Contribution from the Department of Chemistry and Biochemistry,
James Cook University of North Queensland, P. O. James Cook University, Queensland 4811, Australia

Studies Involving Nitrogen–Oxygen Donor Macrocyclic Ligands. I. Nickel(II) Complexes of a New Series of Cyclic Ligands Derived from Salicylaldehyde

L. G. ARMSTRONG and L. F. LINDOY*

Received September 16, 1974 AIC40651I

A new series of nitrogen–oxygen macrocyclic ligands containing cis imine linkages have been prepared both by direct syntheses and by in situ procedures in the presence of nickel salts. The corresponding range of nickel complexes has been characterized and comparison has been made with nickel complexes of a related, previously reported trans-imine macrocycle. A series of novel diamine-exchange reactions has been observed and studied. In each of these, the diamine used to form the imine functions of the cyclic-ligand complex exchanges with 1,3-diaminopropane such that a new macrocyclic ligand derived from this diamine is produced. Comparison of the properties of the cyclic ligand complexes with those of an open-chain analog exemplifies the operation of the "macrocyclic" effect in the cyclic-ligand examples.

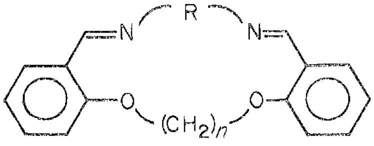
Introduction

The chemistry of synthetic macrocyclic ligands can be conveniently divided into two major divisions. First there are the studies involving cyclic polyether ligands of the "crown" type.[1] These ligands have an affinity for non transition metals such as the alkali and alkaline earth metal ions and, like several naturally occurring antibiotics, often exhibit remarkable selectivity for particular metal ions.[2] They also show considerable potential for the transport of certain of these cations across natural and artificial membranes.[3,4] Because of their possible use as therapeutic agents and also for other (nonbiological) applications, the cyclic polyether ligands have thus aroused considerable recent interest. In contrast to their behavior toward the above metal ions, this ligand type generally shows much less tendency to coordinate to transition metal ions.[3,5]

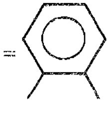
The other category of macrocyclic ligands are those which usually form quite stable complexes with transition metal ions. A number of donor atom types (mainly nitrogen or sulfur) have been incorporated in such ligands[6] and typical examples are the four-nitrogen quadridentates of the Curtis type.[7] Such transition metal complexes often show special properties which in some instances are related to those of the naturally occurring macrocyclic systems.[8] Compared to the polyethers, these ligands usually show much less tendency to form stable complexes with non transition ions such as those of the alkali and alkaline earth metals.[6]

Both categories of cyclic ligand thus often yield complexes which have unusual properties.

In this, the first paper of the series, the synthesis of a new series of cyclic ligands which are intermediate in structure between the above ligand categories is reported. The ligands are of type I and were prepared by both direct and in situ procedures in the presence of nickel(II) salts. Studies involving these and other related ligands with both transition and non transition metal ions will be reported subsequently. The aim of all these studies is to investigate more fully the chemistry (and, in particular, the metal ion specificity) of these intermediate ligand types in terms of the unusual properties of the well-studied categories of macrocycles mentioned above.



I

	Abbreviations when $n = 2$	 when $n = 3$
R = $-CH_2CH_2-$	*O*-en-*N*-en	*O*-tn-*N*-en
R = $-CH_2CH_2CH_2-$	*O*-en-*N*-tn	*O*-tn-*N*-tn
R = $-CH_2CH(CH_3)-$	*O*-en-*N*-pn	*O*-tn-*N*-pn
R = 	*O*-en-*N*-phen	*O*-tn-*N*-phen

Experimental Section

Analyses for carbon, hydrogen, and nitrogen were determined by Mr. J. Kent of the Microanalytical Laboratory, University of Queensland. Nickel was determined by atomic absorption spectroscopy. NMR spectra were obtained on a Jeol JNH-MH-100 spectrometer; ir spectra were recorded on a Jasco IRA-I spectrophotometer using Nujol mulls. The reflectance electronic spectra were determined on a Zeiss PMQ II spectrophotometer fitted with a RA3 reflectance attachment. We thank Dr. G. M. Mockler, Wollongong University College, for these spectra. Mass spectra were obtained on a CH-7 mass spectrometer by Dr. J. MacLeod, Australian National University. Magnetic moments were determined by the Gouy method using $HgCo(CNS)_4$ as calibrant. Conductance measurements were obtained using a Philips bridge, Model PR9501.

Preparation of Organic Compounds. Preparation of 1,5-Bis(2'-formylphenyl)-1,5-dioxapentane, *O*-tn. To salicylaldehyde (24.4 g, 0.2 mol) in alcohol (20 ml) was added sodium hydroxide (8.0 g, 0.2 mol) in water (400 ml). The mixture was warmed and 1,3-dibromopropane (20.2 g, 0.1 mol) was added. Sufficient alcohol (300 ml) to produce a homogeneous solution was then added. The solution was refluxed under nitrogen for 100 hr and then cooled and let stand at 0°. The cream-colored crystals produced were washed with water. Recrystallization was performed using an ether–chloroform mixture; yield 17.8 g (63%); mp 99° (lit.[9] mp 99°). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.68. Found: C, 71.82; H, 5.79.

Preparation of 1,4-Bis(2'-formylphenyl)-1,4-dioxabutane, *O*-en. By a procedure similar to that described above 1,2-dibromoethane (18.4 g, 0.1 mol) yielded the analogous product as white needles. The reaction time was 44 hr; yield 10.8 g (40%); mp 129°. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.87; H, 5.20.

Preparation of 3,4:9,10-Dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-1,11-diene, *O*-en-*N*-tn. To a solution of *O*-en (2.7 g, 0.01 mol) in absolute methanol (150 ml) was added slowly 1,3-diaminopropane (0.74 g, 0.01 mol) in absolute methanol (30 ml). The solution was refluxed for 1 hr. To the cool solution was added distilled water (200 ml) and the suspension was let stand at 0°. The white needles which deposited were washed with water and recrystallized from ether; yield 3.0 g (97%); mp 164°. Mass spectrum (70 eV): 308.4 (30%, parent ion), 280 (15%), 270 (15%), 162 (15%), 149 (20%), 122 (20%), 121 (20%), 105 (100%), 77 (30%). Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.01; H, 6.54; N, 9.08. Found: C, 73.74; H, 6.67; N, 9.19.

Preparation of 3,4:10,11-Dibenzo-1,13-diaza-5,9-dioxacyclohexadecane-1,12-diene, *O*-tn-*N*-tn. By a procedure similar to that described above *O*-tn (2.84 g, 0.01 mol) in absolute methanol (1500 ml) and 1,3-diaminopropane (0.74 g, 0.01 mol) in absolute methanol (200 ml) were refluxed for 3 hr and cooled; then excess distilled water was added. The white crystals were recrystallized from petroleum ether; yield 2.32 g (72%); mp 129°. Mass spectrum (17.5 eV): 322.4 (100%, parent ion), 294 (40%), 176 (30%), 152 (60%), 148 (50%), 134 (70%), 118 (50%), 107 (60%), 91 (70%), 77 (60%). Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.68. Found: C, 74.32; H, 7.08; N, 8.75.

Preparation of Macrocyclic-Ligand Complexes. Procedure A. The in Situ Synthesis of Nickel(II) Macrocyclic Complexes. To a hot butanol solution of dialdehyde (1 mol) and the corresponding nickel(II) salt (1 mol) was added slowly with stirring a hot butanol solution of diamine (1 mol). The solution was stirred and heated for 2 hr and then cooled. The product was filtered off, was washed sparingly with butanol and then ether, and was dried over P_2O_5 in vacuo.

Procedure B. The Direct Synthesis of Nickel(II) Macrocyclic Complexes. A solution of macrocyclic ligand (1 mol) in butanol was added to the nickel(II) salt (1 mol) in butanol. The mixture was stirred and heated for 30 min during which time the product precipitated. It was filtered off, was washed sparingly with butanol and then ether, and was dried over P_2O_5 in vacuo.

Ligand Isolation. General Procedure for the Removal of *O*-en-*N*-tn or *O*-tn-*N*-tn from Their Nickel Complexes. To a stirred suspension of the nickel complex (2 mmol) in absolute methanol (20 ml) was added 1,3-diaminopropane (6 mmol) in absolute methanol (10 ml). The suspension was stirred at room temperature for 30 min and the Ni(1,3-diaminopropane)$_3$X$_2$ was removed by filtration. The macrocycle was precipitated by the addition of water. It was recrystallized from ether. The melting points and infrared and NMR spectra of all products corresponded to those of authentic samples prepared as described above.

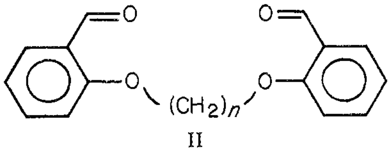
Diamine-Exchange Reactions. Isolation of *O*-en-*N*-tn by the Reaction of 1,3-Diaminopropane with Ni(*O*-en-*N*-pn)X$_2$ (X = Br, I) (in a 3:1 Molar Ratio). General Procedure. To a stirred suspension of the nickel complex (6 mmol) in absolute methanol (20 ml) was added 1,3-diaminopropane (18 mmol) in absolute methanol. The mixture was stirred at room temperature for 30 min. The precipitated tris(diamine)nickel(II) halide was filtered off. The macrocycle *O*-en-*N*-tn was recovered from the filtrate by the addition of water. It was recrystallized from ether; typical yield 65%; mp 164°.

Isolation of Ni(*O*-en-*N*-tn)(NCS)$_2$ by Reaction of 1,3-Diaminopropane with Ni(*O*-en-*N*-en)(NCS)$_2$ or Ni(*O*-en-*N*-pn)(NCS)$_2$ (in a 1:1 Molar Ratio). General Procedure. To a stirred suspension of the nickel complex (0.55 mmol) in dry methanol (10 ml) at room temperature was added 1,3-diaminopropane solution (1 ml of a 0.55 *M* solution in methanol). The resulting suspension was stirred for 30 min during which time a color change occurred. The precipitate was filtered off, was washed with methanol then ether, and was dried over P_2O_5 in vacuo; typical yield 35%. In each case the amine-exchanged product gave an infrared spectrum identical with that of an authentic sample prepared directly from *O*-en-*N*-tn as described previously.

Preparation of Ni(trans-MC)(NCS)$_2$. A solution of trans-MC ligand (0.5 g, 1.7 mmol) in alcohol (30 ml) was added with stirring to nickel perchlorate hexahydrate (0.62 g, 1.7 mmol) and potassium thiocyanate (0.34 g, 3.5 mmol) in butanol (30 ml). A gray precipitate of Ni(trans-MC)(NCS)$_2$ formed. This was filtered, washed with ether, and dried in vacuo over P_2O_5; yield 0.15 g (20%). Anal. Calcd for $C_{20}H_{18}N_4O_2NiS_2$: C, 51.20; H, 3.87; N, 11.94. Found: C, 51.09; H, 3.87; N, 11.68.

Results and Discussion

Dialdehydes have been used previously as precursors for macrocyclic-ligand syntheses since they can often be induced to undergo Schiff base cyclization reactions when allowed to react with diamines.[6] Williamson condensations between salicylaldehyde and the appropriate dibromoalkanes have been used in the present work to obtain dialdehydes of type II. The infrared spectra of these products each show a carbonyl mode at 1680 cm^{-1} and an aromatic mode at 1600 cm^{-1}. The NMR spectra are summarized in Table I and these spectra are in accord with the proposed structures. Both direct synthesis and in situ procedures, in the presence of nickel salts, have been used to obtain the cyclic ligands I which in the case of the in situ reactions were obtained as their nickel complexes. Condensation of 1,3-diaminopropane with each of the dialdehydes yields in each case the corresponding macrocyclic ligand which can be isolated from the methanol reaction solution by the addition of water.[10] The ligand *O*-en-*N*-tn appeared particularly resistant to hydrolysis. The high yield obtained for this product indicated that side reactions, such as formation of polymers, are insignificant under the conditions used for the synthesis. On the other hand, the attempted synthesis of *O*-tn-*N*-tn did not yield a single product. Although the major product isolated was the required one, it was contaminated with an impurity which appeared to be polymeric. However the crude product can be successfully recrystallized from petroleum ether from which pure *O*-tn-*N*-tn is obtained as white needles.



II

Table I. NMR Spectral Data for Organic Products

Compd	Chem shifts[a]
O-en	4.53 (singlet, CH$_2$), 7–8 (multiplet, aromatic), 10.38 (singlet, CHO)
O-tn	2.44 (quintet, CH$_2$), 4.34 (triplet, CH$_2$), 7–8 (multiplet, aromatic), 10.47 (singlet, CHO)
O-en-*N*-tn	2.29 (quintet, CH$_2$), 3.63 (triplet, N–CH$_2$), 4.35 (singlet, O–CH$_2$), 6.8–8.0 (multiplet, aromatic), 8.70 (singlet, CH=N)
O-tn-*N*-tn	2.20 (multiplet, CH$_2$), 3.64 (multiplet, N–CH$_2$), 4.20 (multiplet, O–CH$_2$), 6.8–8.0 (multiplet, aromatic), 8.66, 8.70 (singlets, CH=N)

[a] All resonances in ppm downfield from TMS. $CDCl_3$ was used as solvent in each case. In every case the integral peak heights are in accord with the proposed assignments.

Infrared spectra of the products confirm that Schiff base condensation has occurred by the absence of amine or carbonyl absorption bands and by the presence of imine and aromatic stretching modes at approximately 1640 and 1600 cm^{-1}. The NMR spectrum of *O*-en-*N*-tn (Table I) shows the expected pattern confirming the presence of imine, aromatic, and methylene protons. The spectrum of *O*-tn-*N*-tn, on the other hand, is a little more complex (Table I). This additional complexity presumably results from the presence of conformational isomers in solution. For both ligands, the integral peak values are in accord with the assignments given in the table. Mass spectral data (see Experimental Section) and elemental analyses also support the proposed cyclic Schiff base structures.

Reaction of these macrocyclic ligands with various nickel(II) salts in butanol yields complexes of the type [Ni(*O*-en-*N*-tn)X$_2$] and [Ni(*O*-tn-*N*-tn)X$_2$] where X = Cl, Br, I, NCS. In situ condensation of the dialdehydes and various diamines in butanol also leads to an additional series of nickel macrocyclic complexes, viz., [Ni(*O*-en-*N*-en)X$_2$], [Ni(*O*-tn-*N*-en)X$_2$], [Ni(*O*-en-*N*-pn)X$_2$], [Ni(*O*-tn-*N*-pn)X$_2$], [Ni(*O*-en-*N*-phen)X$_2$], and [Ni(*O*-tn-*N*-phen)X$_2$] where X = Br, I, NCS. The reactions should be performed in dry solvent as many of the complexes are quite susceptible to hydrolysis. In addition, if the diamine is added too fast, a competitive reaction was usually observed to occur with the precipitation of the corresponding tris(diamine)nickel(II) complex.

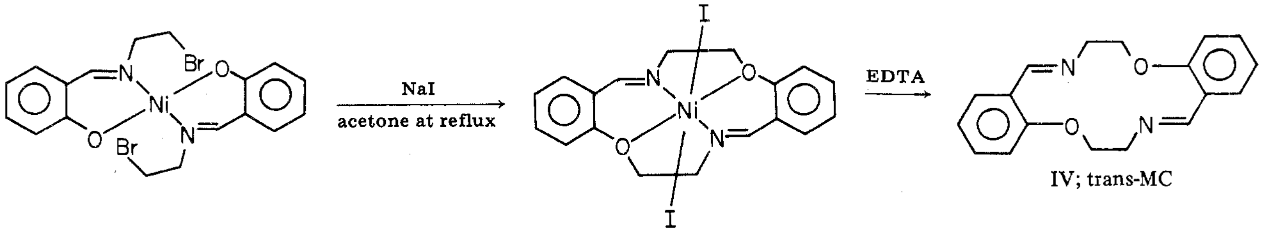
Table II lists selected infrared data for all the complexes. The spectra are all typical of aromatic imine complexes with major bands at approximately 1640 and 1600 cm^{-1}. The spectra are devoid of amine or aldehyde stretching modes thus strongly suggesting that cyclization *via* the Schiff base reaction has occurred. All the thiocyanate complexes exhibit thiocyanate absorptions near 2070 and 790 cm^{-1} and such values are typical of this anion when it is N bonded.[11]

Table II. Properties of Nickel(II) Macrocyclic Complexes

Compd	Method of prepn[a]	Color	% C		% H		% N		% Ni		Infrared spectra, cm^{-1}		Magnetic moment[b]	Electronic spectra, major solid-state bands,[c] cm^{-1}
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Aromatic and imine modes	Anion modes		
Ni(*O*-en-*N*-en)Br$_2$	A	Yellow	42.15	42.28	3.54	3.63	5.46	5.20	11.45	11.4	1660, 1650 sh, 1630 sh, 1600, 1570, 1550 sh		3.19 (297°)	18,600, 15,600, 9200
Ni(*O*-en-*N*-en)I$_2$	A	Brown	35.63	35.63	2.99	3.22	4.62	4.59	9.67	9.5	1650, 1630 sh, 1620 sh, 1595, 1570 sh, 1555 sh		3.12 (297°)	23,400, 15,500, 8300
Ni(*O*-en-*N*-en)(NCS)$_2$	A	Gray	51.20	50.96	3.87	3.94	11.94	11.7	12.51	12.4	1645, 1630 sh, 1595, 1565 sh	2065, 790	3.17 (297°)	19,000, 9800
Ni(*O*-en-*N*-pn)Br$_2$	A	Green-yellow	43.31	43.45	3.83	3.87	5.32	5.29	11.14	11.4	1645, 1630 sh, 1625 sh, 1595, 1570, 1560 sh		3.18 (297°)	18,600, 15,000, 9100
Ni(*O*-en-*N*-pn)I$_2$	A	Brown	36.75	37.04	3.25	3.45	4.51	4.61	9.46	9.4	1640, 1620 sh, 1595, 1570 sh		3.08 (296°)	23,800, 15,400, 8700
Ni(*O*-en-*N*-pn)(NCS)$_2$	A	Green	52.20	52.10	4.17	4.00	11.59	11.3	12.15	12.5	1640, 1615 sh, 1600, 1570 sh, 1555 sh	2075, 790	3.15 (297°)	16,000, 9800
Ni(*O*-en-*N*-tn)Cl$_2$	B	Green	52.10	52.18	4.60	4.47	6.40	6.41	13.40	13.5	1635, 1595, 1570 sh, 1550 sh		3.21 (297°)	20,000, 15,800, 9500
Ni(*O*-en-*N*-tn)Br$_2$	A + B	Green	43.31	43.58	3.83	3.84	5.32	5.31	11.14	11.2	1635, 1620 sh, 1595 1570, 1555 sh		3.23 (297°)	19,100, 15,500, 8900
Ni(*O*-en-*N*-tn)I$_2$	A + B	Green-yellow	36.75	37.00	3.25	3.44	4.51	4.63	9.46	9.5	1635, 1620 sh, 1595, 1570, 1555 sh		3.26 (298°)	18,500, 15,700, 8400
Ni(*O*-en-*N*-tn)(NCS)$_2$	A + B	Blue	52.20	52.16	4.17	4.25	11.59	11.52	12.15	12.1	1635, 1620 sh, 1595, 1570, 1555 sh	2070, 2100, 795	3.25 (297°)	17,600, 11,000
Ni(*O*-en-*N*-phen)I$_2$	A	Orange	40.35	40.49	2.77	3.00	4.28	4.40	8.96	8.9	1620, 1595, 1580 sh, 1565 sh		3.21 (297°)	21,500, 14,500, 8200
Ni(*O*-en-*N*-phen)(NCS)$_2$	A	Green	55.73	55.48	3.51	3.74	10.83	11.1	11.35	11.3	1615, 1595, 1570 sh, 1555 sh	2060, 790	3.19 (297°)	17,600, 11,200
Ni(*O*-tn-*N*-en)Br$_2$	A	Green	43.31	43.49	3.83	3.95	5.32	5.23	11.14	10.9	1630, 1620 sh, 1600, 1580 sh, 1550		3.20 (297°)	16,300, 12,000, 8500
Ni(*O*-tn-*N*-en)I$_2$	A	Green	36.75	36.48	3.25	3.22	4.51	4.58	9.46	9.4	1660, 1630 sh, 1600, 1580 sh, 1550 sh		3.10 (297°)	23,600, 16,400, 8300
Ni(*O*-tn-*N*-en)(NCS)$_2$	A	Blue	52.20	52.47	4.17	4.47	11.59	11.3	12.15	11.9	1650, 1630 sh, 1600, 1580 sh, 1570 sh, 1550	2070, 790	3.15 (297°)	17,900, 11,100
Ni(*O*-tn-*N*-pn)I$_2$	A	Yellow	37.83	37.54	3.49	3.75	4.41	4.62	9.25	9.3	1650, 1630 sh, 1600, 1580 sh, 1560 sh		3.18 (296°)	23,600, 16,100, 8300
Ni(*O*-tn-*N*-pn)(NCS)$_2$	A	Blue	53.14	53.30	4.46	4.72	11.27	11.1	11.81	11.8	1650, 1640 sh, 1620 sh, 1600, 1570 sh	2070, 790	3.26 (296°)	17,500, 11,100
Ni(*O*-tn-*N*-tn)Cl$_2$	B	Green	53.14	53.01	4.90	5.09	6.20	6.04	12.99	13.2	1640, 1630 sh, 1620 sh, 1600, 1580 sh, 1560 sh		3.22 (297°)	20,000, 15,700, 9300
Ni(*O*-tn-*N*-tn)Br$_2$	A + B	Green	44.41	44.19	4.10	4.27	5.18	5.02	10.85	11.0	1635, 1610 sh, 1595, 1565 sh, 1555 sh		3.23 (298°)	19,100, 15,400, 9000
Ni(*O*-tn-*N*-tn)I$_2$	A + B	Yellow	37.83	37.67	3.49	3.62	4.41	4.21	9.25	9.0	1635, 1615 sh, 1595, 1575 sh, 1560 sh		3.21 (297°)	18,200, 15,500, 8100
Ni(*O*-tn-*N*-tn)(NCS)$_2$	A + B	Blue	53.14	53.37	4.46	4.71	11.27	11.23	11.81	11.6	1645, 1630 sh, 1600, 1580, 1560 sh, 1550 sh	2080, 800	3.25 (298°)	17,500, 11,100
Ni(*O*-tn-*N*-phen)Br$_2$	A	Green	48.05	47.89	3.51	3.52	4.87	5.15	10.21	10.1	1640, 1635 sh, 1620 sh, 1600, 1580 sh, 1570 sh		3.29 (297°)	17,000, 12,100, 8900
Ni(*O*-tn-*N*-phen)I$_2$	A	Brown	41.30	41.56	3.01	3.21	4.19	4.16	8.78	8.8	1630, 1600, 1570 sh, 1560 sh		3.12 (296°)	24,500, 12,300, 8900
Ni(*O*-tn-*N*-phen)(NCS)$_2$	A	Green	56.52	56.54	3.79	4.00	10.55	10.3	11.05	10.8	1630, 1600, 1580 sh, 1570 sh, 1560 sh	2080, 795	3.21 (297°)	17,600, 11,200

[a] Method A, prepared by in situ reaction; method B, prepared directly from free macrocycle. [b] In Bohr magnetons; temperature of determination in parentheses. [c] All spectra also contain a high-energy charge-transfer band. The majority also contain less intense shoulders on the major bands quoted.

Scheme I



III

IV; trans-MC

All complexes have magnetic moments (Table II) in the range 3.1–3.3 BM (at 297°K) and are thus typical of nickel(II) with a triplet ground state. Conductance measurements in methanol indicate that both anions are ionized in this solvent[12] since values in the range 150–180 ohm^{-1} cm^2 mol^{-1} were observed. Conductances in more weakly coordinating solvents such as nitromethane or nitrobenzene could not be obtained because of the low solubility of the complexes. The solid-state spectra show evidence, in all complexes, for distortion from O_h symmetry with the thiocyanates appearing least distorted. The spectra of all iodide complexes are obscured, to a large extent, by charge-transfer bands which extend across the visible region. Apart from charge-transfer transitions, the spectra of the chloride and bromide salts have at least three major bands in the region 25,000–8000 cm^{-1}; however all these spectra contain other less intense shoulders associated with each of these major peaks. Because of the complexity of these spectra it is difficult to make definite spectral assignments for these compounds. As mentioned above, the spectra of the thiocyanate complexes are simpler and two d–d bands can be observed in the visible region. The spectra approximate that expected for an octahedral ligand field with the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ ranging from 9800 cm^{-1} (for *O*-en-*N*-en and *O*-en-*N*-pn) to 11,200 cm^{-1} (for *O*-en-*N*-phen and *O*-tn-*N*-phen); if O_h symmetry is assumed, the energy of this transition gives the value of 10*Dq* directly.

The closely related nickel iodide complex III of the trans-imine ligand (IV; trans-MC) was also prepared in the present study using the previously reported in situ procedure[13] illustrated in Scheme I. This complex has been shown by X-ray diffraction to be tetragonal with the iodide ions occupying axial positions.[14] A new thiocyanate complex Ni(trans-MC)NCS$_2$ was also synthesized directly from the free cyclic ligand (IV). Like that of Ni(trans-MC)I$_2$, the reflectance spectrum of the thiocyanate complex is similar in overall pattern to the halide complexes of the cis-imine ligands and contains major d–d absorptions at 19,000, 13,900, and 8300 cm^{-1}. The infrared spectrum of this complex shows the expected imine and aromatic bands at 1660 and 1600 cm^{-1} together with thiocyanate modes at 2070 and 780 cm^{-1}. The positions of the latter absorptions are once again indicative of N-bonded terminal thiocyanate groups.[11] This complex, like all the complexes prepared in the present study, very likely has a tetragonal geometry with the macrocycle coordinating in a planar conformation.

Although a number of polydentate macrocyclic ligands incorporating both oxygen and nitrogen donor atoms have been synthesized recently,[15–21] apart from the present ligands of type I, IV appears to be the only unsaturated quadridentate macrocycle of this type to be reported previously.[13]

Attempts to remove the macrocyclic ligands of type I from their respective nickel complexes using conventional sequestering reagents such as dimethylglyoxime, cyanide, or ethylenediaminetetraacetic acid were not satisfactory, under the conditions of our experiments, owing to competing solvolysis and/or other reactions which yielded contaminated products. However addition of 3 molar equiv of 1,3-diaminopropane to a suspension of Ni(*O*-en-*N*-tn)X$_2$ or Ni(*O*-tn-*N*-tn)X$_2$ (where X = Br, I) in dry methanol leads to precipitation of Ni(1,3-diaminopropane)$_3$X$_2$, and the corresponding macrocycle, *O*-en-*N*-tn or *O*-tn-*N*-tn, can be isolated from the filtrate. As discussed previously, these two macrocycles were also the only two which were obtained by direct synthesis.

Related attempts to remove the ligand from Ni(*O*-en-*N*-en)X$_2$ or Ni(*O*-en-*N*-pn)X$_2$ by a similar procedure to the above using ethylenediamine or 1,2-diaminopropane were not successful and the free macrocycles could not be isolated intact from the reaction solution. However when 1,3-diaminopropane was used in the above procedure, then novel amine-exchange reactions were observed and the amine-exchanged free macrocycle *O*-en-*N*-tn was isolated in each case

$$\text{Ni}(O\text{-en-}N\text{-en})\text{X}_2 + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{\text{X = Br, I}} O\text{-en-}N\text{-tn} + \text{Ni(diamine)}_3{}^{2+}$$

From this reaction it seems likely that macrocyclic ring opening occurs in each of the above cases in which the free cyclic ligand is recovered from the reaction solution. Such a mechanism would facilitate removal of the ligand since, in the absence of ring opening, dissociation of a cyclic ligand from its metal ion is usually kinetically slow (the kinetic inertness coupled with the usual considerable thermodynamic stability of most macrocyclic-ligand complexes has been collectively termed the "macrocyclic effect").[22,23] When the amount of 1,3-diaminopropane is restricted to 1 molar equiv, then simple amine exchange occurs and the new macrocycle is obtained as its nickel complex

$$\text{Ni}(O\text{-en-}N\text{-pn})\text{NCS}_2 + \text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{Ni}(O\text{-en-}N\text{-tn})(\text{NCS})_2 + \text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$$

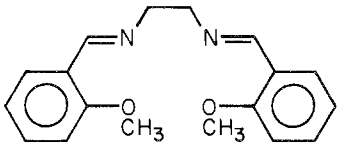
Such reactions very likely proceed by nucleophilic attack of the exchanging amine on the imine carbon atoms of the coordinated macrocycle.

Other amine-exchange reactions involving coordinated imine functions have previously been reported for a series of complexes of bidentate Schiff base ligands.[24,25] For these, amine exchange occurred only when the exchanging amine is considerably more basic than the amine initially used to form the imine complex. In addition, such reactions appear to be equilibrium controlled and the presence of a large excess of exchanging amine favors the reaction.

In the present reactions the exchanging amine [1,3-diaminopropane (pK_{a_1} = 8.98, pK_{a_2} = 10.72)] is more basic than the amines it replaces [1,2-diaminoethane (pK_{a_1} = 7.18, pK_{a_2} = 9.96) or 1,2-diaminopropane (pK_{a_1} = 7.13, pK_{a_2} = 10.00)[26]]. However, as mentioned previously, the diamine does not need to be present in excess for exchange to occur. Undoubtedly other factors also operate in the present reactions since the cyclic ligands which incorporate three methylene groups separating the imine groups are, once again, the only ones which are stable enough to be isolated in the absence of a metal ion. It is uncertain whether the enhanced stabilities of these particular ring systems arise solely from favorable steric or electronic factors or from a combination of both.

Comparison of the behavior of the present ligands toward nickel with that of the previously reported[27] open-chain analog

V illustrates dramatically the operation of the macrocyclic



V

effect. Whether in solution or in the solid, the open-chain ligand V shows no evidence of coordinating as a quadridentate ligand toward nickel;[27] it is bidentate using only the two nitrogen atoms as donors.

Acknowledgment. The authors acknowledge the Australian Research Grants Committee for support and wish to thank Dr. H. C. Lip for assistance.

Registry No. Ni(*O*-en-*N*-en)Br$_2$, 52442-21-4; Ni(*O*-en-*N*-en)I$_2$, 52442-23-6; Ni(*O*-en-*N*-en)(NCS)$_2$, 54484-47-8; Ni(*O*-en-*N*-pn)Br$_2$, 52442-27-0; Ni(*O*-en-*N*-pn)I$_2$, 52442-29-2; Ni(*O*-en-*N*-pn)(NCS)$_2$, 54484-48-9; Ni(*O*-en-*N*-tn)Cl$_2$, 52613-91-9; Ni(*O*-en-*N*-tn)Br$_2$, 52613-92-0; Ni(*O*-en-*N*-tn)I$_2$, 52613-93-1; Ni(*O*-en-*N*-tn)(NCS)$_2$, 54484-46-7; Ni(*O*-en-*N*-phen)I$_2$, 52442-35-0; Ni(*O*-en-*N*-phen)(NCS)$_2$, 54484-45-6; Ni(*O*-tn-*N*-en)Br$_2$, 52442-22-5; Ni(*O*-tn-*N*-en)I$_2$, 52442-24-7; Ni(*O*-tn-*N*-en)(NCS)$_2$, 54484-44-5; Ni(*O*-tn-*N*-pn)I$_2$, 52442-30-5; Ni(*O*-tn-*N*-pn)(NCS)$_2$, 54484-43-4; Ni(*O*-tn-*N*-tn)Cl$_2$, 52659-69-5; Ni(*O*-tn-*N*-tn)Br$_2$, 52659-70-8; Ni(*O*-tn-*N*-tn)I$_2$, 52659-71-9; Ni(*O*-tn-*N*-tn)(NCS)$_2$, 54484-42-3; Ni(*O*-tn-*N*-phen)Br$_2$, 52442-34-9; Ni(*O*-tn-*N*-phen)I$_2$, 52442-36-1; Ni(*O*-tn-*N*-phen)(NCS)$_2$, 54484-41-2; *O*-en, 52118-10-2; *O*-tn, 17954-12-0; *O*-en-*N*-tn, 52026-37-6; *O*-tn-*N*-tn, 51950-95-9; salicylaldehyde, 90-02-8; 1,3-dibromopropane, 109-64-8; 1,2-dibromoethane, 106-93-4; 1,3-diaminopropane, 109-76-2; Ni(trans-MC)(NCS)$_2$, 54484-49-0.

References and Notes

(1) C. J. Pederson, *J. Am. Chem. Soc.*, **89**, 2495, 7017 (1967); **92**, 386, 391 (1970).
(2) R. M. Izatt, D. J. Eatough, and J. J. Christensen, *Struct. Bonding (Berlin)*, **16**, 161 (1973); *Chem. Rev.*, **74**, 351 (1974).
(3) C. J. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).
(4) W. Simon, W. E. Morf, and P. Ch. Meier, *Struct. Bonding (Berlin)*, **16**, 113 (1972).
(5) A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, **7**, 176 (1968).
(6) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(7) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(8) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, **No. 100**, 44 (1971).
(9) E. E. Schweizer, C. J. Beringer, D. M. Crouse, R. A. Davies, and R. S. Logothetis, *J. Org. Chem.*, **34**, 207 (1969).
(10) Prepared in collaboration with J. Rea, James Cook University.
(11) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961); J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).
(12) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(13) R. W. Kluiber and G. Sasso, *Inorg. Chim. Acta*, **4**, 226 (1970).
(14) D. L. Johnston and W. D. Horrocks, *Inorg. Chem.*, **10**, 687 (1971).
(15) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885, 2889 (1969).
(16) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Chem. Commun.*, 1055 (1970).
(17) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).
(18) J. Cheney and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 487 (1972).
(19) P. A. Tasker and E. B. Fleischer, *J. Am. Chem. Soc.*, **92**, 7072 (1970).
(20) J. Lehn, J. Simon, and J. Wagner, *Angew. Chem., Int. Ed. Engl.*, **12**, 578, 579 (1973).
(21) G. R. Newkome and J. M. Robinson, *J. Chem. Soc., Chem. Commun.*, 831 (1973); J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974).
(22) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **91**, 6540 (1969); **92**, 2151 (1970).
(23) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, **12**, 1961 (1973).
(24) E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 345 (1965).
(25) L. F. Lindoy, *Q. Rev., Chem. Soc.*, 379 (1971), and references therein.
(26) L. Mites, "Handbook of Analytical Chemistry", McGraw-Hill, New York, N.Y., 1963.
(27) L. Sacconi and I. Bertini, *Inorg. Chem.*, **7**, 1178 (1968); L. G. Armstrong and L. F. Lindoy, unpublished work.

Contribution from the Department of Chemistry,
The University of Texas at Arlington, Arlington, Texas 76019

Kinetic, Thermodynamic, and Spectral Study of Fluorine-Substituted Acetyl and Methyl Complexes of Iridium(III)

DANIEL M. BLAKE,* ALAN WINKELMAN, and YEN LUNG CHUNG

Received October 24, 1974 AIC40740V

Five- and six-coordinated acyl complexes having the formula $IrCl_2[C(O)CF_nH_{3-n}][P(C_6H_5)_3]_2$ ($n = 1$ or 2) and $IrCl_2[C(O)CF_nH_{3-n}](CO)[PCH_3(C_6H_5)_2]_2$ ($n = 1$, 2, or 3) have been prepared for the first time. The five-coordinated complexes undergo an alkyl group migration reaction upon heating in solution or as a solid to give new six-coordinated complexes, $IrCl_2(CF_nH_{3-n})(CO)[P(C_6H_5)_3]_2$. They reversibly add carbon monoxide in solution and form adducts with dimethylformamide. New trifluoromethyl complexes, $IrXICF_3(CO)[PCH_3(C_6H_5)_2]_2$ (X = Cl or Br), have been prepared via an oxidative addition reaction of trifluoromethyl iodide. The ir, ^1H and ^{19}F NMR, and electronic spectra of series of iridium(III) complexes containing the fluorine-substituted acyl group, $C(O)CF_nH_{3-n}$, and fluorine-substituted methyl group, CF_nH_{3-n} (where $n = 3$, 2, 1, or 0), have been studied to determine the effect of fluorine substitution in methyl and acetyl groups on the physical and chemical properties of both five- and six-coordinated complexes. The trans influence of acetyl groups, evaluated from ν(Ir–Cl) data, decreases with increasing fluorine substitution. The trans influence of the substituted methyl group decreases in the order $CH_3 > CHF_2 \approx CH_2F > CF_3$. The kinetics of the migration reaction in which the five-coordinated acyl complexes are converted to six-coordinated alkyl–carbonyl complexes have been studied in toluene. The rate of the migration decreases in the order $CFH_2 > CF_3 > CF_2H$. Calorimetric measurements for the same compounds establish that the enthalpy change for the migration becomes less exothermic in the order $CF_3 > CF_2H > CFH_2$. The calorimetric data allow determination of an approximate value for the difference between Ir–CF_3 and Ir–CH_3 bond strengths. A combination of the calorimetric and kinetic data is used to predict activation parameters for insertion of carbon monoxide into metal–fluorocarbon bonds.

Stable transition metal complexes containing acyl groups, –C(O)R, as ligands are useful as models for intermediates postulated to occur in a variety of catalytic and stoichiometric reactions of transition metal complexes.[1] Of particular significance are the coordinatively unsaturated iridium(III) complexes $IrCl_2[C(O)R][P(C_6H_5)_3]_2$, where R is a substituted benzyl group,[2] $IrCl_2[C(O)CF_3][P(C_6H_5)_3]_2$,[3] and similar rhodium(III) complexes which have been reported (see ref 4