sodium salts with strongly coordinating anions were tried. We are continuing our efforts to prepare species with coordinated anions since some of these complexes should have interesting five-coordinate geometries with five different donor groups.

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Registry No. Ni(ad)PF$_6$, 50601-07-5; Ni(ad)I, 50601-06-4; Ni(tad)PF$_6$, 50600-69-6; Ni(tad)I, 50600-70-9; Cu(ad)PF$_6$, 50600-72-1; Cu(ad)I, 50600-73-2; Cu(tad)PF$_6$, 50600-75-4; Cu(tad)I, 50600-76-5.

Notes

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Structural Assignments of Some Nickel(II) Complexes Containing Macrocyclic Ligands Derived from Benzilmonohydrazone

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Condensation reactions between amines and nickel(II) complexes containing tetradentate ligands with an N_2O_2 donor set derived from benzilmonohydrazone[1] have recently been described.[2] With ethylenediamine and 1,2-propanediamine, low-spin square-planar nickel(II) complexes containing macrocyclic ligands were obtained. Although the ligand structures were established unequivocally, the mode of coordination of the ligands to nickel(II) was assumed and the stereochemistry of the new chelate rings within the macrocycles was not established.

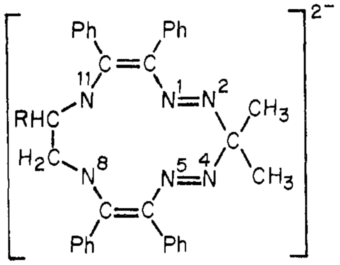
This note reports a study of the proton magnetic resonance spectra of these complexes and circular dichroism spectra of the macrocyclic complex obtained from (–)-1,2-propanediamine. The data obtained has enabled detailed structural assignments to be made for the complexes.

Experimental Section

3,3-Dimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenatonickel(II), (NiHcyclo13),[3] and 3,3,9-trimethyl-6,7,12,13-tetraphenyl-1,2,4,5,8,11-hexaazacyclotrideca-1,4,6,12-tetraenatonickel(II), (NiMcyclo13),[3] were prepared as previously reported[2] from α,α'''-[isopropylidenebis(azo)]di-α-stilbenolatonickel(II), NiMMK,[1,3] and ethylenediamine or 1,2-propanediamine, respectively. *R*-(–)-1,2-Propanediamine was kindly supplied by Professor F. L. Urbach of Case Western Reserve University for the synthesis of (–)-NiMcyclo13. Proton magnetic resonance spectra were obtained using a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal standard. Circular dichroism spectra for (–)-NiMcyclo13 were obtained by Professor F. L. Urbach using techniques previously described.[4]

Results and Discussion

The proton magnetic resonance spectrum of NiHcyclo13, a nickel(II) complex containing the ligand Ia, R = H, is recorded in Table I. Resonances are observed in three distinct regions of the spectrum, each of which may be correlated with protons of the ligand. The singlet (relative intensity 6) at 1.74 ppm is assigned to the hydrogens of the geminal methyls attached to the carbon bridging N^2 and N^4. This is in a similar position to the geminal methyl hydrogens of the parent compound NiMMK[1] from which NiHcyclo13 is derived. The methyl groups are thus in equivalent positions, located above and below the plane of the macrocyclic ligand in the complex. The multiplet centered at about 7.14 ppm is assigned to the hydrogens of the phenyl groups, again in a position similar to those in NiMMK.



I

The most informative region of the spectrum from a structural viewpoint is that between 3 and 4 ppm. In this region, a complex, but symmetrical, pattern is observed (Figure 1, upper spectrum) with integrated relative intensity 4. This absorption is thus due to the protons of the dimethylene chain. The observed pattern may be simulated[5] (Figure 1, lower spectrum) by assuming an A_2B_2 system for these protons. Thus, within the dimethylene chain, there are two sets A and B of equivalent hydrogens, with $n_A = n_B = 2$. Such a system may be described by two parameters only, the coupling constant between the nonequivalent protons, J_{AB}, and δ, the chemical shift difference.[6] For NiHcyclo13, $J_{AB} = 6.5$ Hz and $\delta = 32$ Hz. The value of J_{AB} suggests vicinal coupling between the nonequivalent protons.[7] The spectrum does not change either on increasing the temperature to 80° in bromoform (decomposition takes place above this temperature) or decreasing the temperature to –40° in deuteriochloroform.

The macrocyclic ligand I has six potential donor nitrogen atoms, although the magnetic properties and visible spectrum of the nickel(II) complex suggest it coordinates by four nitrogens in a square planar manner.[2] Three modes of coordination are possible depending on which donor atoms are involved: (a) N^1, N^5, N^8, and N^{11}; (b) N^1, N^4, N^8, and N^{11} (or its equivalent N^2, N^5, N^8, and N^{11}); (c) N^2, N^4, N^8, and N^{11}. Possibilities a and c cause the dimethylene carbons to be equivalent, but this is not the case for possibility b. A

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[1] C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 11, 726 (1972).

[2] C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 12, 2410 (1973).

[3] The abbreviations used in this paper are the same as those used in ref 1 and 2.

[4] R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, 91, 5977 (1969).

[5] Simulation achieved using NMRCAL, a Nuclear Magnetic Resonance Spectrum Calculation Program, Nicolet Instrument Corp., 1971.

[6] P. L. Corio, *Chem. Rev.*, 60, 363 (1960); "Structure of High Resolution NMR Spectra," Academic Press, New York, N. Y., 1966, p 235.

[7] J. S. Waugh, Ed., *Advan. Magn. Resonance*, 1, 195 (1965).

Table I. Proton Magnetic Resonance Spectra for the Complexes[a]

Compd	δ, ppm[b]	Type	Rel inten	Assignment
NiHcyclo13	1.74	Singlet	6	CH_3-[c]
	3.46[d]	"Triplet	4	$-CH_2CH_2-$
	3.78[d]	components"		
	~7.14[d]	Multiplet	~20	C_6H_5-
NiMcyclo13	0.96[d]	Doublet ($J = 6.5$ Hz)	3	CH_3-[e]
	1.67	Singlet	3	CH_3-[c]
	1.79	Singlet	3	CH_3-[c]
	3.31	Doublet ($J = 13$ Hz)	1	H_a[f]
	~3.95[d]	Multiplet	2	H_b and H_c[f]
	~7.20[d]	Multiplet	~20	C_6H_5-

[a] 100-MHz spectra obtained in $CDCl_3$ at ambient temperature.
[b] Chemical shift in parts per million downfield from an internal TMS standard. [c] Geminal methyl groups. [d] Centers of complex patterns. [e] Methyl group from 1,2-propanediamine residue. [f] Hydrogens from 1,2-propanediamine residue.

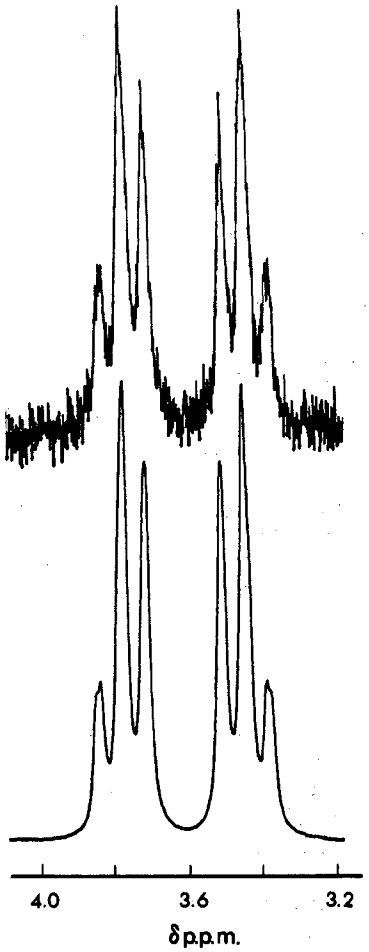
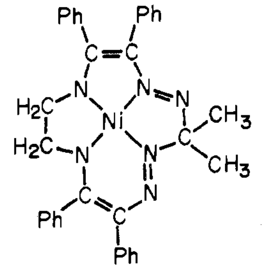


Figure 1. Proton magnetic resonance spectrum for NiHcyclo13 between 3.2 and 4.0 ppm. Upper curve experimental. Lower curve computer simulated.

singlet resonance corresponding to an A_4 pattern is expected for a and c, if rapid flexing of the dimethylene chain takes place, or a more complex A_2B_2 pattern, with J_{AB} corresponding to coupling between geminal hydrogens, if a rigid, staggered conformation is adopted. A variety of nickel(II) complexes containing both macrocyclic and noncyclic ligands with dimethylene chains containing equivalent carbon atoms have been shown to exhibit a singlet resonance for the methylene protons,[8-12] suggesting that rapid flexing of these chains takes place. For b, an A_2B_2 pattern, with J_{AB} corresponding to vicinal coupling between the nonequivalent hydrogens, is expected if rapid flexing is taking place or a complex ABCD pattern for a rigid, staggered conformation.

The observed temperature-independent A_2B_2 pattern for the hydrogens of the dimethylene chain, with $J_{AB} = 6.5$ Hz, suggests that the carbon atoms are nonequivalent and thus we conclude that the ligand is coordinated to the nickel(II) ion in mode b, as in II. It is further concluded that rapid

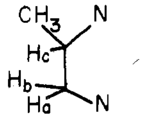


II

flexing of the dimethylene chain is taking place, at least in solution, over the temperature range studied.

The proton magnetic resonance spectrum of NiMcyclo13 containing the ligand Ib, R = Me, is recorded in Table II and shown partly in Figure 2, the multiplet assigned to the phenyl hydrogens centered at ~7.20 ppm being omitted. The macrocyclic ligand Ib is similar to Ia and similar regions of resonance are observed for the nickel(II) complexes containing these two ligands. However, there are significant differences between the spectra and these may be used to provide structural information for NiMcyclo13.

First, the geminal methyls are observed as two singlets, each of relative intensity 3 with a separation of 12 Hz in the 100-MHz spectrum. This separation decreases (to 7 Hz) in the 60-MHz spectrum, indicating that these methyl groups are in different chemical environments in NiMcyclo13. Magnetic anisotropy due to the nickel(II) ion[11] is not thought to be the cause of the nonequivalence, since the geminal methyls are equivalent in NiHcyclo13 and in similar nickel(II) complexes derived from some butanedione monohydrazones.[13] The remaining peaks in the spectrum are associated with the 1,2-propanediamine residue of the macrocyclic ligand.



The doublet centered at 0.96 ppm (relative intensity 3) is assigned to the methyl group of this residue, the resonance being split by H_c ($J = 6.5$ Hz). The location, at higher field than the geminal methyls, suggests it is shielded by its position close to a phenyl ring of the macrocycle. The methine and methylene protons comprise a complex region of absorption between 3.0 and 4.2 ppm, consisting of a doublet centered at 3.31 ppm (relative intensity 1) and a multiplet at ~3.95 ppm (relative intensity 2). Spin decoupling experiments have enabled assignments to be made for these hydro-

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(13) G. A. Melson and D. B. Bonfoey, *Inorg. Nucl. Chem. Lett.*, 9, 875 (1973).

Table II. Circular Dichroism Spectra for (–)-NiMcyclo13

Solvent	$\bar{\nu}$, cm^{-1} ($\Delta\epsilon$)
Chloroform	17,250 (–0.2); 20,400 (1.1); 23,870 (–0.50); 28,500 (6.3); 31,500 sh (1.3); 32,900 (–0.70); 36,750 (5.0)
Pyridine	17,750 (–0.4); 20,750 (1.0); 23,900 (–0.5); 28,500 (7.3); 32,000 (–0.70)

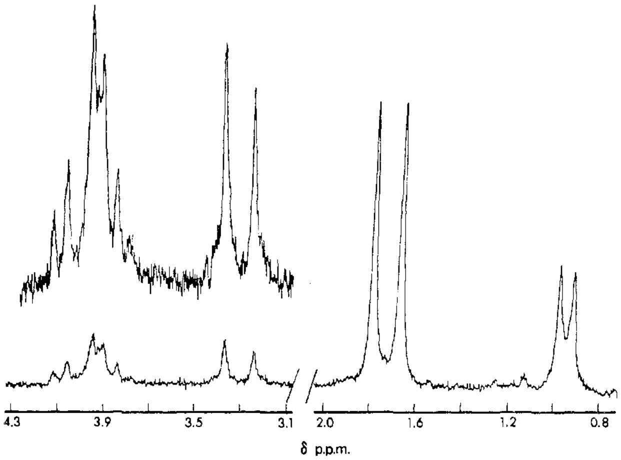

Figure 2. Proton magnetic resonance spectrum for NiMcyclo13 between 0.8 and 4.3 ppm.

gens. Irradiation at 3.93 ppm causes the doublet at 0.96 ppm assigned to the CH_3 group to collapse to a singlet but leaves the doublet at 3.31 ppm unchanged. Thus, part of the multiplet centered at 3.93 ppm is assigned to H_c. Decoupling of the CH_3 resonance is expected to produce an ABC system from H_a, H_b, and H_c. Irradiation at 0.96 ppm simplifies the multiplet although resolution into individual components is not achieved. The doublet at 3.31 ppm remains unchanged. This doublet must correspond to either H_a or H_b with $J_{ab} = 12.5$ Hz, corresponding to the geminal pair of hydrogens. Irradiation at 3.96 ppm converts this doublet into a singlet. If we assign H_a to the resonance at 3.31 ppm, then H_b is at 3.96 ppm, *i.e.*, it is part of the multiplet with H_c. Since no further splitting of the doublet assigned to H_a is observed, $J_{ac} \sim 0$ Hz and thus H_a and H_c must be in similar environments. Irradiation at 3.31 ppm again simplifies the multiplet, but resolution still is not achieved. Since signals for both methylene and methine protons are observed, rapid flexing of the ring does not take place in this ligand, and a fixed conformation is adopted.

There are two possible conformations for the chelate ring containing the propanediamine residue, corresponding to an axial or an equatorial orientation for the CH_3 group. These orientations correspond to δ-gauche and λ-gauche ring conformations, respectively.[14] With the CH_3 in an axial position, one side of the macrocyclic ligand is different from the other. Since the geminal methyls are nonequivalent in NiMcyclo13, the CH_3 group of the propanediamine ring is placed in an axial position. An equatorial location would not be expected to have much influence on the geminal methyl groups. It thus follows that H_c and H_a must be equatorial, H_b axial, and the ring conformation δ-gauche. Further evidence in support of this conformation is obtained from studies on the complex obtained from *R*-(–)-propanediamine. The proton magnetic resonance spectrum of this compound is identical with that obtained from the racemic diamine. Thus, the conformation of the ring is the same for both the optically active and the racemic products. Circular dichroism (CD) spectra of (–)-NiMcyclo13 are recorded in Table II and shown in Figure 3 together with the absorption spectrum in chloroform. The CD spectrum for (–)-NiMcyclo13 is very similar to those found for some complexes containing tetradentate Schiff base ligands derived from *R*-(–)-propanediamine.[4,15] It has been concluded that these latter complexes have a δ-gauche conformation for the propanediamine ring with the methyl group in an axial position. We conclude, therefore, that a similar conformation is present in both the optically active and racemic NiMcyclo13 complexes. Models indicate that in this conformation there is little steric interaction between the methyl group and the closest phenyl group of the ligand. In the equatorial position, however, considerable interaction is apparent. Presumably the δ-gauche conformation is adopted over the λ-gauche to minimize the steric interaction. In this axial position, the methyl group is located over and is thus shielded by the phenyl ring. The high-field location for the doublet (0.96 ppm) assigned to this methyl group is further indication of its axial position.

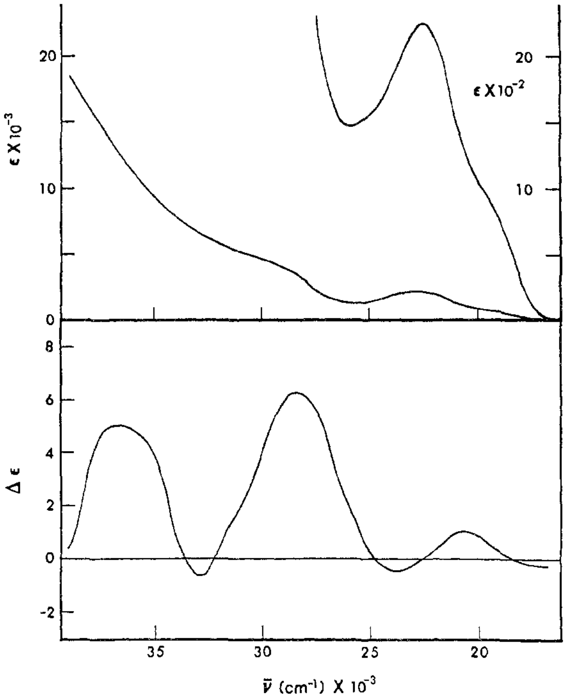

Figure 3. Absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) for (–)-NiMcyclo13 in $CHCl_3$.

Finally, since the proton magnetic resonance spectrum is temperature independent (up to 80°), the conformational lability of the propanediamine backbone is considerably less than that of the dimethylene chain in NiHcyclo13, presumably due to the steric effect of the methyl group.

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Registry No. NiHcyclo13, 50306-62-2; NiMcyclo13, 50306-63-3; (–)-NiMcyclo13, 50306-64-4.

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(14) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, 42, 3184 (1969).

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