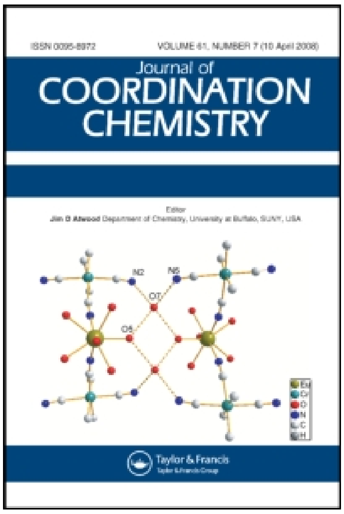


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

TEMPLATE REACTIONS: AXIAL-LIGATION AND MACROCYCLIZATION OF ALPHA-FURILGLYOXIMATES AND ALPHA-AMINEDIOXIMATES OF COBALT(III) AND RHODIUM(III)

M. Sakhawat Hussain[a]; H. M. Al-mohdhar[a]; A. R. Al-arfaj[a]
[a] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

To cite this Article Hussain, M. Sakhawat , Al-mohdhar, H. M. and Al-arfaj, A. R.(1988) 'TEMPLATE REACTIONS: AXIAL-LIGATION AND MACROCYCLIZATION OF ALPHA-FURILGLYOXIMATES AND ALPHA-AMINEDIOXIMATES OF COBALT(III) AND RHODIUM(III)', Journal of Coordination Chemistry, 18: 4, 339 — 349

To link to this Article: DOI: 10.1080/00958978808080974

URL: http://dx.doi.org/10.1080/00958978808080974

J. Coord. Chem. 1988, Vol. 18. pp. 339–349
Reprints available directly from the publisher
Photocopying permitted by license only

TEMPLATE REACTIONS: AXIAL-LIGATION AND MACROCYCLIZATION OF ALPHA-FURILGLYOXIMATES AND ALPHA-AMINEDIOXIMATES OF COBALT(III) AND RHODIUM(III)

M. SAKHAWAT HUSSAIN,* H. M. AL-MOHDHAR and A. R. AL-ARFAJ

Department of Chemistry, King Fahd University of Petroleum and Minerals, KFUPM Box 1830, Dhahran 31261, Saudi Arabia

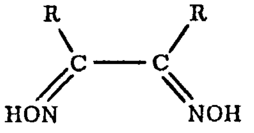
(Received March 18, 1988; in final form May 27, 1988)

A series of cobaloximes were synthesized from α-furilglyoximates and α-aminedioximates of cobalt(II), cobalt(III) and rhodium(III) and monodentate ligands having different inductive and steric requirements. The six-coordinate H-bonded macrocycles initially formed were used as metal templates to prepare the corresponding BF_2-capped macrocycles. Characterization of the complexes was carried out by magnetic, spectroscopic, ^1H and ^{13}C nmr measurements as well as elemental analysis. The cobaloximes reported are quite stable and mimic the metal core of several biological molecules such as vitamin B_{12}.

Keywords: macrocyclic, glyoximes, cobalt, rhodium, synthesis

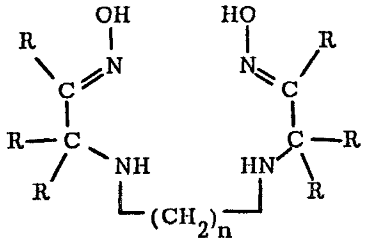
INTRODUCTION

Coordination compounds of vicinal glyoximes and tetradentate α-aminedioximes (Structures I and II) have been widely investigated as analytical reagents,[1] models for biological systems such as vitamin B_{12},[2-4] compounds having columnar stacking thought to be the reason for their semiconducting properties,[5] and recently, in macrocyclization reactions.[6-8] The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes *vic*-glyoximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with metal ions such as nickel(II), cobalt(II) and cobalt(III) as central atoms.[9-10]



R = alkyl or furane group

(I)



n = 2 or 3; R = CH_3

(II)

---

* Author for correspondence

In common with corrins, metal glyoximates undergo facile axial ligation with monodentate N-donors without effecting the planar arrangement around the central metal atom[4,7] and the relevant chemical analogies with vitamin B_{12} resides in the reactivity of the axial positions of these macrocycles.[4]

The pertinent glyoximates or macrocycles studied so far are principally derived from dimethylglyoxime, H_2dmg.[11-12] Recent investigations[8,13-15] of chelates of α-furilglyoxime (H_2afdo) have revealed that the presence of electron-accepting substituents on the α-carbon atoms in *vic*-glyoximes effects the distribution of electron density in the metal–nitrogen bonds and in the short intramolecular hydrogen bonds of the planar chelate compounds. Thus, the structures of α-furilglyoximates and their corresponding BF_2-macrocycles differ in many respects from those of their H_2dmg counterparts. For example, [M(Hdmg)$_2$] complexes (M = nickel(II), palladium(II) and platinum(II)) have columnar stacked structures[5] with metal–metal distances ranging from 3.25 to 3.46 Å whereas the BF_2-capped macrocycle [Ni(BF_2dmg)$_2$] is a dimer and forms 1:1 diadducts of N-bases with complete retention of the dimeric nature of the parent molecule.[11-12] Contrary to the H_2dmg complexes, the macrocyclic H_2afdo complex [Ni(BF_2afdo)$_2$] is a monomer without any columnar stacking[13] though the uncyclized [Pd(H_2afdo)$_2$] did reveal[14] a columnar structure which would be expected to exhibit semiconducting properties.

As a part of our continuing research dealing with template reactions, we report here synthesis and characterization of a series of novel glyoximates and their BF_2-capped macrocycles using cobalt(II), cobalt(III) and rhodium(III) as central metal atoms and α-furilglyoxime and/or α-aminedioximes as ligands. Macrocyclization was carried out with $Et_2O:BF_3$and monodentate ligands of different inductive and steric requirements were used for axial ligation.

EXPERIMENTAL

Chemicals and Materials

All chemicals and solvents were of analytical grade and used without further purification except for $Et_2O:BF_3$ which was freshly distilled before use. The ligand α-furilglyoxime was obtained from the Fluka Chemical Company while α-aminedioximes were prepared using known procedures[17] with some modifications. The elemental analyses were carried out with a Carlo Erba 1106 instrument.

Axial Ligation Reactions

The following general procedure was used for the preparation of most of the complexes. An aqueous solution of the metal salt was added to the dioxime which was dissolved in ethanol. The mole ratio metal:dioxime:ligand was kept close to 1:2:3 with the ligand in a slight excess. The pH of solution, in the cases of [M(Hafdo)$_2$(H_2O)$_2$] (M = cobalt(II), rhodium(III)), was adjusted close to 5, for precipitation of the corresponding products. In most cases cobalt(II) was oxidized to cobalt(III) upon stirring the solution for an hour without using any oxidizing agent. In some cases, however, oxygen was passed through the solution for complete oxidation. All products were washed with distilled water and ether and dried under vacuum. Recrystallization of the products was carried out from acetone.

BF_2-Macrocyclization Reactions

Macrocyclization was carried out either by treating the six-coordinate complexes with an excess of freshly distilled $Et_2O:BF_3$ or by stirring the metal salt solution, the complexing agent and the monodentate ligand in the presence of excess of $Et_2O:BF_3$ in dichloromethane for 6–8 hours at room temperature. Elemental analyses were in satisfactory agreement with the proposed stoichiometries.

Spectroscopic Measurements

The electronic spectra of DMSO solutions of the complexes in the range 200–700 nm were recorded on a Varian UV-VIS-NIR, Cary 2390 or DMS90 instrument. The solid state infrared spectra of KBr pellets in the range 4600–400 cm^{-1} were recorded with a Nicolet FTIR 5DXB or DX20 spectrophotometer and λ_{max} data, molar absorptivities and characteristic infrared absorptions are given in Table I.

TABLE I

Electronic and infrared spectral data for cobaloxime-type complexes of alpha-furilglyoximates and their macrocycles.*

	concentration (mol dm^{-3})	λ_{max} (nm)	(cm^{-1})	ε (M^{-1} cm^{-1})
(A) Electronic Spectra:				
Six-Coordinated complexes, and ligands				
H_2afdo	0.363	270	37040	2.31
[Co(Hafdo)$_2$(H$_2$O)]	0.12	285	35090	3.25
[Co(Hafdo)$_2$(Py)(Cl)]	1.370	280	35710	0.37
		370	27030	0.14
[Co(Hafdo)$_2$(TPPSe)$_2$]ClO$_4$.2H$_2$O	0.170	270	37040	2.76
[Co(Hafdo)$_2$(*p*-Tolu)$_2$]NO$_3$	0.285	285	35090	2.45
		372	26880	1.48
[Co(Hafdo)$_2$(DEtOHA)$_2$]NO$_3$	0.170	270	37040	2.76
[Co(Hafdo)$_2$(TPAs)$_2$]ClO$_4$	0.044	270	37040	8.11
		370	27030	1.80
[Co(Hafdo)$_2$(TPAsO)$_2$]ClO$_4$.H$_2$O	0.199	270	37040	3.42
[Co(HBuAO]Cl$_2$.H$_2$O	0.924	270	37040	0.85
[CoHpnAO]Cl.H$_2$O	1.07	285	35090	5.49
[Rh(Hafdo)$_2$(TPAs)$_2$]NO$_3$.2H$_2$O	0.192	270	37040	4.00
[Rh(Hafdo)$_2$(Anil)Cl].5H$_2$O	0.284	285	35090	1.94
[Rh(Hafdo)$_2$(H$_2$O]$_2$)	0.139	280	35700	5.34
		360	27780	0.94
[Rh(Hafdo)$_2$(Pip)Cl].4H$_2$O	0.081	285	35090	6.97
[Rh(Hafdo)$_2$(DEtA)$_2$]Cl	0.158	280	35700	3.57
[Rh(HBuAO)Cl$_2$]2H$_2$O	1.50	270	37040	0.67
[Ni(HpnAO)]Cl	0.536	280	35700	1.19
BF_2-Macrocycles				
[Co(BF$_2$afdo)$_2$(PY)$_2$]	0.127	270	37040	4.66
		325	30770	2.37
	0.844	430	23260	0.50
[Co(BF$_2$afdo)$_2$(H$_2$O)$_2$]	0.082	285	35090	2.90
		310	32260	1.81
	2.07	540	18520	0.33
[Co(BF$_2$afdo)$_2$(TPP)$_2$]NO$_3$.H$_2$O	0.045	280	35710	14.6
		380	26320	2.65
[Rh(BF$_2$afdo)$_2$(H$_2$O)Cl]	0.101	280	35700	4.34
[Ni(BF$_2$PnAO)]BF$_4$.H$_2$O	0.312	270	37040	2.44

(TABLE I *continued*)

(B) Infrared Spectra

Six-Coordinated Complexes and ligands	*O–H*	*O–H–O*	*C=N*	*N–O*
H_2afdo	3200		1550	1234 1140
H_2pnAO	3323		1623	1174 1111
[Co(Hafdo)$_2$(H_2O)]	3417	1280	1520	1218 1126
[Co(Hafdo)$_2$(Py)Cl]	3440	1650 1710	1522	1229 1140
[Co(Hafdo)$_2$(TPPSe)$_2$]ClO_4.2H_2O	3148	1680 1745	1515	1179 1097
[Co(Hafdo)$_2$(TPAs)$_2$]ClO_4	3452	1681 1725 1745	1512	1220 1140
[Co(Hafdo)$_2$(TPAsO)$_2$]ClO_4.H_2O	3154	1669	1522	1220 1091
[Co(Hafdo)$_2$(*p*-Tolu)$_2$]NO_3	3460	1760	1515	1223
[Co(Hafdo)$_2$(DEtOHA)$_2$]	3395	1707	1520	1221 1128
[Rh(Hafdo)$_2$(H_2O)$_2$]	3156	1640 1680 1720 1737	1483	1204 1098
[Rh(Hafdo)$_2$(TPAs)$_2$]NO_3.2H_2O	3452	1663 1721		1196 1081
[Rh(Hafdo)$_2$(Anil)Cl].5H_2O	3493	1754 1754	1516	1226 1116
[Rh(Hafdo)$_2$(DEtA)$_2$]Cl.2H_2O	3123	1289	1520	1227 1122
[Co(HBuAO)Cl_2].H_2O	3376	1729	1619	1284 1156
[Co(HpnAO)Cl_2].H_2O	3446	1780	1601	1224 1111
[Rh(HBuAO)Cl_2].2H_2O	3391	1705	1630	1235 1157
[Ni(HpnAO)]Cl		1649 1800	1593	1200 1100
BF_2-Macrocycles	*C=N*	*N–O*	*B–O*	*B–F*
[Co(BF_2afdo)$_2$(H_2O)$_2$]	1592	1223 1129	1170 849	1017 946
[Co(BF_2afdo)$_2$(Py)$_2$]	1566	1226 1133	1175 832	1056 956
[Co(BF_2pnAO)]BF_4.H_2O	1645	1188 1068	1032 882	1001 936
[Ni(BF_2pnAO)]BF_4.H_2O	1637	1199 1096	1035 868	 992

---

* H_2afdo = alpha-furilglyoxime, H_2dmg = dimethylglyoxime, Hafdo = alpha-furilglyoxime anion; Hdmg = dimethylglyoxime anion,H_2pnAO = 3,3′(trimethylenediimino)bis(3-methyl-2-butanoneoxime), H_2BuAO = 4,4′(tetramethylenediimino)bis(4-methyl-2-pentanoneoxime), TPPSe = triphenylphosphine-selenide, TPAs = triphenylarsine, TPAsO = triphenylarsine-oxide, DEtOHA = diethanolamine, DEtA = diethylamine, Py = pyridine, Pip = pipyridine, *p*-Tolu = *p*-toludine, Anil = aniline, Thio = thiourea.

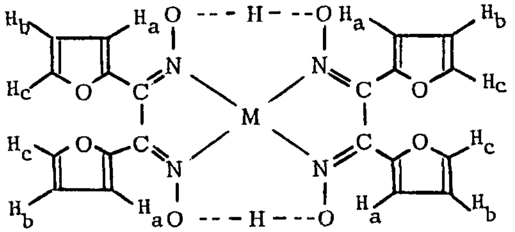
Proton and carbon-13 nmr spectra were recorded either with a JEOL GX 270 or a Bruker AC80 FT-nmr spectrometer using d_6-DMSO as solvent. Because of the very low solubility of some of the complexes in d_6-DMSO and other solvents such as methanol, acetone and acetonitrile, the proton and carbon-13 nmr spectra of these complexes could not be obtained. The nmr data for the soluble complexes are given in Tables II and III.

TABLE II

^1H NMR spectral data for some alpha-furilglyoximates in d_6-DMSO.*

	O-H-O	H_a	H_b	H_c
H_2afdo	12.4	7.8	7.4	6.6
[Co(Hafdo)$_2$(Thio)$_2$]NO$_3$.2H$_2$O	18.2	8.0	7.4	6.8
[Co(Hafdo)$_2$(TPAs)$_2$]ClO$_4$.2H$_2$O	18.2	7.8	7.7	6.5
[Co(Hafdo)$_2$(TPAsO)$_2$]ClO$_4$.H$_2$O	12.0	7.8	7.4	6.6
[Co(Hafdo)$_2$(TPPSe)$_2$]ClO$_4$.2H$_2$O	18.3	7.7	7.4	6.5
[Co(Hafdo)$_2$(*p*-Tolu)$_2$]NO$_3$	9.3	7.8	7.2	5.9
[Rh(Hafdo)$_2$(H$_2$O)$_2$]	11.2	7.7	7.4	6.5
[Rh(BF$_2$afdo)$_2$(H$_2$O)Cl]	10.2	7.8	7.5	6.6
[Rh(Hafdo)$_2$(DEtA)$_2$]Cl.2H$_2$O	12.0	7.7	7.5	6.6
	O-H-O	H-CH$_3$	H-CH$_2$	NH
[Ni(BF$_2$pnAO)]BF$_4$.H$_2$O		1.4	1.7	3.5
[Co(HBuAO)Cl$_2$].H$_2$O	10.4	1.0		3.3
[Rh(HBuAO)Cl$_2$].2H$_2$O	9.5	1.3	2.5	4.1

* The proton assignments are shown below:



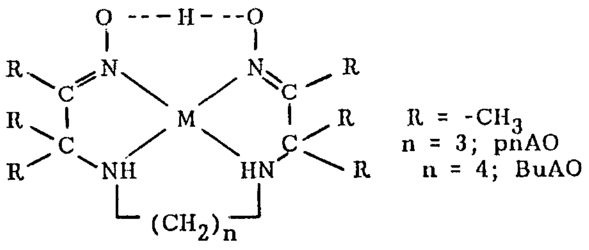
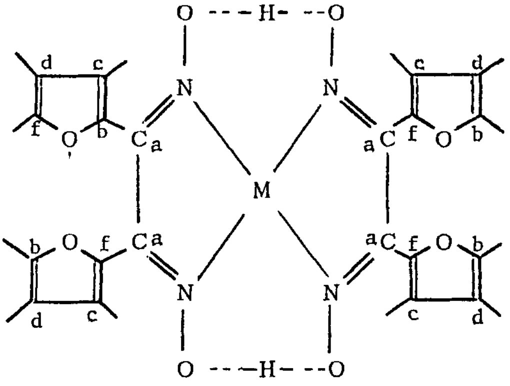


TABLE III
^{13}C-NMR Chemical shifts for some alpha-furilglyoximates in d_6-DMSO.[a]

	C_a	C_b	C_c	C_d	C_f
H_2afdo	150.0	144.0	117.0	112.0	145.1
$[Co(Hafdo)_2(H_2O)]$		141.2	116.0	108.5	142.0
$[Co(Hafdo)_2(Thio)_2]NO_3.2H_2O$	141.8	140.2	115.0	109.7	141.0
$[Co(Hafdo)_2(Anil)_2]NO_3$[b]	143.8	141.5	117.0	111.5	143.2
$[Rh(Hafdo)_2(H_2O)_2]$	153.5	145.3	120.0	114.0	148.1

[a] Resonance for the C=S carbon at 172.9 ppm

[b] Resonance for the aromatic carbons in aniline were observed at 138.5, 122.5, 128.7 and 125.2 ppm. Numbering scheme is shown below:



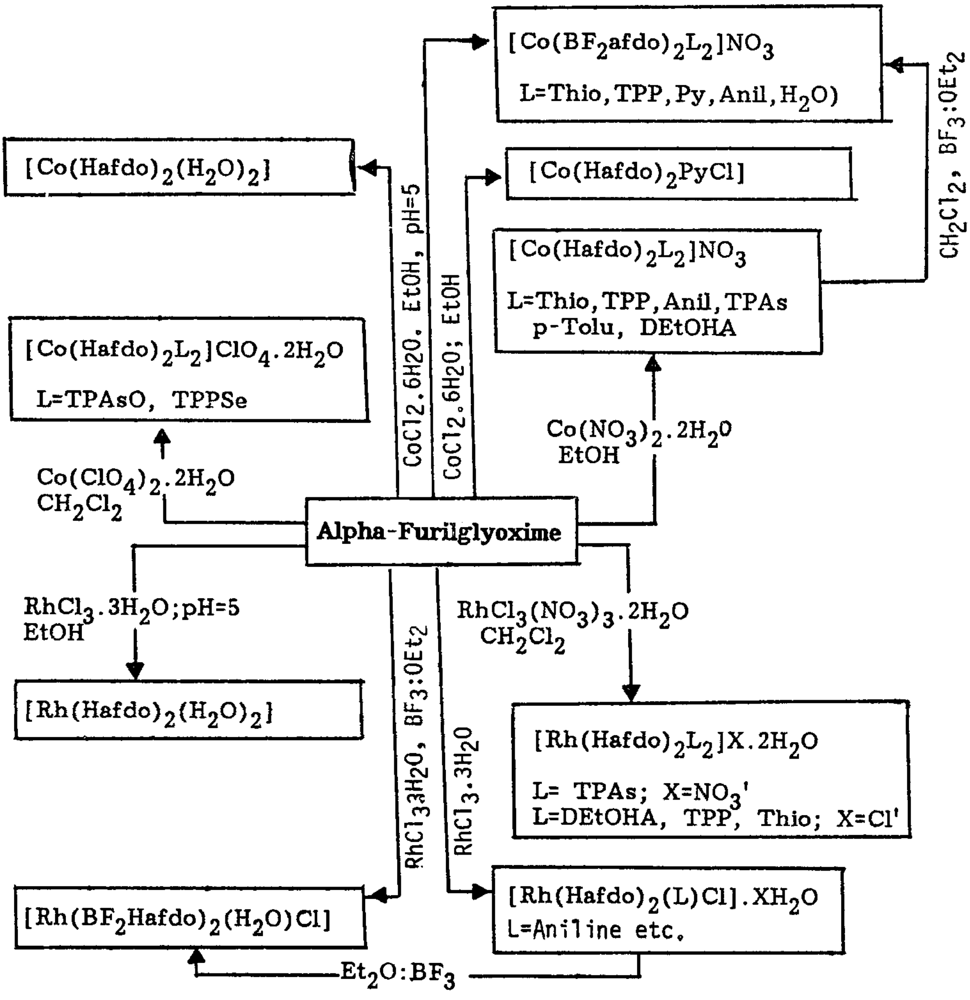
Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were carried out in the temperature range 4.2 to 20 K with a vibrating sample magnetometer (VSM) incorporating a 50 KG superconducting magnet and a precise temperature controller for the temperature range of 4.2 to 150 K. The temperatures above 4.2 K were measured using a calibrated Ga–As diode which also served as the sensor for the temperature controller. The ac susceptibility measurements were made in a double-can ^3He cryostat using a mutual inductance technique[18] at a frequency of 250 Hz and a field of 0.3 G. The magnetic susceptibility was measured only for $[Co(Hafdo)_2(H_2O)_2]$ as a representative cobalt(II) complex.

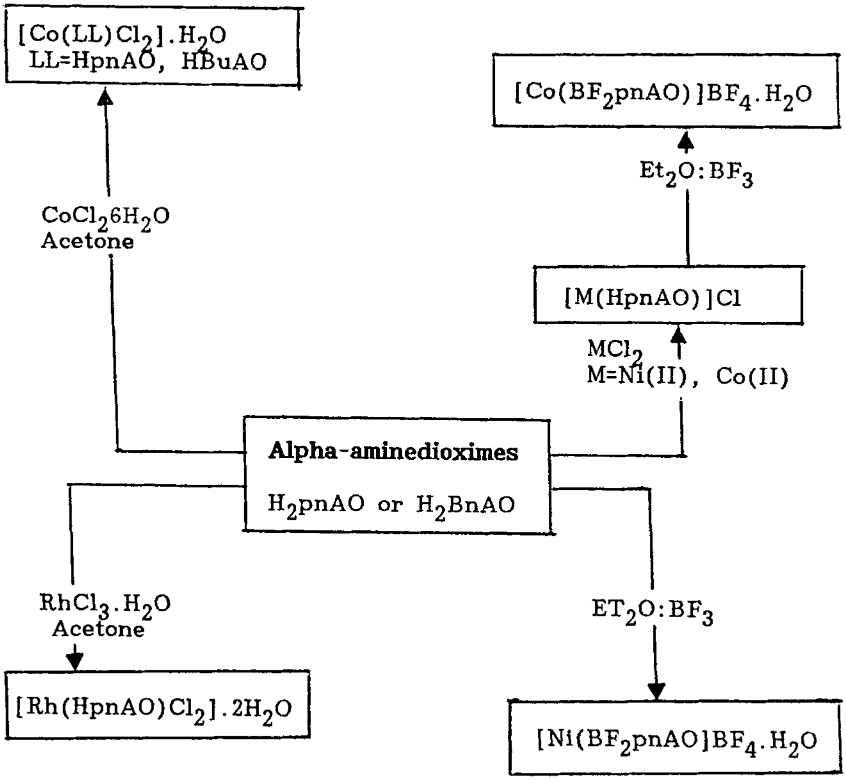
RESULTS AND DISCUSSION

Synthesis of Novel Cobaloximes

As mentioned above, the BF_2-capped macrocycles could be prepared either by adding $Et_2O:BF_3$ to a dichloromethane solution of the H-bonded glyoximates or by stirring the metal salt, the dioxime and the monodentate ligand in an excess of borontrifloride etherate. The latter procedure was preferred due to the better yield and because prior isolation of the glyoximate was not necessary. Beside commonly used N-bases such as pyridine, aniline, piperidine, *p*-toludine, diethylamine and diethanolamine as donors, other monodentate ligands such as thiourea, triphenylphosphine, triphenylphosphine selenide, triphenylarsine and triphenylarsine oxide havng S-, P-, Se-, As-, and O-donors, respectively, were used for the first time for axial ligation of the H-bonded pseudomacrocycles. BF_2-macrocyclic adducts were prepared only with thiourea, pyridine, triphenylphosphine and water, these representing axial ligation through S-, N-, P-, and O-donors. The general synthesis is summarized in Schemes I and II.



SCHEME I
Synthesis of Alpha-furilglyoximates and their Macrocycles
(see Table I for abbreviation)



SCHEME II Macrocyclization of Alpha-aminedioximates. For abbreviations, see Table I.

Spectroscopic (electronic and IR) data

As is quite typical of cobaloxime-type compounds[19] the π–π* transition, observed at 270 nm (37040 cm^{-1}) in free α-furilglyoxime[14] was bathochromically shifted by about 1350–2300 cm^{-1} in the H-bonded complexes. In addition to the strong band at 285 nm (35090 cm^{-1}), the macrocyclic cobalt(II) complexes (*e.g.*, $[Co(BF_2afdo)_2(H_2O)_2]$) exhibited another absorption at 310 nm (32260 cm^{-1}) and a broad visible band at 540 nm (18520 cm^{-1}) with molar absorptivities of 0.33–1.8 × 10^4 M^{-1} cm^{-1}. Similar strong absorptions were also reported for the $[Co(BF_2dmg)_2(H_2O)_2]$ complex.[19] The cobalt(III) species, on the other hand, exhibited featureless visible spectra and two bands at 270 and 370 nm. By analogy with previously reported compounds, the broad band at 370–375 nm (27030–26670 cm^{-1}) is assigned to monodentate thiourea ligands or aromatic molecules *trans* to one another. The molar absorptivities of the BF_2-macrocycles of cobalt(III) are at least an order of magnitude higher than those of the corresponding H-bonded species. The strong absorption at 270 nm in these complexes is characteristic of cobaloximes and owing to its position and intensity is often used to follow complexation, axial ligation and macrocyclization steps during synthesis.

The neutral *trans* ligated H-bonded complexes of the type [Rh(Hafdo)$_2$LL′)].xH$_2$O with L = L′ = H$_2$O, TPAs, DEtA; and L = Anil, Pip with L′ = Cl$^-$, prepared from RhCl$_3$ in aqueous ethanol, exhibited only one strong band at 270–280 nm. The BF$_2$-macrocycles for rhodium(III) could not be obtained. The α-aminedioximato complexes of the type [M(dioxime)$_2$Cl$_2$].xH$_2$O with dioxime = HPnAO, HBuAO, M = cobalt(III) and rhodium(III) also exhibited a strong absorption around 280 nm.

In addition to the infrared peaks listed in Table I, absorptions characteristic of the monodentate axial ligands and strong bands at 1570, 1020, 885, and 770 cm^{-1} for the furane groups[20] were observed for all complexes. A downward shift (relative to free H$_2$afdo) of about 30–40 cm^{-1} for the C=N absorption in the H-bonded complexes indicated coordination through the N-atoms. Contrary to this downward shift, the BF$_2$-macrocycles exhibited upward shifts of about 30 cm^{-1} due to the strong electron-withdrawing influence of the BF$_2$ groups incorporated in the macrocycle. The broad band in the region 1790–1680 cm^{-1} characteristic of O- -H- -O in-plane deformation of the short hydrogen bond,[21–22] disappeared upon encapsulation of the H-bonded complex with BF$_2$ with the concomitant appearance of peaks around 1193–1032 and 882–834 cm^{-1} for the B–O and B–F groups.

Proton and Carbon-13 nmr Spectra

The ^{1}H nmr resonances with expected integrated intensities were observed at 6.5–7.8 ppm (relative to Me$_4$Si) for the furane protons, 4.0 ppm for the –NH protons, and 12.0 or 18.0 ppm for the normal and the intramolecular strong H-bonded protons, respectively. The intramolecular H-bonded proton and the –NH proton could not be detected in the nmr of some complexes because of the rapid exchange of these protons with solvent at room temperature or due to the presence of trace amounts of moisture in the solvent (or compound) combined with very low solubility of these complexes. The ^{1}H nmr spectra of [Co(Hafdo)$_2$L$_2$]NO$_3$ where L = thiourea, TPPSe or PH$_3$As clearly revealed the presence of short intramolecular hydrogen bonded protons at 18.0 ppm, as was previously observed for several α-aminedioximates.[14] The O–H proton resonance observed at 12.00 ppm in the free ligand and at 9.3–11.2 ppm in all rhodium(III) complexes and in TPAsO, *p*-Tolu, DEtA and diaqua cobalt(II) complexes are indicative of weak hydrogen bonding.

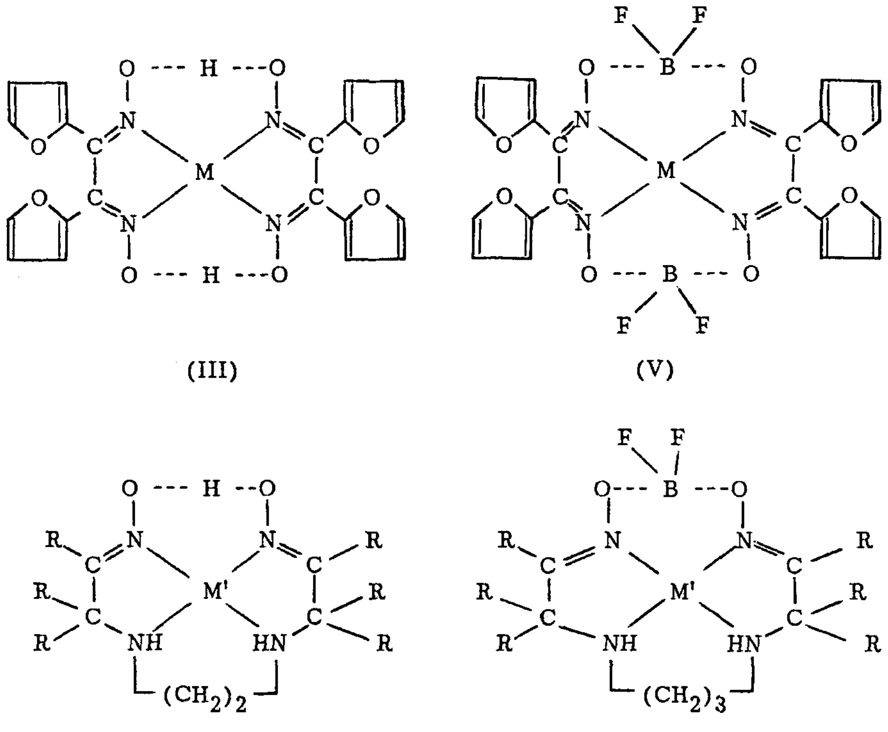
The ^{13}C-nmr measurements were limited to only a few complexes, again due to solubility problems. The complexes which dissolved in d_6-DMSO revealed characteristic resonances for the five magnetically unique carbon nuclei in the [M(Hafdo)$_2$] unit, in addition to ^{13}C resonances corresponding to the axial ligands.

Magnetic Susceptibilities

Magnetic susceptibility measurements were carried out only for [Co(Hafdo)$_2$(H$_2$O)$_2$] as a representative cobalt(II) complex. The effective magnetic moment of the complex calculated from the inverse susceptibility *vs* T plot was 4.387 μ_B, which is close to typically found values (4.9–5.2 μ_B) for the high spin Co^{2+} ion in a distorted octahedral environment.[19] The observed magnetic moment of [Co(Hafdo)$_2$(H$_2$O)$_2$] is distinctly different from the spin-only value (1.73 μ_B, and typically 1.82–1.92 μ_B) for the single unpaired electron in [Co(Hdmg)$_2$(H$_2$O)$_2$], [Co(BF$_2$dmg)$_2$(H$_2$O)$_2$] and a number of other 14-membered macrocyclic complexes of cobalt(II) with ligands of sufficiently high field strength to stabilize cobalt(II) in low-spin environment.[19] Thus, H$_2$afdo acts as a low field strength ligand for cobalt(II) in [Co(Hafdo)$_2$(H$_2$O)$_2$] as compared to H_2dmg in [Co(Hdmg)$_2$(H_2O)$_2$] or [Co(BF_2dmg)$_2$(H_2O)$_2$]. The general features of the $1/\chi$ *vs* T plot are similar to those observed for a ferromagnetic material except for the fact that no spontaneous magnetization was observed as is usually the case at the Curie temperature.

The present study shows that the α-furilglyoximates and α-aminedioximates of cobalt(II), cobalt(III) and rhodium(III) form six-coordinated complexes upon addition of monodentate ligands such as H_2O, Ph_3P, Ph_3PSe, Ph_3As, Ph_3AsO, C_5H_5N, $(NH_2)C{=}S$, $C_6H_5NH_2$, $(C_2H_5)_2NH$, and piperidine with these ligands occupying *trans* axial sites and that the inductive and/or steric requirements of the axial ligands appear to have no significant effects on the mode of axial ligation. Reactions of the pseudo-octahedral or 4-coordinated H-bonded glyoximates with $Et_2O{:}BF_3$ resulted in the replacement of O--H--O hydrogen bonding by O--BF_2--O linkages, forming the macrocyclic complexes [M(BF_2afdo)$_2$L$_2$] (M = cobalt(II), cobalt(III) or rhodium(III)). The furane groups in the α-furilglyoximates are not engaged in any kind of intra- or intermolecular bond formation.

On the basis of the above results Structures III to VI (Scheme III) are proposed for the pseudo-octahedral H-bonded α-furilglyoximates, α-aminedioximates and their corresponding macrocycles, respectively.



(III) (V)

(IV) (V)

M = Co(II), Co(III) or Rh(III); R = CH_3

M' = Ni(II) or Co(III)

SCHEME III
Proposed structures of uncyclized and cyclized glyoximates with monodentate ligands occupying axial positions

Our single crystal X-ray structure analysis[23] of $[Co(Hafdo)_2(thio)_2]NO_3$ is in agreement with the structures proposed above. The spectral behaviour of the pseudo-octahedral α-furilcobaloximes resembles that of dimethyl-cobaloximes and thus, the complexes reported here would serve as models for vitamin B_{12}, and related biological molecules.

ACKNOWLEDGEMENTS

The authors acknowledge the facilities provided by the King Fahd University of Petroleum and Minerals for this research.

REFERENCES

1. F. J. Welcher, *Organic Analytical Reagents*, **3**, 154 (1947).
2. M.N. Hughes, 'Inorganic Chemistry of Biological Precesses', Second Edition (Wiley, New York, 1981).
3. D. Dolphin, Ed., 'B-12', Vols 1 and 2 (Wiley, New York, 1982).
4. N.B. Phor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, *Coord. Chem. Rev.*, **63**, 1 (1985).
5. T.W. Thomas and A.E. Underhill, *Chem. Soc. Rev.*, **99** (1972).
6. G.N. Schrauzer, *Ber*, **95**, 1438 (1962).
7. G.N. Schrauzer, *Angew. Chem., Internl. Ed.*, **15**, 417 (1976).
8. M.Z. El-Faer, A. Khan and M.S. Hussain, *J. Coord. Chem.*, **16**, 81 (1987).
9. A. Chakravorty, *Coord. Chem. Rev.*, **13**, 1, (1974).
10. N.M. Samus and A.V. Ablov, *Coord. Chem. Rev.*, **29**, 177 (1979).
11. F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **43**, 72 (1980).
12. F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **42**, 139 (1980).
13. M.S. Hussain, M.Z. El-Faer, Aqil Khan and E.O. Schlemper, *Inorg. Chim. Acta*, **128**, 81 (1987).
14. M.S. Hussain, S.A. Al-Hamoud, M.Z. El-Faer and Aqil Khan, *J. Coord. Chem.*, **14**, 91 (1985).
15. Z.Y. Vaisbien, O.A. Bologa, N.N. Proskina and A.V. Ablov, *Russ. J. Inorg. Chem.*, **24**, 404 (1979).
16. M.S. Hussain, B.E.V. Salinas and E.O. Schlemper, *Acta Cryst.*, **B35**, 628 (1979).
17. R.K. Murmann, *J. Am. Chem. Soc.*, **79**, 524 (1957).
18. T.A. Meert, Ph. D. Thesis, Wayne State University, (1982).
19. A. Bakac, M.E. Brynildson and J.H. Espenson, *Inorg. Chem.*, **25**, 4108 (1986).
20. D.R. Boston and N.J. Rose, *J. Am. Chem. Soc.*, **90**, 6859 (1968).
21. A. Bigotto, V. Galasso and G. Dealti, *Spectro Chim. Acta*, **27**, 1659 (1970).
22. E. Emsely, *Chem. Soc. Rev.*, **91**, (1981).
23. M.S. Hussain, H.M. Al-Mohdhar and E.O. Schlemper, *J. Cryst. & Spectro. Res.*, in press (1988).