Preparation and Characterization of Oxochromium(IV) and Nickel(II) Complexes with 5,14-Dihydro-7,16-diethyl-(*E*)- or -(*Z*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine

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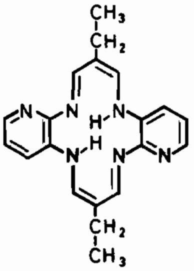
Abstract

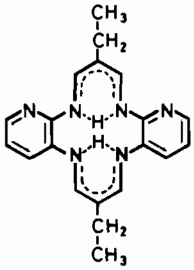
The reaction of 5,14-dihydro-7,16-diethyl-(*E*) or -(*Z*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine with chromium hexacarbonyl produced the corresponding oxochromium(IV) complexes. These compounds had intense bands in the infrared region at 985 cm^{-1}, which are attributed to the Cr=O stretching modes. The two complexes gave mass spectra with prominent parent and parent-O peaks. On the other hand the mass spectra for the nickel(II) complexes showed parent and parent-CH_3 peaks. The absorption bands appearing in the energy range greater than 19 000 cm^{-1} were attributable to the $\pi \rightarrow \pi^*$ and CT transitions. Consistent with their diamagnetism, the oxochromium complexes gave well-resolved proton NMR and carbon-13 NMR spectra. The magnitude of downfield shifts for the oxochromium(IV) complex is much larger than that observed for the corresponding nickel(II) complex. This is due to the fact that the positive charge provided by chromium(IV) is greater in magnitude than that by nickel(II).

Introduction

A transition-metal oxo complex is an available reagent for the oxidation of an organic molecule [1]. Oxo-metalloporphyrin complexes of vanadium(IV) [2], chromium(IV) [3], molybdenum(IV) [4] and molybdenum(V) [5] and oxo related complexes of chromium(V) [6] and molybdenum(V) [7] have been prepared and have been widely investigated to the present time because of their biochemical interest [8]. Nevertheless, unsaturated N_4-macrocycles, namely, 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine (**1-E**) and 5,14-dihydro-7,16,-diethyl-(*Z*)-dipyrido[b,i]-[1,4,8,11] tetraazacyclotetradecine (**1-Z**) have never been studied as ligands of metal oxo complexes.



1-E



1-Z

In the present research, we prepared oxochromium(IV) and nickel(II) complexes of **1-E** and **1-Z**. This is the first example of a well-characterized oxochromium complex formed with unsaturated macrocyclic N_4-ligands. We have undertaken to elucidate the correlation between the valence state of chromium and nickel in complexes. We characterized the spectral and magnetic properties of oxochromium(IV) and nickel(II) complexes of the present macrocycles by the use of mass, vibrational and electronic spectroscopies as well as magnetic susceptibility measurements. The detailed proton and carbon-13 NMR studies for the oxochromium(IV) and nickel(II) complexes are also provided.

Experimental

Physical Measurements

Mass spectral measurements were taken using a JEOL JMS-DX 300 gas chromatograph–mass spectrometer at 70 eV. Magnetic susceptibility measurements of solid powdered samples were performed by the

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Faraday method at room temperature. Infrared spectra in the region of 400–4000 cm^{-1} were carried out with a Hitachi 260-10 spectrophotometer at room temperature using a KBr disk method. Ultraviolet and visible spectra covering the 12 500–40 000 cm^{-1} range were obtained on a Shimadzu UV 200S double beam spectrophotometer for chloroform solutions at room temperature. Proton (60 MHz) and carbon-13 (15 MHz) measurements were measured with a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were run in chloroform-d or hexamethylphosphoric triamide-d_{18} and chemical shifts are reported in ppm relative to tetramethylsilane as an internal reference standard.

Preparation of Macrocyclic Ligands

5,14-Dihydro-7,16-diethyl-(E)-dipyrido[b,i]-[1,4,8,11]tetraazacyclotetradecine (1-E) and 5,14-dihydro-7,16-diethyl-(Z)-dipyrido[b,i][1,4,8,11]-tetraazacyclotetradecine (1-Z)

The synthetic procedures for **1-E** and **1-Z** have been described previously [9].

Preparation of Complexes

(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxochromium(IV) (CrO(1-E))

Chromium(0) hexacarbonyl (1.5 g) and **1-E** (0.177 g) were dissolved in 68 ml of decaline, and the mixture was heated at 180–190 °C under argon atmosphere with stirring for 4 h. Solvent and unreacted chromium hexacarbonyl were removed under reduced pressure. The residue was extracted with toluene (800 ml), concentrated to *ca.* 30 ml *in vacuo*, and red needles were obtained; yield 0.091 g (43%), melting point >300 °C. The mass spectrum showed M^+ at m/z 412 and peaks for $[M - CH_3]^+$ and $[M - CH_3 - O]^+$ at m/z 397 and 381, respectively. IR (KBr disk): 1595 (C=C str. (conjugated ring)), 1560 (C=N str.), 1415 (macrocyclic skeletal str.) and 985 (Cr=O str.) cm^{-1}.

(7,16-Diethyl-(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)oxochromium(IV) (CrO(1-Z))

A mixture of **1-Z** (0.177 g), chromium(0) hexacarbonyl (1.5 g) and decalin (68 ml) was heated at 180–190 °C under argon atmosphere with stirring for 3 h. Solvent and unreacted chromium hexacarbonyl were eliminated under diminished pressure. The residue was dissolved in toluene (800 ml), the solution concentrated to *ca.* 30 ml *in vacuo*, and red plates were obtained by the addition of hexane (20 ml); yield 0.090 g (43%), melting point >300 °C. The mass spectrum showed M^+ at m/z 412 and peaks for $[M - CH_3]^+$ and $[M - CH_3 - O]^+$ at m/z 397 and 381, respectively. IR (KBr disk): 1595 (C=C str. (conjugated ring)), 1570 (C=N str.), 1422 (macrocyclic skeletal str.) and 985 (Cr=O str.) cm^{-1}.

(7,16-Diethyl-(E)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (Ni(1-E))

A mixture of **1-E** (0.175 g), nickel(II) acetate tetrahydrate (0.150 g) and *N,N*-dimethylformamide (5.5 ml) was heated under reflux with stirring for 4 h. After the reaction mixture was cooled down with ice-water, the precipitated crystalline solid was recrystallized from benzene to give glittering blue–violet needles; yield 0.160 g (80%), melting point >300 °C. The mass spectrum showed M^+ at m/z 402 and peak for $[M - CH_3]^+$ at m/z 387. IR (KBr disk): 1600 (C=C str. (conjugated ring)), 1565 (C=N str.) and 1422 (macrocyclic skeletal str.) cm^{-1}.

(7,16-Diethyl-(Z)-dipyrido[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (Ni(1-Z))

The reaction of **1-Z** (0.175 g) and nickel(II) acetate tetrahydrate (0.150 g), following the above procedure, gave glittering dark red needles; yield 0.150 g (75%), melting point >300 °C. The mass spectrum showed M^+ at m/z 402 and peak for $[M - CH_3]^+$ at m/z 387. IR (KBr disk): 1601 (C=C str. (conjugated ring)), 1563 (C=N str.) and 1440 (macrocyclic skeletal str.) cm^{-1}.

Results and Discussion

Synthesis of Complexes

Treatment of 5,14-dihydro-7,16,-diethyl-(*E*)- or -(*Z*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine in decalin with chromium hexacarbonyl led to the isolation of a red crystalline, **CrO(1-E)** or **CrO(1-Z)**, in 43% yield. The analytical and magnetic data for the macrocyclic complexes are summarized in Table I. Elemental analyses of crystalline complexes were in accord with compounds for the formula macrocyclic oxochromium(IV) and nickel(II) chelates, respectively. The two chromium complexes gave mass spectra with the prominent parent peak at mass number 412, which were observed to have the same characteristic structure as that of $Cr(1\text{-}E)^+$ or $Cr(1\text{-}Z)^+$ shifted by 16 mass units to higher numbers. This peak was therefore assigned to originate from $CrO(1\text{-}E)^+$ or $CrO(1\text{-}Z)^+$. On the other hand the mass spectra of the nickel complexes revealed parent and parent-CH_3 peaks. Spectral and physical characterization indicated that **CrO(1-E)** and **CrO(1-Z)** were diamagnetic oxochromium(IV) complexes.

Vibrational Spectra

The infrared spectra of **CrO(1-E)**, **CrO(1-Z)**, **Ni(1-E)** and **Ni(1-Z)** are shown in Fig. 1 for the range of 900–1100 cm^{-1}. All the compounds exhibit medium

TABLE I. Analytical and Magnetic Data for Macrocyclic Complexes

Complex	Found (%)			Calc. (%)			μ_{eff}[a] (BM)
	C	H	N	C	H	N	
CrO(1-E)	58.34	4.92	20.15	58.25	4.89	20.38	dia.
CrO(1-Z)	58.46	5.03	20.20	58.25	4.89	20.38	dia.
Ni(1-E)	59.79	5.07	20.68	59.59	5.00	20.85	dia.
Ni(1-Z)	59.37	4.95	20.79	59.59	5.00	20.85	dia.

[a] dia = diamagnetism.

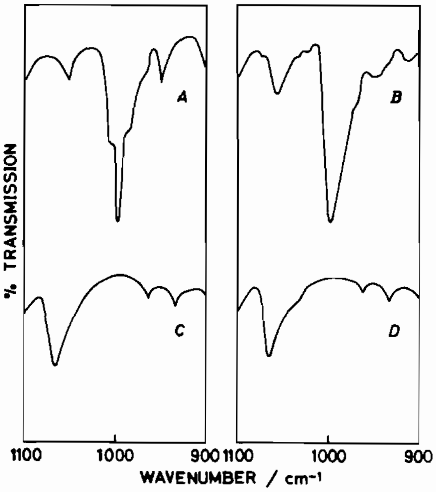


Fig. 1. Infrared spectra for macrocyclic metal complexes by a KBr disk technique. (A) CrO(1-E); (B) CrO(1-Z); (C) Ni(1-E); (D) Ni(1-Z).

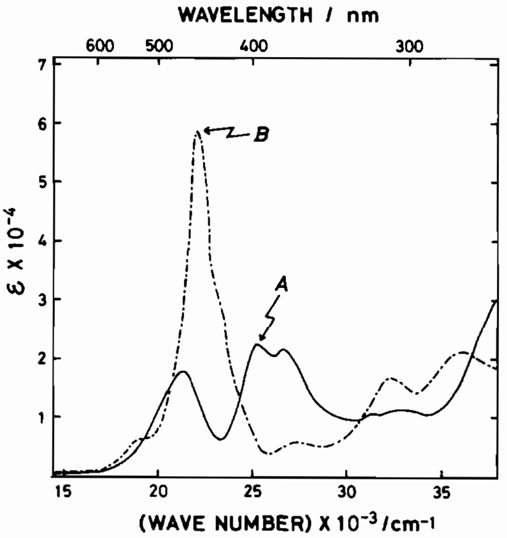


Fig. 2. Electronic spectra of 5,14-dihydro-7,16-diethyl-(*E*)-dipyrido[b,i] [1,4,8,11] tetraazacyclotetradecine chelates in chloroform at room temperature. (A) CrO(1-E); (B) Ni(1-E).

absorption bands at around 1060 cm^{-1}. Intensity of this characteristic band for **Ni(1-E)**, **1-E** **Ni(1-Z)** and **1-Z** is comparable to each other assigned to the ligand vibration. As reported in porphyrin and related oxochromium complexes previously [3(a), (b), 6], the Cr=O stretching mode gives rise to a strong absorption in the range of 950–1050 cm^{-1}. The absorption band at 985 cm^{-1} observed for **CrO(1-E)** and **CrO(1-Z)** shows a strong intensity and, accordingly, is attributable to the Cr=O stretching mode.

Electronic Spectra

Visible and ultraviolet spectra covering the 15 000–38 000 cm^{-1} region are shown in Fig 2 for **CrO(1-E)** and **Ni(1-E)** as an example. General features of the spectra for **CrO(1-E)** and **CrO(1-Z)**, and **Ni(1-E)** and **Ni(1-Z)** respectively, are similar to each other. This suggests that the delocalization of a conjugated system in complexes of *cis* and *trans* isomers in relative positions of N atoms to heteroatoms of other pyridine rings is approximately analogous to one another. Since the molar extinction coefficients of the absorption bands observed above the 19 200 cm^{-1} range are larger in magnitude than those assigned to ligand-field transitions, these bands are attributed to CT or $\pi \rightarrow \pi^*$ transitions. In addition, the general feature of the spectra for **Ni(1-E)** and **Ni(1-Z)** is analogous to those obtained for the macrocyclic nickel(II) complex including benzene rings described previously [10].

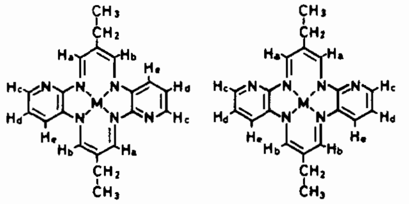
NMR

^{1}H NMR data and their assignments for the macrocyclic oxochromium(IV) and nickel(II) complexes are compiled in Table II. The signal for amine protons (N-*H*) was found to be extinguished on metal coordination, and the H_a- and H_b-methine proton signals turned to be singlets owing to no coupling with amine protons. The H_a-proton peak observed in the lowest field is shifted downfield by 0.10–0.37 ppm (nickel complex) and 1.07–1.26 ppm (oxochromium complex) upon complex formation. The downfield shift for the oxochromium(IV)-coordination is larger in magnitude than that observed for the nickel(II)-coordination. This may be attributable to the fact that the oxidation number of the chro-

TABLE II. Proton NMR Data for the Macrocyclic Metal Complexes[a]

Complex	Ethyl		Aromatic			Methine	
	$-CH_3$	$-CH_2-$	$-H_c$	$-H_d$	$-H_e$	$-H_a$	$-H_b$
Ni(1-E)	1.20(t) (J = 7.0 Hz)	2.46(q) (J = 7.0 Hz)	7.87(dd) (J = 4.6 Hz) (J = 1.5 Hz)	6.75(dd) (J = 8.1 Hz) (J = 4.6 Hz)	7.45(dd) (J = 8.1 Hz) (J = 1.5 Hz)	8.50(s)	7.59(s)
Ni(1-Z)	1.17(t) (J = 7.3 Hz) 1.22(t) (J = 7.3 Hz)	2.36(q) (J = 7.3 Hz) 2.48(q) (J = 7.3 Hz)	7.84(dd) (J = 4.6 Hz) (J = 1.5 Hz)	6.72(dd) (J = 8.1 Hz) (J = 4.6 Hz)	7.44(dd) (J = 8.1 Hz) (J = 1.5 Hz)	8.48(s)	7.50(s)
CrO(1-E)	1.33(t) (J = 7.5 Hz)	2.72(q) (J = 7.5 Hz)	8.17(dd) (J = 4.7 Hz) (J = 1.0 Hz)	7.09(dd) (J = 8.1 Hz) (J = 4.7 Hz)	7.89(dd) (J = 8.1 Hz) (J = 1.0 Hz)	9.39(s)	8.60(s)
CrO(1-Z)	1.30(t) (J = 7.6 Hz) 1.34(t) (J = 7.6 Hz)	2.64(q) (J = 7.6 Hz) 2.75(q) (J = 7.6 Hz)	8.16(dd) (J = 4.6 Hz) (J = 1.0 Hz)	7.00(dd) (J = 8.1 Hz) (J = 4.6 Hz)	7.85(dd) (J = 8.1 Hz) (J = 1.0 Hz)	9.45(s)	8.49(s)

[a] Chemical shifts are given in ppm for TMS. Measured in chloroform-d with TMS as an internal reference. Multiplicity of a proton signal is given in parentheses after δ-values: s = singlet, t = triplet; q = quartet; dd = doublet of doublets.



M(1 - E)   M(1 - Z)

M = Ni,CrO

mium is greater than that of the nickel and, hence, the electron-withdrawing effect of the former is greater than that of the latter. A similar shift is observed for the H_b-methine proton signal.

The H_c-aromatic proton couples with both H_e and H_e-aromatic protons, the H_c-signal being split into a doublet of doublets, which was observed as a quartet. A similar signal pattern is observed for H_d- and H_e-aromatic protons. Upon formation of metal complexes the H_c-, H_d- and H_e-aromatic proton signals show downfield shifts. The downfield shifts with regard to the oxochromium and the nickel complexes are comparable to those observed for each of the methine protons described above. The magnitude of the downfield shifts for the aromatic protons is much smaller than those observed for the methine protons. This is primarily due to the fact that the aromatic proton groups are placed further from the positive charge of the metal ion which provides a deshielding effect.

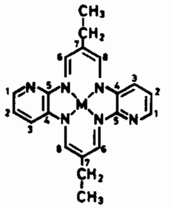
The methyl and methylene proton signals of the 7- and 16-ethyl groups in complexes are observed in a lower field, compared to those of metal-free macrocycles, upon the electron-withdrawing effect of the metal ions as observed for the methine and aromatic proton signals. These methyl and methylene proton signals for **Ni(1-E)** and **CrO(1-E)** are split into a triplet and a quartet, respectively, due to coupling with each other. On the other hand, the methyl and methylene proton signals for **Ni(1-Z)** and **CrO(1-Z)** are split into a quintet and a sextet, respectively. Consequently, the quintet signal is referred to the overlap of two quartets and the sextet signal is explained as the stagger of two triplets. This seems to indicate that each of the groups is placed in distinct spaces from the neighboring pyridine nitrogens.

Carbon-13 NMR data and their assignments for these macrocycles and their metal complexes are collected in Table III. All carbon signals for **1-E**, **Ni(1-E)**, **CrO(1-E)** and **CrO(1-Z)** exhibit a singlet, but the methyl, methylene and 7-position carbon signals for **1-Z** and **Ni(1-Z)** are observed as a 1:1 doublet. These peaks were analysed as two signals caused by the different chemical shift with the lowering of symmetry, as judged by the peak number of off-resonance decoupling. The magnitude of downfield shifts for the oxochromium(IV) complex at 4-, 5-, 6-, 7- and 8-position carbons in the chelating rings is much larger than that observed for nickel(II) complex. This is attributed to the deshielding effect due to the more positive charge provided by the

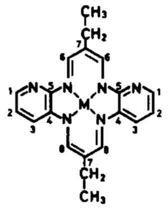
TABLE III. Carbon-13 NMR Data for the Macrocyclic Metal Complexes[a]

Complex	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	Ethyl	
									$-CH_2-$	$-CH_3$
Ni(1-E)	144.03(2)	119.01(2)	122.04(2)	138.61(1)	156.26(1)	148.63(2)	113.49(1)	142.86(2)	25.23(3)	17.89(4)
Ni(1-Z)	145.40(2)	119.20(2)	121.55(2)	138.90(1)	155.96(1)	146.73(2)	112.50(1)	142.27(2)	24.93(3)	17.55(4)
							113.87(1)		25.62(3)	17.99(4)
CrO(1-E)	144.08(2)	120.08(2)	121.99(2)	140.42(1)	158.55(1)	153.96(2)	117.29(1)	150.05(2)	25.77(3)	17.41(4)
CrO(1-Z)	143.94(2)	119.89(2)	121.84(2)	140.22(1)	158.36(1)	153.77(2)	117.15(1)	149.86(2)	25.57(3)	17.21(4)
1-E	144.67(2)	118.27(2)	122.67(2)	132.40(1)	148.58(1)	158.94(2)	112.06(1)	136.85(2)	25.91(3)	16.87(4)
1-Z	147.95(2)	120.28(2)	121.50(2)	132.99(1)	147.95(1)	149.12(2)	111.13(1)	142.57(2)	25.47(3)	16.77(4)
							112.16(1)		26.21(3)	17.26(4)

[a] Chemical shifts are given in ppm for TMS. Measured in hexamethylphosphoric triamide-d_{18}. Peaks by the off-resonance decoupling are given in parentheses after δ-value.



M(1 – E)



M(1 – Z)

M = Ni,CrO

chromium ion. This result is consistent with the corresponding proton NMR spectral behavior. The difference of chemical shifts between the two types of metal-free macrocycles decreased with the complex formation. This is attributable to the electron-withdrawing effect of the metal ion which is greater in magnitude than that of the pyridinic nitrogens. Accordingly, the metal-coordination partly closes the structural gap between the two types.

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