Nickel(II) Complexes of Cyclic Tetradentate Thioethers

William Rosen and Daryle H. Busch

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received February 24, 1969*

Abstract: Three tetradentate ligands, 1,4,8,11-tetrathiacyclotetradecane (TTP), 2,5,9,12-tetrathiatridecane (TTT), and 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane (TTX), have been prepared. The nickel(II) tetrafluoroborate complexes of these ligands are the first low-spin nickel(II) species reported having four thioethers as donors. $Ni(TTP)^{2+}$ and $Ni(TTX)^{2+}$ constitute the first reported complexes of tetradentate macrocyclic ligands containing only sulfur donor atoms. Tetragonal $Ni(TTP)X_2$ species, where X = NCS, Cl, Br, and I, have been prepared and their electronic spectra used to calculate a Dq^{xy} of 1070 cm^{-1} for the macrocycle. The $Ni(TTP)I_2$ complex exhibits behavior in nitromethane solution which is best interpreted as involving two consecutive ionization equilibria. The predominant species is low-spin, five-coordinate $Ni(TTP)I^+$.

The occurrence of sulfur as a donor atom for transition metals is a well-known phenomenon.[1] It acts as a very good ligating atom when in the form of the sulfide ion (S^{2-}) or as a mercaptide ion (RS^-), but complexes of sulfur as a thioether (RSR) are much less abundant.[1,2-5] When nickel(II) is the central metal atom, thioether chelates are quite unstable toward displacement by good class a ligands (like H_2O) despite the fact that the thioethers prove to have spectrochemical field strengths that are "fairly strong"[5] or "almost as strong as ammonia."[3]

In this paper we report the synthesis and properties of nickel(II) complexes of some tetradentate ligands having thioethers as the exclusive donors. These new materials include the first low-spin nickel(II) complexes having four thioethers as the donors, and a number of tetragonal complexes formed from one of these low-spin complexes by coordination of various axial ligands. The useful synthetic method which makes these complexes readily available is also discussed.

Experimental Section

All chemicals used in this work were either prepared by the following procedures or were commercially available from outlets mentioned in the body of this section. The nitromethane used was spectrograde from Eastman Organic Chemicals which had been purified by known procedures.[6] All nmr spectra were run on a Varian A-60 spectrometer while infrared spectra were recorded on a Perkin-Elmer 337 recording spectrophotometer. Visible and near-infrared spectra were recorded on a Cary 14 spectrophotometer either of nitromethane solutions or by diffuse transmittance of Nujol mulls. Chemical analyses were performed by Galbraith Laboratories, Inc., of Knoxville, Tenn. Mass spectral data were provided by Mr. Dick Weisenberger of the Department of Chemistry at The Ohio State University. Conductivity measurements were obtained on 10^{-3} to 10^{-4} *M* nitromethane solutions in a standard 15-ml conductivity cell in conjunction with an Industrial Instruments conductivity bridge, Model RC 16B. Magnetic susceptibilities were measured by both Faraday and nmr techniques.[7]

Preparation of 1,11-Dioxa-4,8-dithiaundecane. In 500 ml of absolute ethanol under nitrogen, 11.5 g (0.5 g-atom) of sodium metal was dissolved. This mixture was heated gently and 27.0 g (0.25 mole) of 1,3-propanedithiol (Aldrich) was slowly added. To the resulting solution, 40.25 g (0.5 mole) of 2-chloroethanol (Eastman) was cautiously added and the mixture was then refluxed for several hours. The mixture was cooled and filtered and the ethanol was removed from the filtrate by evaporation. A thick liquid remained which was distilled at reduced pressure. After a small forerun, a thick, viscous liquid was collected, bp 179–181.5° (0.5 mm), yield 39.0 g (80%).

Preparation of 1,4,8,11-Tetrathiaundecane (TTU). In a 1-l. flask were placed 39.0 g (0.2 mole) of 1,11-dioxa-4,8-dithiaundecane, 30.5 g (0.4 mole) of thiourea (Matheson), and 105 ml of concentrated HCl, and the mixture was refluxed for 12 hr. The resulting solution was then cooled and 67 g (1.2 moles) of KOH in 400 ml of H_2O was very cautiously added. This mixture was refluxed and stirred for an additional 3 hr. The two-phase system which resulted was cooled and separated, and the upper aqueous phase was acidified with dilute HCl and extracted with 200 ml of ether. The ether layer was combined with the oily organic layer from the reaction mixture, and this solution was dried over anhydrous $MgSO_4$ (Mallinckrodt). The dried ether solution was filtered and the ether evaporated leaving a thick liquid which was distilled. The fraction boiling between 145 and 180° (0.5 mm) was collected and then redistilled to give the desired product, bp 159–161° (0.5 mm), yield 23.4 g (50%). *Anal.* Calcd for $C_7H_{16}S_4$: C, 36.80; H, 7.06; S, 56.14. Found: C, 37.05; H, 7.20; S, 56.29. The infrared spectrum displayed a sharp band at 3.9 μ due to SH.

Preparation of 1,4,8,11-Tetrathiacyclotetradecane (TTP). In 700 ml of absolute ethanol, under nitrogen, 4.7 g (0.204 g-atom) of Na metal was dissolved. To this solution 23.4 g (0.102 mole) of 1,4,8,11-tetrathiaundecane was slowly added and the mixture was refluxed gently. To the resulting mixture 21.0 g (0.102 mole) of 1,3-dibromopropane (Eastman) was added cautiously, with stirring, and after the addition the mixture was refluxed for several hours. The mixture was filtered hot and the ethanol was removed. The solid that remained was Soxhlet extracted with anhydrous ether for 24 hr. The ether was evaporated leaving a white solid which was sublimed and then resublimed at 0.5 mm and 110° to give a white solid, mp 115–117°. Recrystallization of this solid from ethanol gave beautiful white needles, mp 119–120°, yield 2.0 g (7.5%). *Anal.* Calcd for $C_{10}H_{20}S_4$: C, 44.79; H, 7.51; S, 47.77. Found: C, 44.69; H, 7.71; S, 47.83. The infrared spectrum showed no S–H. The mass spectrum had a parent peak at *m/e* 268; theory, 268. The nmr spectrum displayed overlapping singlet and triplet patterns at τ 7.25 of area 16 and a pentuplet at τ 8.02 of area 4.

Preparation of 13,14-Benzo-1,4,8,11-tetrathiacyclopentadecane (TTX). A procedure similar to that above was employed using 31.7 g (0.102 mole) of α,α'-dibromo-*o*-xylene (Eastman). After refluxing for several hours the mixture was filtered hot and the filtrate allowed to cool. The solid that crystallized was filtered and recrystallized several times from chloroform–ethanol mixtures to a constant mp of 84–86°, yield 12.5 g (38%). *Anal.* Calcd for $C_{15}H_{22}S_4$: C, 54.55; H, 6.72; S, 38.80. Found: C, 54.07; H, 6.90; S, 39.08. The infrared spectrum showed no S–H. The mass spectrum was not obtained because the compound decomposed on the probe of the instrument. The nmr spectrum displayed a singlet at τ 2.95 of area 4, a singlet at τ 6.40 of area 4, an overlapping singlet and triplet pattern at τ 7.67 of area 12, and a pentuplet at τ 8.41 of area 2.

Preparation of 2,5,9,12-Tetrathiatridecane (TTT). In a 1-l., three-necked flask was placed 0.96 g (0.020 mole, 50% oil dis-

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Table I. Analytical Data for Ni(TTP)X_2

X	% C Found	% C Calcd	% H Found	% H Calcd	% S Found	% S Calcd	% N or Cl Found	% N or Cl Calcd
NCS	32.83	32.51	4.12	4.55	44.06	44.39	7.04	6.32
Cl	29.87	30.09	4.92	5.06	...	...	18.02	17.76
Br	24.31	24.56	3.89	4.11	...	...	...	...
I	20.34	20.60	2.87	3.45	...	...	...	...
ClO_4	23.19	22.83	3.68	3.83	23.88	24.38	13.56	13.47

persion) of NaH (Alfa Inorganics). The NaH was washed three times with 50-ml portions of dry *n*-hexane. Each time the solid was allowed to settle and the hexane was decanted off. After the third decantation the NaH was covered with 500 ml of dry dimethylformamide and the slurry was placed under dry nitrogen. A solution of 2.28 g (0.01 mole) of 1,4,8,11-tetrathiaundecane in 100 ml of dry DMF was added and the mixture heated until the NaH had dissolved. The solution was then cooled and a solution of 1.30 g (0.01 mole) of anhydrous $NiCl_2$ (made by heating $NiCl_2 \cdot 6H_2O$ *in vacuo* for 24 hr at 110°) in 50 ml of dry DMF was added slowly. To the resulting reddish brown solution was then added 2.84 g (0.02 mole) of CH_3I (Eastman) in 10 ml of dry DMF quickly, and the entire mixture was heated to 75° for 2 hr. This mixture was cooled and the volume reduced to about 40 ml. The reddish solution was added to 200 ml of chloroform and extracted with three 150-ml portions of water. The $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and filtered; the solvent was removed, leaving a red oil which was distilled, bp 138–140° (0.5 mm), yield 1.4 g (55%). *Anal.* Calcd for $C_9H_{20}S_4$: C, 42.14; H, 7.86; S, 50.00. Found: C, 42.37; H, 7.84; S, 50.13. The infrared spectrum showed no S–H. The mass spectrum had a parent peak at *m/e* 256; theory, 256. The nmr spectrum displayed overlapping singlet and triplet patterns at τ 7.25 of area 12, a singlet at τ 7.84 of area 6, and a pentuplet at τ 8.12 of area 2.

Preparation of Ni(TTP)$(BF_4)_2$. To 1.11 g (0.0033 mole) of $Ni(BF_4)_2 \cdot 6H_2O$ (Baker and Adamson) in 40 ml of dry nitromethane was added 2 g of acetic anhydride (Matheson). The mixture was stirred for 10 min or until the solid dissolved and was then filtered. To this stirring, filtered mixture was added 0.89 g (0.0033 mole) of 1,4,8,11-tetrathiacyclotetradecane, all at once. The solution immediately changed its color from a green to orange-red. The volume was reduced to 10 ml, and 30 ml of anhydrous ether was added, whereupon a solid precipitated. (If an oil separates at this point, the solution should be cooled until the oil solidifies.) The solid was filtered and recrystallized from a nitromethane–ether mixture, yield 1.1 g (80%). *Anal.* Calcd for $C_{10}H_{20}S_4NiB_2F_8$: C, 23.98; H, 4.03; S, 25.61. Found: C, 24.20; H, 4.04; S, 25.04.

Preparation of Ni(TTX)$(BF_4)_2$. A similar procedure to the one above was followed. After addition of the ligand, anhydrous ether was added to cause the product to separate as an oil. The solvent was decanted from the oil and the oil was dried *in vacuo*. The resulting glass was dissolved in a large amount of nitromethane and ether was added until the mixture turned cloudy. The cloudy mixture was placed in the refrigerator and crystallization was allowed to proceed. The crystals were collected and the procedure was repeated on the mother liquor until a substantial amount of the product had been crystallized. The crystals were dried *in vacuo*, yield 0.90 g (50%). *Anal.* Calcd for $C_{15}H_{22}S_4NiB_2F_8$: C, 31.98; H, 3.94; S, 22.77. Found: C, 31.99; H, 3.98; S, 22.44.

Preparation of Ni(TTT)$(BF_4)_2$. A procedure similar to those above was followed. After adding the ligand, anhydrous ether was added and a red oil separated. The solvent was decanted away and the oil was dried *in vacuo*. The resulting glass was crystallized from dry acetone to give red needles which were dried at room temperature *in vacuo*, yield 0.70 g (45%). *Anal.* Calcd for $C_9H_{20}S_4NiB_2F_8$: C, 22.11; H, 4.12; S, 26.24. Found: C, 22.13; H, 4.07; S, 26.34.

Preparation of Ni(TTP)X_2 (where X = NCS, Cl, Br, I, or ClO_4). The following general procedure for the metathesis of Ni(TTP)$(BF_4)_2$ was followed. To 0.1 mmole of Ni(TTP)$(BF_4)_2$ in 10 ml of dry nitromethane was added 0.2 mmole of the alkali metal salt with stirring (either KSCN, NaCl, LiBr, NaI, or $NaClO_4$ in the anhydrous orm, Baker and Adamson) (5 ml of acetone was added when NaCl was used). The mixtures were stirred for from 12 to 24 hr during which time a white powder precipitated and the color of the solution changed. The mixture was heated to about 60° and filtered. The volume of the filtrate was slowly reduced with a stream of dry nitrogen until it reached 1 or 2 ml. The solid which had precipitated was filtered and dried *in vacuo*.

Results and Discussions

Syntheses. The ligands synthesized for this study all contained four thioether sulfur atoms and were all prepared from the same precursor, 1,4,8,11-tetrathiaundecane (TTU).[8] Synthesis of TTU was accomplished in 40% over-all yield as shown in Figure 1. The ligands were then prepared by straightforward organic reactions using the dianion of TTU and the appropriate alkyl halide as outlined.

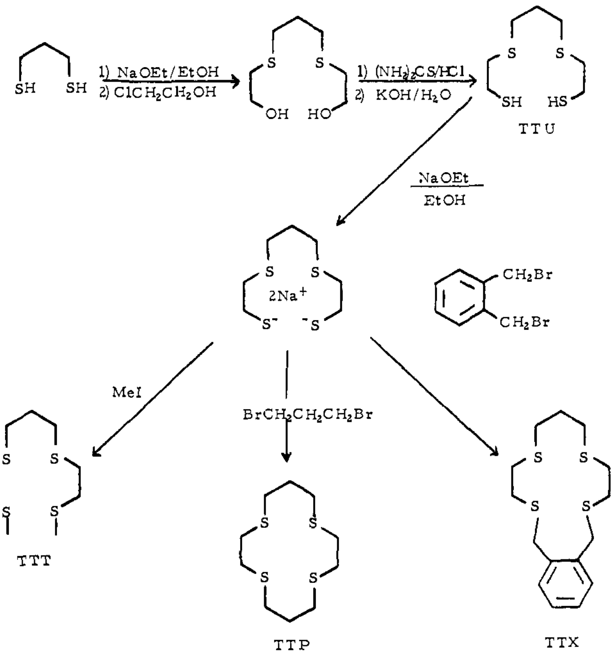

Figure 1. Syntheses of the ligands TTT, TTP, and TTX.

The structures of the ligands were proven by a combination of nmr, elemental analysis, and mass spectral data, as well as by disappearance of the S–H stretching band in the ir. The mass spectra of the ligands show that they are monomers while the elemental analyses give the correct empirical formulas. The nmr spectra of all the ligands are very similar, their spectra approximating the one displayed by TTP in Figure 2. The overlapping singlet–triplet pattern at τ 7.25 is assigned to the methylene groups adjacent to the sulfur atoms while the pentuplet at τ 8.00 is the methylene protons not adjacent to the sulfur atoms. In addition TTT has a singlet at τ 7.84 assigned to the methyl protons while TTX displays two singlets at τ 2.95 and 6.40 assigned to

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[8] A. M. Reeves and E. E. Reid, Abstracts, 115th National Meeting of the American Chemical Society, San Francisco, Calif., 1949, p 651.

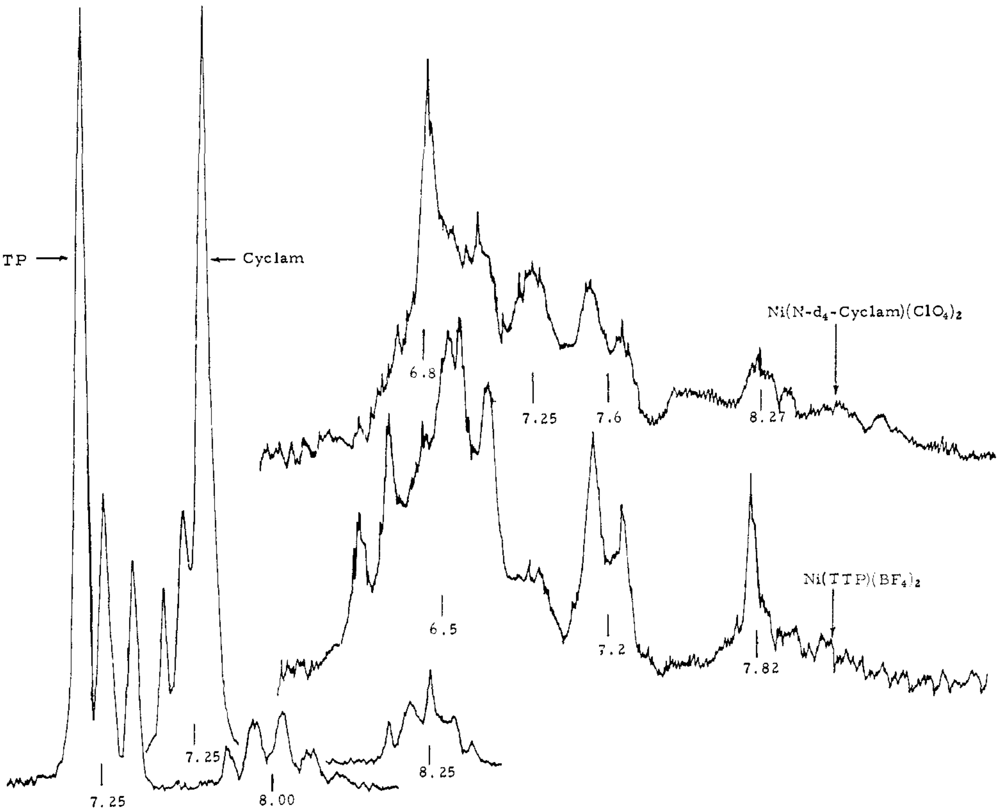

Figure 2. Nmr spectra of TTP and its nickel(II) tetrafluoroborate complex as compared to cyclam[15] and its complex. Units in τ.

the aromatic and benzylic protons, respectively. The Experimental Section contains all pertinent data.

Attempts were made to synthesize the ligands by means of template reactions,[9] but the yields were not improved when nickel(II) was used as a template over that in the absence of a template. (The exception is the synthesis of TTT, described in the Experimental Section, where the use of nickel(II) is involved in the preferred method.)

Complexation of the ligands was accomplished by reaction with the hexaacetic acid derivative of nickel(II) tetrafluoroborate[10] in nitromethane. All of the tetrafluoroborates are reddish orange solids soluble in nitromethane and acetone. They react instantaneously with solvents of good class a donor ability, such as water, ethanol, and dimethyl sulfoxide, to liberate free ligand, which was identified by comparison with the known compounds, and to produce the nickel(II) hexasolvated tetrafluoroborate. This reactivity therefore necessitated the use of the above synthetic procedure where other more common methods failed.

Metathetical reactions producing the tetragonal species were carried out exclusively on the Ni(TTP)(BF$_4$)$_2$ complex in nitromethane with various salts in order to introduce anions into the structure. The resulting tetragonal complexes are also reactive toward water and again produce the free ligand TTP[11] upon reaction. We chose this ligand and its complexes for extensive study because of the similarity it shares with many macrocycles having nitrogen as the donor atom.[12]

Low-Spin Nickel(II) Complexes. The tetrafluoroborate complexes are all diamagnetic, 2:1 electrolytes as is Ni(TTP)(ClO$_4$)$_2$. They exhibit electronic spectra in nitromethane solution typical of square-planar nic-

Table II. Physical Properties of the Complexes Ni(L)X$_2$

L	X	μ, BM	Λ_M, (mho cm^2) mole)	$\lambda^{-1}{}^{CH_3NO_2}_{max}$, cm^{-1} [d]	$\lambda^{-1}{}^{solid}_{max}$, cm^{-1}
TTT	BF$_4$	d[a]	186	20,200 (268)	
TTX	BF$_4$	d	187	19,600 (273) 22,200 (142) sh	19,420 22,000 sh
TTP	BF$_4$	d	194	20,250 (263) 24,000 (97.5) sh	20,160 24,150
TTP	ClO$_4$	d	189	20,320 (270) 23,810 (100) sh	20,140 24,390 31,250
TTP	I	3.10	. . .[c]	14,290 (58) sh 18,520 (315)	8,260 sh 10,990 16,530 26,320
TTP	Br	3.18	18.1	9,010 (16) sh 10,640 (48) 16,390 (53)	8,930 10,990 16,950 29,410
TTP	Cl	3.04[b]	23.9	9,260 (25) sh 10,640 (48) 16,390 (28)	9,170 sh 11,110 16,950 29,410
TTP	NCS	3.11	27.7	9,900 (34) sh 10,930 (54) 17,540 (28)	9,900 11,100 17,540 28,570

[a] d = low spin. [b] Obtained by nmr measurement.[7] [c] Concentration dependent. [d] Molar extinction coefficient in parentheses.

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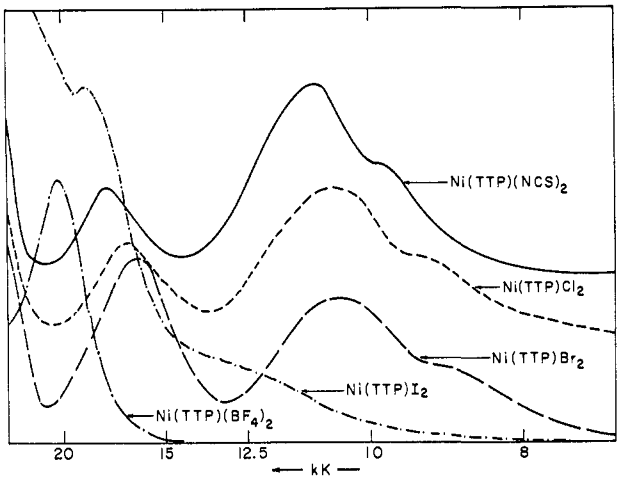

Figure 3. Electronic spectra of Ni(TTP)X$_2$ species, where X = BF$_4$, I, Br, Cl, NCS, as solutions in nitromethane.

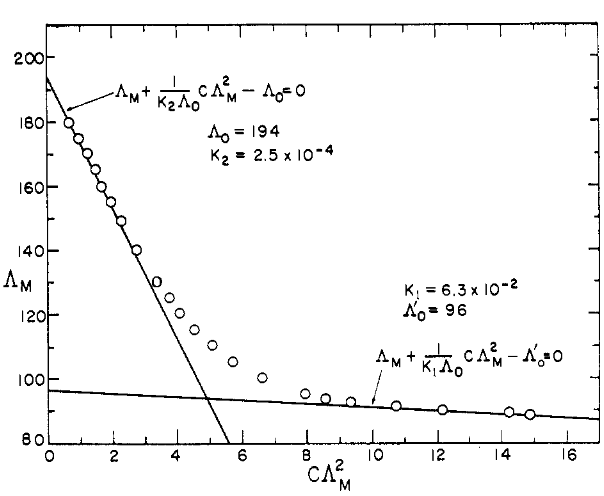

Figure 4. Ostwald dilution law plot showing two consecutive equilibria for Ni(TTP)I$_2$ in nitromethane. Λ_M = molar conductance, C = concentration in moles/l., Λ_0 = molar conductance at infinite dilution, K_1 and K_2 are consecutive equilibrium constants.

kel(II) complexes,[13] having a single strong band near 500 mμ with a molar extinction coefficient approximating 270 (see Table II). The infrared spectra displayed bands for ionic BF_4^- and ClO_4^- [14] which is compatible with a square-planar stereochemistry for these complexes. These complexes are therefore the first examples of low-spin nickel(II) with four thioethers as the donors.

The nmr spectrum of Ni(TTP)(BF$_4$)$_2$ is shown in Figure 2 as well as a spectrum of Ni(N-d_4-cyclam)(ClO$_4$)$_2$.[15] The great similarity between the two is to be noted indicating that the configuration of TTP about the metal is very much like that of the known cyclam complex.[15] Nmr spectra of Ni(TTT)(BF$_4$)$_2$ and Ni(TTX)(BF$_4$)$_2$ show similar patterns in the methylene region except that the TTT complex has a sharp singlet at τ 7.50 for the methyl groups while TTX has a broad singlet at τ 2.49 for the aromatic protons.

High-Spin Nickel(II) Complexes. A series of complexes of empirical formula Ni(TTP)X$_2$, where X = NCS, Cl, Br, or I, were prepared as described. All are paramagnetic solids displaying diffuse transmittance spectra having four discernible bands in the near-infrared and visible region (see Table II). Spectra of nitromethane solutions, Figure 3, are essentially identical with those of the solid samples, with the exception of the iodide which will be discussed below. From the spectra of these tetragonal species a Dq^{xy},[12,16] value for the ligand TTP of 1070 cm^{-1} can be calculated, which is the weakest field yet observed for a symmetrical tetradentate macrocycle.[12]

The thiocyanate, chloride, and bromide are paramagnetic, nonelectrolytes in nitromethane solution, whereas the iodide has a conductivity which is concentration dependent in this solvent as is shown in Figure 4. Two successive equilibria were implicated by application of the Ostwald dilution law and these may be described as involving 2:1 and 1:1 electrolytes at low concentrations while at higher concentrations the 1:1 electrolyte is in equilibrium with a nonelectrolyte. Solution spectra of the iodide in nitromethane (about 10^{-3} M) are very different from the spectra of either the square-planar or tetragonal complexes already presented. Attempts to measure the magnetic susceptibility of these solutions by the nmr technique[7] failed because the amount of paramagnetic species in solution was not sufficient to be observed. The data necessitated that the predominant 1:1 electrolyte in solution be five-coordinate and diamagnetic and thus placed the iodide on the borderline where six-coordinate, high-spin species are very similar in stability to low-spin species of reduced coordination number.[17] The equilibria can be described by the following equations.

$$\mathrm{Ni(TTP)I_2} \rightleftharpoons \mathrm{Ni(TTP)I^+} + \mathrm{I^-} \qquad K_1 = 6.3 \times 10^{-2}$$

$$\mathrm{Ni(TTP)I^+} \rightleftharpoons \mathrm{Ni(TTP)^{2+}} + \mathrm{I^-} \qquad K_2 = 2.5 \times 10^{-4}$$

The unexpectedly high spectrochemical Dq values encountered with thioethers in comparison to the high reactivity of their complexes toward nucleophiles of moderate donor strength is an anomaly which cannot be satisfactorily explained at present. Arguments based on bonding alone are not adequate, and, in fact, other thermodynamic factors must be considered.

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