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Studies Involving Nitrogen–Oxygen-Donor Macrocyclic Ligands. 4. Interaction of Nickel(II) with New 14- to 17-Membered Crown Macrocycles[1]

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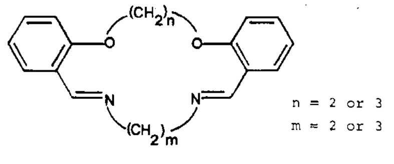
New nickel(II) complexes of 11 O_2N_2-donor macrocycles incorporating 14- to 17-membered macrocyclic rings have been synthesized. Physical measurements indicate that the complexes are of the type Ni(macrocycle)X_2 (X = Cl, Br, or NCS) and that the ether oxygens as well as the amines of the respective macrocycles coordinate; a pseudooctahedral geometry occurs for each complex. A correlation between macrocycle ring size (as well as some macrocycle substituents) and spectral properties of the resulting complexes is observed.

Introduction

Although the interaction of metal ions with the polyether "crown" macrocycles has now been studied in considerable depth,[2,3] related studies involving mixed nitrogen–oxygen-donor macrocycles are also receiving increasing attention.[1,3-9] The latter macrocycles might be expected to span the coordination behavior of the "crown" polyethers and the other well-studied group of macrocyclic ligands which incorporate only nitrogen donor atoms.[10]

The synthesis[1,5] and kinetics[11] of imine hydrolysis of a series of metal complexes of 14-, 15-, and 16-membered macrocyclic ligands of type **1** have been studied previously. The investigation has now been extended to include a study of the complexing behavior with nickel(II) of macrocycles **2–12**;[12] the ligands were obtained by the hydrogenation of the imine linkages of corresponding ligands of type **1**. A feature of the reduced ligands is that they are not susceptible to the metal-ion promoted imine hydrolysis found for their precursors.[1,5,11] The tendency to hydrolyze has inhibited the use of ligands of type **1** for a number of quantitative investigations originally planned.



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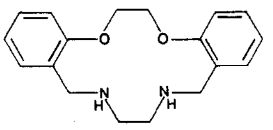

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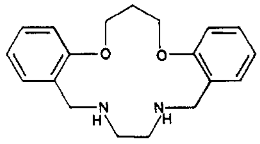

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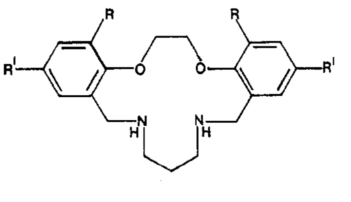
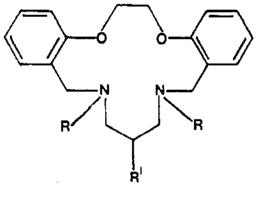
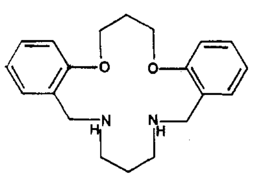




4 R = R^1 = H
5 R = H, R^1 = Cl
6 R = H, R^1 = Br
7 R = OCH$_3$, R = H

8 R = H, R^1 = OH
9 R = CH$_3$, R^1 = H
10 R = CH$_3$, R^1 = OH



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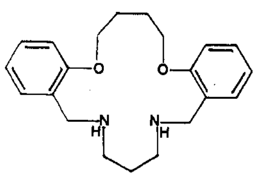

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A motivation for the present work was to obtain a range of closely related macrocycles which would enable the effects of minor ligand changes on metal-ion complexation to be evaluated. Thus, apart from their intrinsic interest, the synthetic results now presented will also provide a foundation for kinetic and thermodynamic studies which will be reported subsequently.

Experimental Section

Analyses for carbon, hydrogen, and nitrogen were determined by Mr. J. Kent, University of Queensland. Nickel was determined gravimetrically as its DMG complex. All compounds were dried over P_4O_{10} in vacuo before analyses. The solution infrared spectra were obtained on a Perkin-Elmer-297 spectrophotometer; other physical measurements were obtained as outlined previously.[1]

Preparation of Ligands. The preparation and characterization of macrocycles **2–5** and **11** from the corresponding diimine precursors[5] are described elsewhere[13] and ligands **6–8** and 12 were obtained by a similar procedure. Typically, yields of between 40 and 80% were obtained based on the diimine precursors. Ligands **9** and **10** were obtained from **4** and **8**, respectively, by N-methylation using formaldehyde in formic acid.[14] The following data were obtained for the new ligands.

Ligand 6: white solid, mp 225 °C. Anal. Calcd for $C_{19}H_{22}N_2O_2Br_2$: C, 48.6; H, 4.7; N, 6.0. Found: C, 48.4; H, 4.9; N, 5.9. Mass spectral parent ion: *m/e* 468 (based on ^{79}Br). ^{1}H NMR (δ, ppm): 1.68, quintet ($CH_2–CH_2–CH_2$); 1.78, s (–N*H*); 2.58, t ($N–CH_2$); 3.61, s (arom–CH_2–); 4.27, s (O–CH_2–); 6.78–7.42, m (arom).

Ligand 7: white solid, mp 100 °C. Anal. Calcd for $C_{21}H_{28}N_2O_4$: C, 67.7; H, 7.6; N, 7.5. Found: C, 67.4; H, 7.5; N, 7.6. Mass spectral parent ion: *m/e* 372. ^{1}H NMR (δ, ppm): 1.77, quintet ($CH_2–CH_2–CH_2$); 2.02, s (–N*H*); 2.74, t (N–CH_2–); 3.67, s (arom–CH_2–); 3.76, s (O–CH_3); 4.35, s (O–CH_2–); 6.80–7.28, m (arom).

Ligand 8: white solid, mp 156 °C. Anal. Calcd for $C_{19}H_{24}N_2O_3$: C, 69.5; H, 7.4; N, 8.5. Found: C, 69.3; H, 7.3; N, 8.2. Mass spectral parent ion: *m/e* 328. ^{1}H NMR (δ, ppm): 2.55, s (–N*H*); 2.61, d (N–CH_2–); 3.73, m (arom–CH_2–, –C*H*OH–); 4.34, s (O–CH_2–); 6.70–7.40, m (arom). ^{13}C NMR (δ, ppm): 51.2, t (N–CH_2–); 53.0, t (arom–CH_2–); 65.7, t (O–CH_2–); 67.9, d (–CHOH); 110.1, 120.6, 127.7, 128.6, 131.1, 157.6 (arom).

Ligand 9: white solid, mp 100 °C. Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.1; H, 8.3; N, 8.2. Found: C, 74.2; H, 8.4; N, 8.2. Mass spectral parent ion: *m/e* 340. ^{1}H NMR (δ, ppm): 1.62, quintet ($CH_2–CH_2–CH_2$); 2.18, s(N–CH_3); 2.49, t (N–CH_2–); 3.61, s (arom–CH_2–); 4.32, s (O–CH_2–); 6.80–7.30, m (arom). ^{13}C NMR (δ, ppm): 26.1, t ($CH_2–CH_2–CH_2$); 41.4, quartet (N–CH_3); 55.7, t (N–CH_2–); 57.2, t (arom–CH_2–); 66.6, t (O–CH_2–); 111.0, 120.1, 126.7, 128.4, 132.3, 157.4 (arom).

Ligand 10: white solid, mp 144 °C. Anal. Calcd for $C_{21}H_{28}N_2O_3$: C, 70.8; H, 7.9; N, 7.9. Found: C, 70.5; H, 8.0; N, 7.9. Mass spectral parent ion: *m/e* 356. ^{1}H NMR (δ, ppm): 2.25, s (N–CH_3); 2.54,

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Table I. Physical Data for the Complexes

complex	magnetic moment[a]	infrared bands, cm^{-1} ν(N–H)	infrared bands, cm^{-1} ν(C=N)	visible reflectance spectra,[b] nm
$NiLCl_2$ (L = **2**)	3.18	3240		580, 765 sh, 1120
$NiLBr_2$ (L = **2**)	3.19	3200, 3160		575, 700 sh, 1170
$NiL(NCS)_2 \cdot 2CH_3OH$ (L = **2**)	3.20	3220	2120	605, 960
$NiLCl_2 \cdot H_2O$ (L = **3**)	3.18	3200, 3180		400, 685, 1070
$NiLBr_2$ (L = **3**)	3.26	3200		400, 640, 875, 1260
$NiL(NCS)_2$ (L = **3**)	3.23	3255, 3220	2110, 2080	600, 925
$NiLCl_2$ (L = **4**)	3.17	3260, 3220		640, 860 sh, 1000, 1175
$NiLBr_2$ (L = **4**)	3.13	3230		640, 720 sh, 940, 1250
$NiL(NCS)_2$ (L = **4**)	3.18	3230	2085, 2060	575, 970
$NiLCl_2$ (L = **5**)	3.22	3210		400, 635, 1145
$NiLBr_2$ (L = **5**)	3.28	3205		410, 630, 1220
$NiL(NCS)_2$ (L = **5**)	3.31	3200	2075	585, 1000
$NiLCl_2$ (L = **6**)	3.18	3258, 3233		400, 640, 1120
$NiL(NCS)_2$ (L = **6**)	3.24	3270, 3223	2073	590, 996
$NiLCl_2 \cdot H_2O$ (L = **7**)	3.29	3260, 3206		395, 635, 1188
$NiLBr_2$ (L = **7**)	3.29	3245		405, 630, 700 sh, 1192
$NiL(NCS)_2$ (L = **7**)	3.23	3273, 3230	2098, 2087	577, 984
$NiLCl_2$ (L = **8**)	3.20	3260		470, 630, 1160
$NiL(NCS)_2$ (L = **8**)	3.14	3285	2117, 2095	570, 960
$NiLCl_2$ (L = **9**)	3.19			420, 700, ~1200
$NiL(NCS)_2$ (L = **9**)	3.18		2100, 2092	620, 1040
$NiLBr_2$ (L = **9**)	3.21			425, 710, ~1200
$NiL(NCS)_2$ (L = **10**)	3.16		2112, 2090	615, 1020
$NiLCl_2$ (L = **11**)	3.20	3260, 3180		410, 680, 1120, 1180
$NiLBr_2$ (L = **11**)	3.30	3220		420, 680, 1240
$NiL(NCS)_2$ (L = **11**)	3.19	3280, 3240	2120, 2080	600, 980
$NiL(NCS)_2$ (L = **12**)	3.11	3252	2100, 2080	635, 1064

[a] In Bohr magnetons, at 25 °C. [b] Spectral range scanned: 390–1350 nm; where no peak is listed for the 400–420-nm region then the edge of an absorption (d–d or charge transfer) occurs in this region.

m (N–C*H*$_2$–); 3.56, 3.79, AB system (arom–C*H*$_2$–); 3.95, quintet (–C*H*OH–); 4.33, s (O–C*H*$_2$–); 6.70–7.30, m (arom). ^{13}C NMR (δ, ppm): 42.6, quartet (N–*C*H$_3$); 56.7, t (N–*C*H$_2$–); 61.3, t (arom–*C*H$_2$–); 65.8, d (–*C*HOH); 66.9, t (O–*C*H$_2$–); 111.2, 120.2, 126.6, 128.5, 132.2, 157.2 (arom).

Ligand 12: white solid, mp 82 °C; isolated as monohydrate. Anal. Calcd for $C_{21}H_{30}N_2O_3$: C, 70.4; H, 8.4; N, 7.8. Found: C, 70.3; H, 8.3; N, 7.8. Mass spectral parent ion: *m/e* 358. ^{1}H NMR (δ, ppm): 1.83, quintet (N–CH$_2$–C*H*$_2$–); 2.06, m (O–CH$_2$–C*H*$_2$–); 2.21, s (–N*H*); 2.75, t (N–C*H*$_2$–); 3.78, s (arom-C*H*$_2$–); 4.04, m (O–C*H*$_2$–); 6.91–7.30, m (arom).

Preparation of Complexes. General Preparation. Macrocycle (1 mmol) in methanol or butanol was added slowly to a stirred hot solution of the required nickel salt (1 mmol) in methanol or butanol. The hot solution was stirred for 5 min and then concentrated whereupon the complex separated. The solution was filtered and the product was washed with methanol or butanol and then ether. The chloride and bromide complexes could be recrystallized from methanol. All complexes were obtained in greater than 70% yield.

Sodium Borohydride Reduction of $NiLBr_2$ (L = 1, n = 2, m = 3) to Yield $NiLBr_2$ (L = 4). Sodium borohydride (0.42 g; 12 mmol) was added quickly to the diimine complex (1.66 g; 3.2 mmol) partially dissolved in dry methanol (100 mL). The solution was stirred for 30 min. The green precipitate was filtered off and recrystallized from methanol. Analytical data as well as the infrared spectrum of the product confirmed that it was the reduced compound; yield 40%.

Satisfactory elemental analyses for carbon, hydrogen, nitrogen and nickel were obtained for each metal complex. A list of these data is available as supplementary material.

Results and Discussion

Unlike the crown polyethers (which usually show low affinity toward transition-metal ions such as nickel)[3] the macrocycles **2–12** readily react with nickel salts in methanol or butanol to yield the corresponding complexes. An alternative method of synthesis, established for $NiLBr_2$ (L = **4**), involved reductive hydrogenation of the imine linkages of $NiLBr_2$ (L = **1**; n = 2, m = 3) by treatment of a suspension of the complex in dry methanol with sodium borohydride.

Table II. Solution Spectra in Dichloromethane for Selected Complexes[a]

complex	visible–near-infrared, nm λ_{max} (ϵ) $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{2g}$	infrared, cm^{-1} ν(C=N)
$NiL(NCS)_2$ (L = **2**)	–[b]	563 (33)	922 (23)	2071
$NiLCl_2$ (L = **4**)[c]	410 (31)	644 (24)	1132 (47)	
$NiL(NCS)_2$ (L = **4**)	368 (60)	587 (39)	969 (35)	2077
$NiLCl_2$ (L = **5**)	400 (33)	637 (26)	1130 (8)	
$NiL(NCS)_2$ (L = **5**)	370 (63)	580 (40)	967 (36)	2077
$NiLCl_2$ (L = **6**)	400 (36)	635 (27)	1120 (10)	
$NiL(NCS)_2$ (L = **6**)	370 (66)	585 (29)	968 (36)	2079
$NiL(NCS)_2$ (L = **7**)	370 (57)	582 (36)	960 (28)	2078
$NiLCl_2$ (L = **9**)	415 (54)	695 (26)	~1160 (3)	
$NiL(NCS)_2$ (L = **9**)	385 (77)	620 (42)	1040 (26)	2083
$NiL(NCS)_2$ (L = **10**)	389 (55)	625 (55)	1032 (45)	2081
$NiLCl_2$ (L = **11**)	418 (37)	670 (22)	1183 (11)	
$NiL(NCS)_2$ (L = **11**)	378 (44)	610 (24)	1009 (37)	2082
$NiL(NCS)_2$ (L = **12**)	382 (46)	620 (24)	1020 (41)	2081

[a] Other compounds in the series are insufficiently soluble to obtain spectra in CH_2Cl_2 or $CHCl_3$. [b] Obscured by the edge of a more intense peak in the ultraviolet region. [c] In $CHCl_3$.

Physical data for the complexes are listed in Table I. All complexes are nonelectrolytes in nitrobenzene and have magnetic moments which are typical of high-spin nickel(II). Apart from the N-methylated derivatives, the infrared spectra of all complexes contain ν(N–H) modes in the region 3285–3160 cm^{-1}; such absorptions are typical of coordinated secondary amines. In most cases the solid-state electronic spectra indicate octahedral coordination; however, for several of the dihalogeno complexes additional spectral complexity is evident. Because of limited resolution, it is difficult to make definite assignments for these latter complexes; nevertheless the spectra approximate those expected for distorted octahedral complexes.

Visible–near-infrared spectra were determined for a selection of the complexes in dichloromethane or chloroform (Table II). Each complex shows only three d–d bands and, since these bands are not split, the solution spectra are all as expected for octahedral ligand fields. The apparent symmetry of these complexes is, perhaps, somewhat surprising when the mixed donor nature of the ligands is considered. Comparison of the position of $^3A_{2g} \rightarrow {}^3T_{2g}$ transition for the various complexes containing similar monodentate ligands but different macrocycles indicates that the ligand field strength of the macrocycles decreases in the order 2 > 4 ~ 5 ~ 6 ~ 7 > 11 > 12.[15] That is, excluding the N-methylated derivatives, there is a consistent decrease of ligand field strength with increase in macrocyclic ring size—a result which has been observed previously for other systems[16] and which can be considered to arise primarily from a forced shortening of the metal–donor bond distances for the smaller rings. It is of interest that incorporation of various substituents in the aromatic rings of the 15-membered macrocycle has little effect on the ligand field produced. However, N-methylation of the macrocyclic ring leads to a decrease in ligand field (9615 cm^{-1} for **9** compared with 10 320 cm^{-1} for **4**). N-Methylation of tetraaza macrocyclic ligands has been shown previously to result in a decrease in ligand field strength.[17]

The infrared spectra of the dithiocyanato complexes in dichloromethane (Table II) show, for each complex, only a single $\nu(C{=}N)$ band which is in the expected range for N-bonded coordination.[18] In addition, there is an interesting correlation between the observed stretching frequency and the macrocyclic ring size (as well as with 10*Dq*)—the $\nu(C{=}N)$ value increases as the ring size increases. In solution, the two thiocyanate groups of each complex are thus effectively in equivalent environments even though several of the thiocyanate complexes show a split $\nu(C{=}N)$ mode in the solid state (Table I).

The overall spectral evidence (and especially that from the solution spectra) suggest that all complexes in the series have a related octahedral (or pseudooctahedral) geometry and such a stereochemistry is also in accord with the other physical measurements. A preliminary X-ray study of $NiLCl_2$ (L = **4**) confirms that this complex adopts a trans-octahedral geometry.[19]

Where soluble, the complexes are dissociated moderately quickly in the presence of dilute hydrochloric acid to give the corresponding free ligand as its hydrochloride salt.[20] Thus the complexes do not show the extreme resistance to ligand dissociation which is a characteristic of the nickel complexes of related cyclic ligands incorporating four nitrogen donor atoms[10] and which is one feature of the "macrocyclic effect".[21] Similarly, dissociation of the macrocyclic ligand also occurs in the presence of strong chelating agents such as 1,10-phenanthroline, 2,2′-bipyridyl, and the tetraaza macrocycle cyclam.

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Registry No. $NiLCl_2$(L = **2**), 66793-50-8; $NiLBr_2$(L = **2**), 66793-51-9; $NiL(NCS)_2$(L = **2**), 66793-52-0; $NiLCl_2$(L = **3**), 66793-53-1; $NiLBr_2$(L = **3**), 66793-54-2; $NiL(NCS)_2$(L = **3**), 66793-55-3; $NiLCl_2$(L = **4**), 66810-83-1; $NiLBr_2$(L = **4**), 66793-56-4; $NiL(NCS)_2$(L = **4**), 66793-57-5; $NiLCl_2$(L = **5**), 66793-58-6; $NiLBr_2$(L = **5**), 66793-59-7; $NiL(NCS)_2$(L = **5**), 66793-60-0; $NiLCl_2$(L = **6**), 66793-61-1; $NiL(NCS)_2$(L = **6**), 66793-62-2; $NiLCl_2$(L = **7**), 66793-63-3; $NiLBr_2$(L = **7**), 66793-37-1; $NiL(NCS)_2$(L = **7**), 66793-38-2; $NiLCl_2$(L = **8**), 66793-39-3; $NiL(NCS)_2$(L = **8**), 66793-40-6; $NiLCl_2$(L = **9**), 66793-41-7; $NiL(NCS)_2$(L = **9**), 66793-42-8; $NiLBr_2$(L = **9**), 66793-43-9; $NiL(NCS)_2$(L = **10**), 66793-44-0; $NiLCl_2$(L = **11**), 66793-45-1; $NiLBr_2$(L = **11**), 66793-46-2; $NiL(NCS)_2$(L = **11**), 66793-47-3; $NiL(NCS)_2$(L = **12**), 66793-48-4; **6**, 66793-33-7; **7**, 66793-32-6; **8**, 66793-31-5; **9**, 66793-30-4; **10**, 66793-28-0; **12**, 66793-29-1.

Supplementary Material Available: A listing of analytical data for the complexes (1 page). Ordering information is given on any current masthead page.

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(12) Apart from yielding complexes of nickel(II) and other transition-metal ions, the present ligands also complex with a number of non-transition ions; an investigation of their interaction with selected alkali and alkaline earth ions is at present underway.

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