III) molecular weight measurements could not be performed due to the scarce solubility of the compounds, conductivity measurements of 10^{-3} M solutions show that the compounds are dissociated to a relatively small extent.

The electronic spectra of the adducts both in water solutions and in the solid state show essentially the same absorptions of the ferricyanide ion but show a sensible bathochromic shift of the copper(II) band with respect to the parent copper(II) complexes (Figure 1 and Table II).

The infrared spectra of the three adducts in the solid state show a clear splitting of the C≡N stretching vibration with respect to the pure $\text{K}_3[\text{Fe}(\text{CN})_6]$ ($\nu_6 = 2119 \text{ cm}^{-1}$).⁹ $\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$ shows three well-resolved bands at 2102, 2113, and 2125 cm^{-1} ; the *N-Pr-en* compound shows two bands at 2105 and 2120 cm^{-1} and a shoulder at ca. 2136 cm^{-1} , while in the *N-Et-en* derivative only one band is apparent, centered at 2108 cm^{-1} , with shoulders at ca. 2118 and 2130 cm^{-1} . The absorptions due to the copper(II) moieties are essentially the same as for the pure copper compounds, indicating that the trans configuration of the asymmetric ethylenediamines is retained.¹⁰

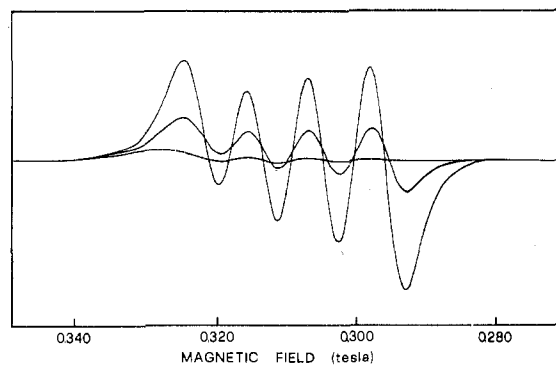


Figure 2. ESR spectra of $[\text{Cu}(\text{N-Pr-en})_2](\text{ClO}_4)_2$ in aqueous solution in the presence of increasing amounts of $\text{K}_3[\text{Fe}(\text{CN})_6]$. The Fe:Cu ratios are 0, 0.5, and 0.7 in order of decreasing signal intensity.

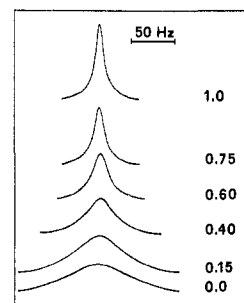


Figure 3. ^1H NMR signal of the methyl group of $[\text{Cu}(\text{N-Pr-en})_2](\text{ClO}_4)_2$ in D_2O solution in the presence of $\text{K}_3[\text{Fe}(\text{CN})_6]$ at various Fe:Cu ratios.

The parent copper complexes show at $[\text{Fe}(\text{CN})_6]^{3-}$ temperature ESR signals typical of tetragonal species: in solution, owing to rapid rotation, a spectrum with a single g value at about 2.10 with four hyperfine lines separated by ca. $80 \times 10^{-4} \text{ cm}^{-1}$ is obtained. In glassy solutions two g values are observed ($g_{\parallel} = 2.21$ and $g_{\perp} = 2.05$) with $A_{\parallel} = 200 \times 10^{-4} \text{ cm}^{-1}$.¹¹ The lines are sharp, the half-width being ca. 40 G. This is consistent with orbitally nondegenerate ground energy levels. $\text{K}_3[\text{Fe}(\text{CN})_6]$, on the contrary, has a $^2\text{T}_1$ ground state and gives rise to a very broad ESR line which becomes detectable only at liquid-hydrogen temperature.¹² The three adducts show a very broad signal which is hardly detectable at room temperature. Even at liquid-nitrogen and liquid-helium temperatures the signal remains almost shapeless and does not allow determination of any g value. At liquid-helium temperature such a signal is broader than that of the pure $\text{K}_3[\text{Fe}(\text{CN})_6]$.

Upon addition of increasing amounts of $[\text{Fe}(\text{CN})_6]^{3-}$ to a solution of $[\text{Cu}(\text{N-R-en})_2]^{2+}$, the intensity of the ESR signal of the copper(II) ion decreases without any broadening (Figure 2). This means that the chemical exchange of the cyanide complex among copper centers is slow on the ESR time scale. From the intensity of the ESR signal upon dilution an apparent affinity constant between $[\text{Cu}(\text{en})_2]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ of ca. 10^3 M^{-1} has been estimated.

When the ^1H NMR of the CH_3 group of $[\text{Cu}(\text{N-Et-en})_2]^{2+}$ or of $[\text{Cu}(\text{N-Pr-en})_2]^{2+}$ is monitored as a function of the amount of $[\text{Fe}(\text{CN})_6]^{3-}$ added to the solution, a dramatic sharpening of the signal occurs (Figure 3), which monotonously increases with the concentration of the iron(III) complex. This

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Table III. Magnetic Data of the Adducts and Parent Complexes

	T, K	χ'_M^a	$\mu_{\text{eff}} \mu_B^b$
K[Cu(en) ₂][Fe(CN) ₆]	295	3930	3.05
	88	11790	2.88
[Cu(N-Et-en) ₂] ₃ [Fe(CN) ₆] ₂ ·4H ₂ O	298	8750	4.57
	88	26920	4.36
[Cu(N-Pr-en) ₂] ₃ [Fe(CN) ₆] ₂ ·5H ₂ O	298	9920	4.87
	88	29550	4.56
K ₃ [Fe(CN) ₆]	298	2360	2.37
	88	6085	2.07
[Cu(en) ₂](ClO ₄) ₂	298	1445	1.86
	88	5050	1.89
[Cu(N-Et-en) ₂](ClO ₄) ₂	295	1465	1.86
[Cu(N-Pr-en) ₂](ClO ₄) ₂	295	1450	1.85

^a Values are $\times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and are inclusive of diamagnetic correction. ^b $1 \mu_B = 9.27 \times 10^{-24} \text{ A m}^2$. For complexes with more than one paramagnetic center $\mu_{\text{eff}}^2 = \Sigma \mu_i^2$.

means that the chemical exchange is rapid on the NMR time scale.

For further information of the type of interaction between the two complexes, the ¹³C NMR spectra of ¹³C-enriched [Co(CN)₆]³⁻ ion have been measured in the presence of increasing amounts of [Cu(en)₂]²⁺. The NMR signal dramatically broadens and the T_1^{-1} values increase; both effects are a function of the cobalt:copper ratio, indicating that the chemical exchange is rapid. For a solution of $1.36 \times 10^{-1} \text{ M}$ [Co(¹³CN)₆]³⁻ and of $1.64 \times 10^{-2} \text{ M}$ [Cu(en)₂]²⁺ T_1^{-1} and T_2^{-1} values of 5.9 and 125 s⁻¹, respectively, are obtained.

A Mössbauer measurement on K[Cu(en)₂][Fe(CN)₆] gave a value of the isomer shift of -0.118 mm s^{-1} and a quadrupole splitting of 0.743 mm s^{-1} . Such parameters are typical of iron(III) in a six-coordinate environment although the quadrupole splitting might be indicative of low-symmetry components.¹³

Magnetic susceptibility measurements of the three adducts have been performed between 293 and 77 K (Table III). The molar susceptibility values at both temperatures are essentially the sum of the susceptibility values of the parent complexes.

Discussion

The disappearance of the ESR signal as well as the effect on the proton line width of the copper ligands suggests that some sort of interaction must exist both in the solid state and in solution. Even conductivity and molecular weight measurements are consistent with [Cu(en)₂Fe(CN)₆]⁻ or [(Cu(N-R-en)₂)_x(Fe(CN)₆)_y] clusters, although such measurements do not give information on the type of interaction and may be misleading owing to the possible formation of ion couples.

The bathochromic shifts of the absorption bands of copper(II) in the electronic spectra of the adducts indicate that extra ligand(s) bind in the axial positions of the [Cu(N-R-en)₂]²⁺ moieties as it has been pointed out for all the axially perturbed planar chromophores.¹⁴ A simple increase in the ionic strength, on the other hand, has been shown to cause a quite smaller shift in the opposite direction,¹⁵ i.e., an ipsochromic shift, since ions decrease the axial perturbation of solvent molecules.

However, the most detailed evidence for an interaction between [Cu(N-R-en)₂]²⁺ moieties and the nitrogen of the cyano complexes comes from the ¹³C NMR data on the Cu(en)₂-Co(CN)₆ system. The experimental values of ¹³C T_1^{-1} and T_2^{-1} for [Co(¹³CN)₆]³⁻ in the presence of Cu(en)₂²⁺ can

be expressed in terms of the following equations¹⁶⁻¹⁸

$$fT_1^{-1} = Kr^{-6} \left(6\tau_c + \frac{14\tau_c}{1 + \omega_s^2\tau_c^2} \right) + K' \frac{2\tau_e}{1 + \omega_s^2\tau_e^2} \quad (1)$$

$$fT_2^{-1} = Kr^{-6} \left(7\tau_c + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2} \right) + K' \left(\tau_e + \frac{\tau_e}{1 + \omega_s^2\tau_e^2} \right) \quad (2)$$

where f is the ¹³C:Cu^{II} molar ratio, K and K' are products of known constants, τ_e is the electronic relaxation time, and τ_c is related to τ_e and to the rotational correlation time τ_r through eq 3. The first term in both eq 1 and 2 represents the dipolar

$$\tau_c^{-1} = \tau_e^{-1} + \tau_r^{-1} \quad (3)$$

contribution, and the second term is the contact contribution due to spin delocalization involving s-type orbitals of ¹³C. In the present case T_2^{-1} is more than one order of magnitude larger than T_1^{-1} ; since the difference in the dipolar contributions to the two relaxation rates cannot be larger than 17% for any value of τ_c , while the two contact terms diverge as long as τ_e values are larger than ω_s^{-1} , the dramatic effect on T_2^{-1} relaxation rates must originate from large unpaired spin delocalization onto the carbon atom, as in the case of a chemical bond.

The occurrence of $T_2^{-1} \gg T_1^{-1}$ is typical for ligand nuclei in copper(II) complexes,¹⁹ which always show $\tau_e \gg \omega_s^{-1}$.

In the present case $\omega_s^{-1} = 3 \times 10^{-12} \text{ s}$, while τ_e can be estimated from the line width of the ESR line to be ca. $3 \times 10^{-9} \text{ s}$, a value in the usual range of 10^{-8} – 10^{-9} s for copper(II) complexes. From estimation of K' in eq 2 through the above values and substitution in eq 1, the contact term in the latter is found to be negligible. Therefore a value of r can be calculated from the dipolar part of eq 1: with a reasonable estimate for τ_r of ca. 10^{-10} s a copper-carbon distance of 340 pm is obtained,²⁰ again in agreement with a chemical bond.

A weak interaction between the two moieties at a very long distance, as it would happen in the case of a water molecule bridging the two ions, is not consistent with the ¹³C relaxation data and would hardly account for the effect of proton and electron relaxations in hexacyanoferrate(III) analogues.

Conclusions

The present data indicate that hexacyanoferrate(III) interacts with planar copper complexes giving rise to discrete adducts whose stoichiometry may depend on the bulkiness and on the ligand field strength of the copper ligands.

The disappearance of the ESR signal of the copper complex in solution as well as the sharpening of the ¹H NMR of the ligand of the copper(II) ion indicates an efficient mechanism of coupling at the level of the electronic relaxation rates. Dramatic effects on the nuclear relaxation times in dimers had already been observed.²¹

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Finally, the present results should be a warning for everyone working with ESR on copper(II) in biological systems after oxidizing the ion with $[\text{Fe}(\text{CN})_6]^{3-}$.²²

Acknowledgment. Thanks are expressed to Professor Luigi

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Sacconi for encouragement and to Professor Nuccio Bertazzi for recording the Mössbauer spectra.

Registry No. $\text{K}[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6]$, 72967-84-1; $\text{K}[\text{Cu}(\text{en})_2][\text{Co}(\text{CN})_6]$, 72967-83-0; $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Fe}(\text{CN})_6]_2$, 73036-60-9; $[\text{Cu}(\text{N-Pr-en})_2]_3[\text{Fe}(\text{CN})_6]_2$, 72967-82-9; $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$, 15444-88-9; $[\text{Cu}(\text{N-Et-en})_2](\text{ClO}_4)_2$, 73036-59-6; $[\text{Cu}(\text{N-Pr-en})_2](\text{ClO}_4)_2$, 72984-95-3; $\text{K}_3[\text{Fe}(\text{CN})_6]$, 13746-66-2.

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Effect of Altering the Ring Sequence in Nickel(II) Complexes Containing a 14-Membered Macrocyclic Ligand

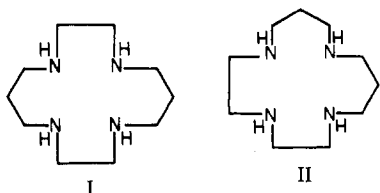
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Nickel(II) complexes of 1,4,7,11-tetraazacyclotetradecane, (1,4,7,11)[14]aneN₄, have been prepared and characterized. Both $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ and $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{SCN})_2$ have been assigned a trans geometry on the basis of electronic and infrared spectral data. On the basis of conductivity data and spectra data, the anions are coordinated to the nickel(II) in nonpolar solvents and in the solid state. The Dq^{xy} for (1,4,7,11)[14]aneN₄ is smaller, 1342 cm⁻¹, than for its isomer (1,4,8,11)[14]aneN₄ (cyclam), 1480 cm⁻¹. Spectral and pH data suggest that in aqueous solution (1,4,7,11)[14]aneN₄ is functioning as a tridentate ligand in the square-planar diamagnetic Ni(II)-(1,4,7,11)[14]aneN₄ complexes. In aqueous solution there is an equilibrium between the six-coordinate $[\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{H}_2\text{O})_2]^{2+}$ and the square-planar species. This equilibrium has been discussed in light of the tridentate nature of the square-planar species in solution.

Introduction

Extensive research has been done to determine the relationship between the size of saturated tetradentate macrocyclic ligands and their effect on the stereochemistry and the physical and chemical properties of their metal complexes.¹⁻⁴ The most detailed comparative studies have been made on derivatives of the 14-membered cyclic ring, [14]aneN₄ (I).³⁻¹² Organic groups have been substituted for hydrogens on the alkyl backbone⁷⁻¹⁰ or on the nitrogen atoms.^{9,11,12} However, there is a paucity of information on how the shape of the macrocycle affects the chemical and physical properties of metal complexes. Until recently all the metal complexes containing the [14]aneN₄ type ligands had alternating ethylene and trimethylene bridges between the nitrogen donors (I). However,



there are now several recent studies on metal complexes

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Table I. Conductivities of Various Nickel(II) Complexes

	Λ^a	solvent	electrolyte type
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$	246	H ₂ O	2:1
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$	82	CH ₃ OH	1:1
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$	0	CCl ₃ H	<i>b</i>
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{SCN})_2$	185	H ₂ O	2:1,1:1
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{SCN})_2$	46	CH ₃ OH	1:1
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{SCN})_2$	17	CH ₃ NO ₂	<i>b</i>
$\text{Ni}[(1,4,8,11)[14]\text{aneN}_4]\text{Cl}_2$	235	H ₂ O	2:1
$\text{Ni}[(1,4,8,11)[14]\text{aneN}_4]\text{Cl}_2$	106	CH ₃ OH	1:1
$\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{ClO}_4)_2$	240	H ₂ O	2:1
$\text{Ni}[(1,4,8,11)[14]\text{aneN}_4](\text{ClO}_4)_2$	179	H ₂ O	2:1

^a All concentrations = 1×10^{-3} M; units $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. ^b Non-electrolyte.

containing the unsymmetrical macrocyclic isomer, (1,4,7,11)[14]aneN₄ (isocyclam) (II).^{13,14} We have extended this research.

Results and Discussion

Characterization of Complexes. $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ and $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{NCS})_2$ were prepared by the addition of LiCl and LiSCN, respectively, to a warm solution of (1,4,7,11)[14]aneN₄ and $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$. Both complexes are purple in both the solid state and nonaqueous solutions. However, in an aqueous solution, these complexes appear orange. The $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4](\text{ClO}_4)_2$ was prepared in a manner similar to one reported by Sabatini and Fabbri.¹⁴

The molar conductivity of a 1×10^{-3} M aqueous solution of $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$, 238 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (Table I), is in the range of a 2:1 electrolyte¹⁵ and in methanol the molar conductivity of $\text{Ni}[(1,4,7,11)[14]\text{aneN}_4]\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$, 82 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, lies in the range of a 1:1 electrolyte.¹⁵

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