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

Acknowledgment. Thanks are expressed to Professor Luigi Sacconi for encouragement and to Professor Nuccio Bertazzi for recording the Mössbauer spectra.

Registry No. $K[Cu(en)_2][Fe(CN)_6]$, 72967-84-1; $K[Cu(en)_2]$-$[Co(CN)_6]$, 72967-83-0; $[Cu(N\text{-Et-en})_2]_3[Fe(CN)_6]_2$, 73036-60-9; $[Cu(N\text{-Pr-en})_2]_3[Fe(CN)_6]_2$, 72967-82-9; $[Cu(en)_2](ClO_4)_2$, 15444-88-9; $[Cu(N\text{-Et-en})_2](ClO_4)_2$, 73036-59-6; $[Cu(N\text{-Pr-en})_2](ClO_4)_2$, 72984-95-3; $K_3[Fe(CN)_6]$, 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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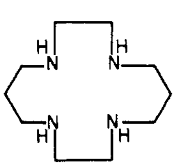
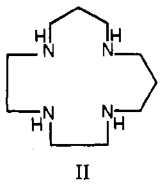
Nickel(II) complexes of 1,4,7,11-tetraazacyclotetradecane, (1,4,7,11)[14]aneN_4, have been prepared and characterized. Both Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$ and Ni[(1,4,7,11)[14]aneN_4]$(SCN)_2$ have been assigned a trans geometry on the basis of electronic and infrared spectral data. On 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]aneN_4 is smaller, 1342 cm^{-1}, than for its isomer (1,4,8,11)[14]aneN_4 (cyclam), 1480 cm^{-1}. Spectral and pH data suggest that in aqueous solution (1,4,7,11)[14]aneN_4 is functioning as a tridentate ligand in the square-planar diamagnetic Ni(II)–[(1,4,7,11)[14]aneN_4] complexes. In aqueous solution there is an equilibrium between the six-coordinate $[Ni[(1,4,7,11)[14]aneN_4](H_2O)_2]^{2+}$ 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]aneN_4 (I).[3-12] Organic groups have been substituted for hydrogens on the alkyl backbone[7-10] 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]aneN_4 type ligands had alternating ethylene and trimethylene bridges between the nitrogen donors (I). However, there are now several recent studies on metal complexes containing the unsymmetrical macrocyclic isomer, (1,4,7,11)[14]aneN_4 (isocyclam) (II).[13,14] We have extended this research.



I



II

Table I. Conductivities of Various Nickel(II) Complexes

	Λ^a	solvent	electrolyte type
Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$	246	H_2O	2:1
Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$	82	CH_3OH	1:1
Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$	0	CCl_3H	*b*
Ni[(1,4,7,11)[14]aneN_4]$(SCN)_2$	185	H_2O	2:1,1:1
Ni[(1,4,7,11)[14]aneN_4]$(SCN)_2$	46	CH_3OH	1:1
Ni[(1,4,7,11)[14]aneN_4]$(SCN)_2$	17	CH_3NO_2	*b*
Ni[(1,4,8,11)[14]aneN_4]Cl_2	235	H_2O	2:1
Ni[(1,4,8,11)[14]aneN_4]Cl_2	106	CH_3OH	1:1
Ni[(1,4,7,11)[14]aneN_4]$(ClO_4)_2$	240	H_2O	2:1
Ni[(1,4,8,11)[14]aneN_4]$(ClO_4)_2$	179	H_2O	2:1

[a] All concentrations = 1 × 10^{-3} M; units Ω^{-1} cm^2 mol^{-1}. [b] Nonelectrolyte.

Results and Discussion

Characterization of Complexes. Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$ and Ni[(1,4,7,11)[14]aneN_4]$(NCS)_2$ were prepared by the addition of LiCl and LiSCN, respectively, to a warm solution of (1,4,7,11)[14]aneN_4 and $Ni(C_2H_3O_2)_2\cdot4H_2O$. Both complexes are purple in both the solid state and nonaqueous solutions. However, in an aqueous solution, these complexes appear orange. The Ni[(1,4,7,11)[14]aneN_4]$(ClO_4)_2$ was prepared in a manner similar to one reported by Sabatini and Fabbrizzi.[14]

The molar conductivity of a 1 × 10^{-3} M aqueous solution of Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$, 238 Ω^{-1} cm^2 mol^{-1} (Table I), is in the range of a 2:1 electrolyte[15] and in methanol the molar conductivity of Ni[(1,4,7,11)[14]aneN_4]$Cl_2\cdot{}^1/_2H_2O$, 82 Ω^{-1} cm^2 mol^{-1}, lies in the range of a 1:1 electrolyte.[15]

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Table II. Electronic Spectral Data for Nickel(II) Complexes of (1,4,7,11)[14]aneN_4 and (1,4,8,11)[14]aneN_4

	λ, nm (ε)				
complex	solid[a]	CH_3OH	CH_3NO_2	H_2O	CCl_3H
Ni[(1,4,7,11)[14]aneN_4]$Cl_2 \cdot {}^1/_2H_2O$	352	356 (29)		340 (44)	359 (26)
	538	470 (47)		475 (60)	548 (14)
	725	690 (7)		710 (8)	725 (8)
				780 (8)	1260 (3.4)
Ni[(1,4,8,11)[14]aneN_4]Cl_2[3]	346			445 (46)	343 (30)
	525				526 (7)
	670				685 (4)
	1190				1185 (3)
Ni[(1,4,8,11)[14]aneN_4](NCS)$_2$[3]	320				
	503				
	920				
Ni[(1,4,7,11)[14]aneN_4](SCN)$_2$		530 (18)	390 (26)		325 (16)
		750 (9)	520 (12)	463 (52)	510 (10)
			728 sh (4)		803 (7)
			744 (4)		915 (10)
			798 (2)		
			956 (4)		

[a] At room temperature.

Table III. Comparison of Experimental and Calculated Spectral Band Positions[a]

	$^3B_{1g} \rightarrow {}^3E_g$	$^3B_{2g}$	$^3A_{2g}$	^3E_g	$^3A_{2g}$
Ni[(1,4,8,11)[14]aneN_4]Cl_2[3]	8 600	14 750	15 200	19 400	27 250 sh
b	8 656	14 793	15 162	19 337	27 359
Ni[(1,4,7,11)[14]aneN_4]Cl_2	8 264	13 333	12 987	18 652	28 169
b	8 263	13 333	13 124	18 695	28 414
Ni[(1,4,8,11)[14]aneN_4](NCS)$_2$[3]	11 080	14 150	17 800 sh	20 225	
b	11 030	14 104	17 849	20 279	30 561
Ni[(1,4,7,11)[14]aneN_4](NCS)$_2$	10 417	13 514	17 241 sh	19 417	28 926 sh
b	10 493	13 514	17 126	19 432	29 416

[a] Diffuse-reflectance spectra taken at 77 K. Spin-forbidden transitions not included. [b] Program-generated spectrum.

However, in $CHCl_3$ this complex appears to be a nonelectrolyte. Such data indicate that in aqueous solution both chlorides are not in the coordination sphere of nickel(II); however, in $CHCl_3$ they are both bonded to the nickel(II). The inference from the conductivity data in $CHCl_3$ is that the chlorides are also coordinated to the nickel(II) in the solid state. The conductivity data in methanol suggest that an average of only one chloride is coordinated to nickel(II). Plots of the equivalent conductance in methanol and H_2O vs. the $C_e{}^{1/2}$ resulted in curves. The conductivity of a 1×10^{-3} M aqueous solution of Ni[(1,4,7,11)[14]aneN_4](SCN)$_2$, 185 Ω^{-1} cm^2 mol^{-1}, lies between that of a 2:1 electrolyte and 1:1 electrolyte,[15] and in methanol the conductivity, 46 Ω^{-1} cm^2 mol^{-1}, is between a nonelectrolyte and a 1:1 electrolyte.[15] Again, plots of Λ_e vs. $C_e{}^{1/2}$ for all solutions of this complex resulted in curves. On the basis of the above results it appears that the two SCN^- groups are both coordinated to the nickel(II) in the solid state and are only partially ionized by polar solvents. The perchlorate salt is a 2:1 electrolyte in H_2O.

Elemental analyses suggest that water is present in Ni[(1,4,7,11)[14]aneN_4]$\cdot Cl_2 \cdot {}^1/_2H_2O$ and is confirmed by a broad absorption at 3375 cm^{-1} found in the infrared spectra taken in Nujol mull. The possibility of coordinated water is also ruled out by the absence of conductivity in $CHCl_3$.

The infrared spectrum of Ni[(1,4,7,11)[14]aneN_4]$Cl_2 \cdot {}^1/_2H_2O$ shows strong bands at 3240 and 3205 cm^{-1} while Ni[(1,4,7,11)[14]aneN_4](NCS)$_2$ exhibited three N–H stretching frequencies at 3280, 3200, and 3170 cm^{-1}. These bands are assigned to the N–H stretches of the coordinated ligand. More than one N–H stretch was expected since there are three different N–H bonds in the ligand. In obvious contrast only one N–H stretch was observed in the complex Ni[(1,4,8,11)[14]aneN_4]Cl_2.[10] All these N–H stretches are at lower energies than the corresponding bands for the free ligand. This is what is expected if all four nitrogens coordinated to the nickel(II).

In Ni[(1,4,7,11)[14]aneN_4](NCS)$_2$, the NCS^- is bonded to the nickel(II) via the nitrogen atom. This is indicated by strong sharp bands at 780, 480, and 490 cm^{-1} and 2075 and 2090 cm^{-1}.[16] However, two bands were not expected in the 480–490 cm^{-1} region and the 2075–2040 cm^{-1} region. Since the conductivity data indicated that both thiocyanates are coordinated to nickel, they must be coordinated in different environments. The configurations of the chelate rings in Ni[(1,4,7,11)[14]aneN_4](SCN)$_2$ are likely to make both sides of the NiN_4 plane have different environments.

The electronic spectra in $CHCl_3$ solution for Ni[(1,4,7,11)[14]aneN_4]$Cl_2 \cdot {}^1/_2H_2O$ and Ni[(1,4,7,11)[14]aneN_4](SCN)$_2$ is consistent with the expected spectra for a six-coordinated complex having approximately D_{4h} symmetry.[17,18] The spectra of Ni[(1,4,7,11)[14]aneN_4]$Cl_2 \cdot {}^1/_2H_2O$ in $CHCl_3$ and in the solid state are quite similar; however, the lowest energy band is not observed in the solid state at room temperature (Table II). The spectrum in water is different than the spectrum in $CHCl_3$, and in general the spectra observed in most solvents are different from each other. Such data suggest that the solid complex and the complex in $CHCl_3$ have identical ligands in the coordination sphere of the nickel(II) and have similar geometries, but in polar solvents the coordinated anions, Cl^- or SCN^-, are ionized by the solvent to various degrees. The conductivity data are consistent with the above model.

Sabatini and Fabbrizzi were able to obtain an estimate of Dq^{xy} value for (1,4,7,11)[14]aneN_4 from the electronic spectrum of Ni[(1,4,7,11)[14]aneN_4]Cl_2. However, to obtain a more accurate Dq^{xy} one must be able to assign the $^3B_{1g} \rightarrow {}^3B_{2g}$ transition. Making such an assignment requires having at least two complexes having D_{4h} symmetry and a stoi-

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Table IV. Spectrochemical Parameters for Metal Complexes Containing Cyclic Rings (cm^{-1})

	Dq^{xy}	$Dq^{z\ a}$	Dt	Ds	B
Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$	1480	379	629	981	831
Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2$	1333	504	474	1425	831
Ni[(1,4,8,11)[14]aneN$_4$]-(NCS)$_2$[3]	1418	876	310	620	860
Ni[(1,4,7,11)[14]aneN$_4$]-(NCS)$_2$	1351	800	315	600	900

[a] Dq^z calculated from $Dt = {}^4/_7(Dq^{xy} - Dq^z)$.

chiometry of the type [NiLX$_2$]$^{n+}$ (L is the macrocycle and X is the apical group). With the availability of such complexes one can readily assign the above transition, and the other transitions can be assigned in a manner similar to Rowley and Drago[19] and to Wentworth and Piper[20] (Table III). Using a weak field model and adjusting the Ds, Dt, and B parameters to a "best fit" and using Dq^{xy} obtained from the $^3B_{1g} \rightarrow {}^3B_{2g}$ band in the electronic spectrum,[18] we are able (Table IV) to obtain a program-generated spectrum which matched the observed spectrum of both complexes (Table III).

The Dq^{xy} for nickel(II) complexes containing the (1,4,7,11)[14]aneN$_4$ ligand is smaller, 1342 cm^{-1} (an average value), than for its isomer (1,4,8,11)[14]aneN$_4$, 1480 cm^{-1} (Table IV). This value for Dq^{xy} is somewhat smaller than the value estimated by Sabatini and Fabbrizi, 1370 cm^{-1}.[14] The smaller Dq^{xy} for (1,4,7,11)[14]aneN$_4$ compared to (1,4,8,11)[14]aneN$_4$ most likely originates from the decreased ligand field strength imposed by fusing two six-membered rings vs. fusing alternating five- and six-membered rings. Busch and co-workers suggested empirical rules that can predict the Dq^{xy} of any simple tetradentate macrocycle.[3] The important parameters included the ring size, the nature of the donor atoms, and organic steric groups on the ring. It appears from our data that the sequence of ring sizes also plays a role, although, not a large one.

As the macrocyclic ligand was varied, Dq^z was shown to increase as Dq^{xy} decreased (Table IV). A comparison of Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2\cdot{}^1/_2$H$_2$O with Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$ showed the expected inverse relationship between the Dq^{xy} and Dq^z. However, the two thiocyanate complexes do not obey this general rule. Busch and co-workers observed a similar linear relationship between Dq^{xy} and Dq^z upon comparing the (1,4,8,11)[14]aneN$_4$ and the [15]aneN$_4$ complexes.[3]

The Tridentate Nature of (1,4,7,11)[14]aneN$_4$. Conductivity and pH data strongly suggest that in aqueous solution (1,4,7,11)[14]aneN$_4$ in the Ni(II)–[(1,4,7,11)[14]aneN$_4$] complex is functioning as a tridentate ligand. Coordinating an amine to a metal ion such as nickel(II) should result in an increase in the amount of positive character of the hydrogen atom bonded to the nitrogen. As a consequence, an uncoordinated amine is basic in aqueous solution but an amine coordinated to a metal ion functions as a Brønsted acid in water. The pHs of an aqueous solution of both Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$ and Ni[(1,4,8,11)[14]aneN$_4$](ClO$_4$)$_2$ are less than the pH of water over a concentration range of 2×10^{-4} M to 2.4×10^{-3} M. (The perchlorate salt is slightly more acidic than the chloride salt.) However, aqueous solutions of Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2\cdot{}^1/_2$H$_2$O and Ni[(1,4,7,11)[14]aneN$_4$](ClO$_4$)$_2$ are more basic than water over the same concentration range. Also the pH of Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2\cdot{}^1/_2$H$_2$O dissolved in a 6 M NaClO$_4$ solution is greater than that of a 6 M NaClO$_4$ solution. Since in 6 M NaClO$_4$ only the square-planar complex exists, we assume that (1,4,7,11)[14]aneN$_4$ is functioning as a tridentate only in the square-planar form of these complexes. In contrast, Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$ dissolved in 6 M NaClO$_4$ is more acidic than a 6 M NaClO$_4$ solution. Such data indicate that the manner of coordination of (1,4,8,11)[14]aneN$_4$ and (1,4,7,11)[14]aneN$_4$ to nickel(II) in water are different.

The conductivity data also suggest that (1,4,7,11)[14]aneN$_4$ is not functioning as a tetradentate ligand in nickel(II) complexes in water. Over a concentration of $(2\text{–}30) \times 10^{-4}$ M, the conductivity at any concentration within this range for Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2\cdot{}^1/_2$H$_2$O and Ni[(1,4,7,11)[14]aneN$_4$](ClO$_4$)$_2$ is greater than that found for Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$ or Ni[(1,4,8,11)[14]aneN$_4$](ClO$_4$)$_2$. The higher conductivity for the (1,4,7,11)[14]aneN$_4$ is expected due to the hydrolysis of the uncoordinated amine producing additional ions.

Even in the solid state it is likely that (1,4,7,11)[14]aneN$_4$ forms nonequivalent nickel-to-nitrogen bonds. The Dq^{xy} value for (1,4,7,11)[14]aneN$_4$ is between that of (1,4,8,11)[14]aneN$_4$ and [15]aneN$_4$.[3] The larger [15]aneN$_4$ is believed to be a "better fit" for nickel(II) than the smaller macrocycle (1,4,8,11)[14]aneN$_4$. This "best fit" suggests the macrocycle [15]aneN$_4$ will result in the least amount of stereoconstrictive effects or stereodilative effects, thereby not resulting in the formation of abnormally short or long nickel(II) to nitrogen bonds, respectively. As a result it was concluded that the strain energy of the [15]aneN$_4$ is similar to that of a saturated linear tetradentate that does not have the constraints of a cyclic ligand.[3,4] On the basis of models it is difficult to rationalize that the size of the hole of (1,4,7,11)[14]aneN$_4$ is closer to that of the [15]aneN$_4$ than (1,4,8,11)[14]aneN$_4$. Therefore we conclude that (1,4,7,11)[14]aneN$_4$ forms nonequivalent bonds to nickel(II). In doing so the (1,4,7,11)[14]aneN$_4$ reduces the constrictive type strain resulting from use of a relatively small cyclic ligand by functioning as a semitetradentate ligand. The net effect of a cyclic tetradentate ligand functioning as a semitetradentate is that the "multiple justapositional fixedness"[21] of a cyclic ligand becomes less operative and the cyclic ligand now affects the metal ion in a similar manner to that of an unstrained linear polydentate. In contrast the symmetric ligand (1,4,8,11)[14]aneN$_4$ cannot reduce the constrictive strain in this manner.

Finally, we have some indication that (1,4,7,11)[14]aneN$_4$ can function as a tridentate ligand in the solid state. We have isolated the complex Co[(1,4,7,11)[14]aneN$_4$H]Cl$_4\cdot$H$_2$O.[22] Analytical and infrared spectral data indicate that one amine is protonated and the other three amines are coordinated to the cobalt(III). Since Co(III) is smaller than nickel(II), we conclude that the cobalt(III) is not able to coordinate to all four nitrogens in (1,4,7,11)[14]aneN$_4$, and as a result, the (1,4,7,11)[14]aneN$_4$ functions as a tridentate ligand. However upon coordination to the larger nickel(II) in a six-coordinate environment, the (1,4,7,11)[14]aneN$_4$ functions as a semitetradentate ligand. The nickel(II) ion in a square-planar environment is smaller than in an octahedral environment, and as a result, the (1,4,7,11)[14]aneN$_4$ functions as a tridentate ligand in a similar manner as it does with cobalt(III).

We conclude that if indeed the (1,4,7,11)[14]aneN$_4$ is functioning as a tridentate ligand in water, the [15]aneN$_4$ might also function in a similar manner. The electronic spectra at 77 K in the solid state for [15]aneN$_4$– and (1,4,7,11)-[14]aneN$_4$–Ni(II) complexes are similar.[3] The pH of the Ni([15]aneN$_4$)Cl$_2$ in H$_2$O is greater than that of pure water over a large concentration range. Kodama and Kimura[23] have shown that the Cu([15]aneN$_4$)$^{2+}$ protonates readily. They claimed that the two adjacent six-membered rings result in

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Table V. Magnetic Moments[a]

	μ_{eff}, μ_B	solvent
$Ni[(1,4,7,11)[14]aneN_4]Cl_2 \cdot {}^1/_2H_2O$	2.78	solid
$Ni[(1,4,7,11)[14]aneN_4]Cl_2 \cdot {}^1/_2H_2O$	3.09	$CHCl_3$
$Ni[(1,4,7,11)[14]aneN_4]Cl_2 \cdot {}^1/_2H_2O$	2.41	H_2O + 2% butyl alcohol
$Ni[(1,4,8,11)[14]aneN_4]Cl_2$[10]	3.09	solid
$Ni[(1,4,8,11)[14]aneN_4]Cl_2$	2.41	5% dioxane
$Ni[(1,4,8,11)[14]aneN_4]Cl_2$	2.35	0.1 $NaClO_4$ + 2% *tert*-butyl alcohol

[a] At room temperature.

Table VI. Thermodynamic Functions for Octahedral to Square-Planar Conversion of Nickel(II) Complexes at 25 °C

ligand	solvent	k_{eq}	$\Delta H°$, kcal/mol	$\Delta S°$, cal deg^{-1} mol^{-1}
$(1,4,7,11)[14]aneN_4$	H_2O	1.04	5.06	17
$(1,4,7,11)[14]aneN_4$	0.100 N $NaClO_4$	1.85	4.98	18
$(1,4,7,11)[14]aneN_4$	5% dioxane + H_2O	0.58	3.14	9.5
$(1,4,8,11)[14]aneN_4$[13]	0.1 N $NaClO_4$	2.45	5.4	20
2,3,2-tet[13]	0.1 N $NaClO_4$	0.29	3.4	9
3,2,3-tet[13]	0.1 N $NaClO_4$	0.08	4.4	15

a weaker nitrogen to copper bond, and as a consequence of this, a lone pair on the nitrogen becomes available for protonation. An X-ray study done by Fabbrizzi, Mealli, and Paoletti[24] on $[Cu([15]aneN_4](ClO_4)_2$ showed that the copper formed four nonequivalent bonds with the nitrogens. However, for full resolution of this issue, a crystal structure of several of the nickel(II) complexes must be done.

Equilibrium between the Square-Planar and Six-Coordinate Nickel(II). The magnetic moments of $Ni[(1,4,7,11)[14]aneN_4]Cl_2 \cdot {}^1/_2H_2O$ were obtained in the solid state by the Gouy method and in solution by the Evans method (Table V).[25] In the solid state and in $CHCl_3$ the moments are consistent with octahedral nickel(II) complexes. However, the magnetic moment of $[Ni[(1,4,7,11)[14]aneN_4]Cl_2] \cdot {}^1/_2H_2O$ in aqueous solution is 2.41 μ_B. This low magnetic moment in water is attributed to the equilibrium between the paramagnetic six-coordinate compound and a diamagnetic square-planar compound.

Like Sabatini and Fabbrizzi[14] we also observed a six-coordinate square-planar equilibrium by use of spectral data and obtained similar $\Delta H°$ and $\Delta S°$ values for the above equilibrium in a 0.1 M $NaClO_4$ solution (Table VI). The difference in our data and Sabatini and Fabbrizzi's data is probably due to our use of the chloride salt while Sabatini and Fabrizzi used the perchlorate salt. Preliminary data indicate that both $NaClO_4$ and NaCl shift the equilibrium toward the square-planar species, although to a different extent. Therefore, the nature of anion influences the magnitude of the equilibrium constant. However, it is unlikely that the chloride anions coordinate to the nickel ion in aqueous solution. This conclusion is based on (a) the similar ΔH and ΔS values obtained for both the chloride and the perchlorate salts of the Ni(II)–$(1,4,7,11)[14]aneN_4$ complexes, (b) the isosbestic point observed on the temperature-dependent spectra (in 0.1 N $NaClO_4$) that indicates that only two species are in solution, (c) similar spectra that were observed in water for both the chloride and perchlorate salts and the addition of 6 M NaCl that did not cause any shift in the band maximum, and (d) the chloride salt that is a 2:1 electrolyte in H_2O. On the basis of above data it is concluded that the six-coordinate species is the *trans*-$[Ni[(1,4,7,11)[14]aneN_4](H_2O)_2]^{2+}$; however, the exact nature of the square-planar species is not obvious.

Since some of the data in Table VI have been interpreted by Sabatini and Fabbrizzi[14] on assumption that in water $(1,4,7,11)[14]aneN_4$ is functioning as a tetradentate ligand in the square-planar nickel(II) species, it is necessary to discuss the equilibrium data in light of our above results. Most of the equilibrium constants in Table VI can be explained on the basis of the potential hydrophobic nature of the square-planar cation, NiL^{2+}. The more carbons on the tetradentate ligand the larger the K_{eq} (more square-planar complex) and the larger ΔS (more disorder in the solvent). Also the strength of the metal–ligand bond should play a role in determining the magnitude of the K_{eq}. The stronger ligand should favor the square-planar complex. For example since Dq^{xy} for the $[13]aneN_4$ is larger than the $(1,4,8,11)[14]aneN_4$, only the square planar form of $Ni([13]aneN_4)^{2+}$ has been isolated from H_2O. Since the Dq^{xy} for $(1,4,8,11)[14]aneN_4$ is larger than for the $(1,4,7,11)$-$[14]aneN_4$, we can assume that the former ligand will stabilize the square-planar geometry to a greater extent than the latter complex. Also since $(1,4,7,11)[14]aneN_4$ is functioning as a tridentate ligand in the square-planar cation, the free amine will protonate in H_2O. The result of increasing the charge on the cation from 2+ to 3+, $[Ni[(1,4,7,11)[14]aneN_4H](H_2O)]^{3+}$, should also make the cation less hydrophobic than the symmetrical $Ni[(1,4,8,11)[14]aneN_4]^{2+}$, and as a result, we would expect a lower K_{eq} and smaller ΔS.

The greater the thermodynamic stability of the square-planar form compared to the six-coordinate compound, the less endothermic will be the ΔH of reaction and the larger the K_{eq}. Because cyclic ligands have more constraints on them than a linear ligand, they have less ability to alter bond angles and bond lengths. As a result, a coordinated cyclic ligand will not be as able to alter its donor atom to metal atom bond lengths to accommodate a square-planar environment around the metal ion as readily as a linear tetradentate ligand. A possible explanation for why the ΔH is less positive for the reaction of $Ni[(1,4,7,11)[14]aneN_4](H_2O)_2^{2+} \rightleftharpoons$ square-planar species + $2H_2O$, than for the reaction $Ni[(1,4,8,11)[14]aneN_4](H_2O)_2^{2+} \rightleftharpoons$ square-planar species + $2H_2O$ is because the unsymmetrical $(1,4,7,11)[14]aneN_4$ has more opportunity to readjust bond lengths and angles to accommodate an unstrained square-planar form of nickel(II) than the more symmetrical $(1,4,8,11)[14]aneN_4$. This is especially true if the $(1,4,7,11)[14]aneN_4$ is functioning as a tridentate ligand in the square-planar species.

The equilibrium between the six-coordinate species and the square-planar species is markedly affected by the nature of this solvent medium. The greater the concentration of $NaClO_4$ or NaCl the more the equilibrium is driven to the square-planar cation (larger K_{eq}) and to smaller ΔH and the larger the ΔS (Table VI). Dioxane has the opposite effect on the ΔS and K_{eq}; i.e., it reduces the K_{eq} and decreases ΔS. If the hydrophobic square-planar cation is structuring the waters (making stronger and more hydrogen bonds), the dioxane should have the opposite effect, i.e., to make the water more monomeric. The less structured the water, the greater its ability to coordinate to $Ni[(1,4,7,11)[14]aneN_4H](H_2O)^{3+}$ and to form the six-coordinate species. The net effect is to reduce the ΔS and K_{eq}. However, the ClO_4^- and Cl^- anion should have a similar affect on the hydrogen bonding in the bulk solvent as the dioxane.[26] However, the anions may selectively interact with the square-planar ion. Selective ion pairing to the square-planar complex is supported by the fact that only

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(25) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(26) J. E. Gorden, "The Organic Chemistry of Electrolyte Solutions", Wiley, New York, 1975, p 182.

the square-planar complex Ni[(1,4,8,11)[14]aneN$_4$](ClO$_4$)$_2$ can be isolated from the six-coordinate square-planar equilibrium in water.

Experimental Section

Materials. (1,4,7,11)[14]aneN$_4$,[22] Ni[(1,4,7,11)[14]aneN$_4$](ClO$_4$)$_2$,[14] and Ni[(1,4,8,11)[14]aneN$_4$](ClO$_4$)$_2$[10] were made according to standard procedures.

Synthesis of Dichloro(1,4,7,11-tetraazacyclotetradecane)nickel(II) Hemihydrate. To a solution of 0.50 g (0.0025 mol) of (1,4,7,11)-[14]aneN$_4$[22] in 50 mL of methanol was added 0.62 g of nickel acetate tetrahydrate. The violet mixture was warmed on a steam bath for 15 min. An excess of LiCl, 0.3 g (0.0071 mol), was added and the warming continued for 10 min. The product was rotoevaporated to dryness to yield a purple solid. The solid was dissolved in a minimum amount of chloroform, and the solution was filtered and evaporated to dryness. This product was then recrystallized from warm acetonitrile; yield 0.71 g (84%). Anal. Calcd for $\mathrm{Ni(C_{10}H_{24}N_4)Cl_2\cdot{}^1/_2H_2O}$: C, 35.44; H, 7.43; N, 16.53. Found: C, 35.56; H, 7.30; N, 16.33.

Synthesis of (Diisothiocyanato)(1,4,7,11-tetraazacyclotetradecane)nickel(II). To 50 mL of water in a 100-mL round-bottom flask was added 0.25 g (0.0012 mol) of (1,4,7,11)[14]aneN$_4$. After the ligand was dissolved, 0.31 g (0.0012 mol) of nickel acetate tetrahydrate was added. The solution was heated on a steam bath for 15 min, during this time the solution changed from light green to dark blue. An excess, 0.29 g (0.003 mol), of LiSCN was added, and a lavender precipitate formed. The product was centrifuged from the suspension and recrystallized from a minimum amount of hot water; yield 0.25 g (53%). Anal. Calcd for $\mathrm{Ni(C_{10}H_{24}N_4)(NCS)_2}$: C, 38.41; H, 6.45; N, 22.40. Found: C, 38.48; H, 6.60; N, 22.32.

Physical Measurements. Conductance measurements were made by using an American Instrument Co. Model 5-2050 conductivity bridge in conjunction with a Beckman Model C1-BB1 conductivity cell. The cell constant was 1.00/cm. Solvents used for making measurements were water, methanol, acetonitrile, and nitromethane. The mass susceptibility was determined by the Evans method by using a Varian A-60 NMR with coaxial NMR tubes. The solvent was water with 2% *tert*-butyl alcohol as the reference. The complex dissolved in solvent was placed in the outer tube, and solvent alone was placed in the inner tube. Concentrations of 4.15–18.93 mg/mL were used depending on the magnitude of the magnetic moment. Diamagnetic corrections were made by using Pascals' constants. A Perkin-Elmer Model 337 spectrophotometer was used to record all infrared spectra. The spectra of complexes were obtained on both Nujol mulls and KBr pressed pellets. The spectra were calibrated by using polystyrene. A Beckman Acta MIV UV–visible near-IR spectrophotometer with 1-cm and 10-cm matched cells was used to obtain visible and near-infrared spectra. The visible spectra of solids were measured in Nujol mulls. The mull was placed on Sharkskin filter paper in the sample beam, and a similar piece of filter paper with Nujol was placed in the reference beam. The electronic spectra were taken at 77 K with a Cary 14 using Nujol mulls at the University of Toledo. Equilibrium constants were calculated from spectra data obtained on a Beckman Acta MIV UV–visible near-IR spectrophotometer. The data were obtained at 470 nm. The 0.1 M NaClO$_4$ was obtained by titrating 1 M HClO$_4$ against a standard NaOH solution and then diluting. The temperature was controlled by using a Haake Model FK thermostated water bath.

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Registry No. Ni[(1,4,7,11)[14]aneN$_4$]Cl$_2$, 72765-27-6; Ni[(1,4,7,11)[14]aneN$_4$](SCN)$_2$, 72893-71-1; Ni[(1,4,8,11)[14]aneN$_4$]Cl$_2$, 15333-47-8; Ni[(1,4,8,11)[14]aneN$_4$](ClO$_4$)$_2$, 15220-72-1; Ni[(1,4,7,11)[14]aneN$_4$](OH$_2$)$_2^{2+}$, 68317-92-0; Ni[(1,4,7,11)[14]aneN$_4$H](OH$_2$)$^{3+}$, 72893-72-2; Ni[(1,4,7,11)[14]aneN$_4$](ClO$_4$)$_2$, 68344-01-4.

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Preparation and Characterization of a Volatile Uranyl Compound, Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)dioxouranium–Tetrahydrofuran

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A volatile uranyl compound $\mathrm{UO_2[(CF_3CO)_2CH]_2\cdot THF}$ with a vapor pressure of 0.7 torr at 100 °C has been prepared. The compound has high thermal stability and is suitable for studies of laser-induced isotope separation. The compound has been characterized by its IR, UV, NMR, fluorescence, and mass spectra and other physical and chemical properties including an X-ray structural determination. The molecule contains a linear uranyl ion equatorially surrounded by a pentagon of oxygen atoms. The chelating anions are tilted slightly in a boatlike configuration from this plane. The crystals are monoclinic, $P2_{1/c}$, with $a = 8.540$ (3) Å, $b = 9.110$ (4) Å, $c = 28.884$ (11) Å, $\beta = 94.26$ (3)°, and $Z = 4$.

Introduction

Recently we reported on an unusually efficient multiple photon CO$_2$ laser driven unimolecular decomposition of a volatile uranyl compound, $\mathrm{UO_2[(CF_3CO)_2CH]_2\cdot THF}$.[1] A key facet of this work was the synthesis of a sufficiently volatile compound. In this report we will discuss its preparation and characterization.

The objective of the synthetic work was to prepare a uranyl compound with a vapor pressure of about 0.1 torr or greater at a temperature below 150 °C. To be suitable for isotope separation studies with a CO$_2$ laser, it must have an asymmetric UO$_2^{2+}$ stretch in roughly the 900–1100-cm^{-1} region that is spectrally isolated from other vibrations of the molecule. At the inception of this work the volatility requirement seemed particularly difficult to attain because of the low vapor pressure of existing uranyl compounds. The THF complex of uranyl hexafluoroacetylacetonate is an unexpectedly volatile and stable complex, which, however, meets these requirements.

A literature search revealed limited vapor pressure data for uranyl compounds. Schlesinger et al.[3] found that the uranyl β-diketonate prepared with 1,1,1-trifluoro-2,4-pentanedione

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