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# Synthesis and Characterization of Several Binuclear and Mononuclear Bis(α-dioximato)nickel(II) Complexes

MARK L. BOWERS and CRAIG L. HILL*

*Department of Chemistry, University of California, Berkeley, Calif. 94720, U.S.A.*

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*Four binuclear bis(α-dioximato)nickel(II) complexes (where the dioxime is 4,5-octanedione dioxime) were prepared by treatment of a monomeric bis(α-dioximato)nickel(II) species with the linking reagents ($F_2B{-}R{-}BF_2$, R = 1,4 $-C_6H_4$ or $-(CH_2)_4-$. The binuclear complexes consist of one F–B–R–B–F moiety linking the two bis(α-dioximato)nickel(II) units together by attachment of each boron to two oxygen atoms of each of the two bis(α-dioximato)nickel(II) units. Several mononuclear bis(α-dioximato)nickel(II) complexes (where the dioxime is either 3,4-hexanedione dioxime or 4,5-octanedione dioxime) containing two RBF units (R = $C_6H_5$, n-$C_4H_9$), one RBF unit (R = $C_6H_5$) and one $BF_2$ unit, or two $BF_2$ units bridging two oxygens of the dioximes were also prepared. The complexes containing two RBF units exist in two isomeric forms that can be separated using adsorption chromatography. The mononuclear and binuclear complexes were characterized by their NMR ($^1H$, $^{13}C$, and $^{19}F$) and IR spectra. The complexes containing RBF units were stable in neutral and basic media but unstable in acidic media. The compounds with RBF units were also unstable in the presence of Lewis acids. Reaction of the complexes containing RBF units with $BF_3$ gave the complexes containing two $BF_2$ units in quantitative yields. Exchange of the α-dioximato ligands between bis(α-dioximato)nickel(II) complexes containing either two hydrogens or two boron moieties bridging the oxime oxygens was unobserved in dichloromethane over a period of at least one month at room temperature. Ligand exchange was observed in acidified dichloromethane for the complexes containing hydrogen bridges but not observed in this medium for the complexes containing $BF_2$ bridges.*

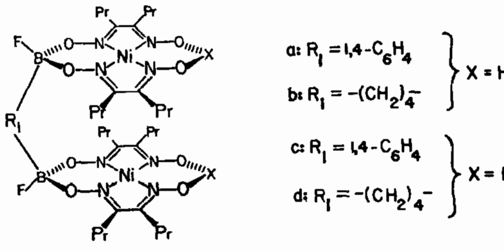

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Fig. 1. Chemical structure of several binuclear bis(α-dioximato)nickel(II) complexes (dimers) containing a single F–B–$R_1$–B–F unit linking the two bis(α-dioximato)nickel(II) complexes together.

## Introduction

In recent years, much attention has been given to binuclear metal complexes because of their role in certain biological systems [1] and their potential to act as multi-electron redox catalysts [2]. Most of the binuclear metal complexes studied to date contain both metals and their ligands in one plane [3]. (Notable exceptions are the cofacial porphyrins [2, 3] and some cryptates [4]). With this in mind, we were interested in synthesizing a new class of cofacial metal complexes with bis(α-dioximato) ligands. It has already been shown that $BF_3$ and $BR_3$ (R = alkyl groups) compounds can be used to bridge the oxygen atoms of several transition metal bis(α-dioximato) complexes [5] and that α-dioximes are robust ligands that are stable to various metals in unusual oxidation states [6].

In this paper, we present the preparation and characterization of several binuclear compounds containing two bis(α-dioximato)nickel(II) complexes linked together by one F–B–R–B–F (R = 1,4-

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*Author to whom correspondence should be addressed. Present address: Department of Chemistry, Emory University, Atlanta, Ga. 30322, U.S.A.

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$C_6H_4$ or $-(CH_2)_4-$) moiety by attachment of each boron to two oxygen atoms of each of the bis($\alpha$-dioximato) units (Fig. 1). (Throughout this paper, the term 'bridging' refers to the binding of the two oxygens of the dioximes by a boron function, whereas 'linking' refers to the connecting of two bis($\alpha$-dioximato)nickel(II) complexes by a FB–R–BF moiety.) The synthesis, characterization, and stability, under various conditions, of several monomeric precursor and model compounds are also reported. The compounds are characterized by NMR ($^1H$, $^{13}C$, and $^{19}F$) and IR spectra [7].

## Experimental

### *Materials*

$BF_3 \cdot Et_2O$ was both distilled and stored under nitrogen. Chloroform and dichloromethane were distilled under nitrogen onto $Na_2CO_3$ and 4-Å molecular sieves and stored at 5 °C. Chloroform-*d* for NMR spectroscopy was stored over $Na_2CO_3$ and 4-Å sieves. The 4,5-octanedione [8], phenyldifluoroborane [9], butyldifluoroborane [10], 1,4-phenylenebis(dichloroborane) [11], and 1,4-butanediboronic acid [11] were prepared by literature methods. The 3,4-hexanedione was a generous gift from BASF corporation.

### *General*

The organodihaloborane and the organobis(dihaloborane) compounds were manipulated in an inert atmosphere due to their sensitivity to moisture. Gel permeation chromatography was performed using polystyrene-divinylbenzene (3%) beads (Bio Beads SX-3, Bio Rad Corporation) packed in a 3.3 × 110 cm glass column fitted with a 2-L solvent reservoir. THF distilled from $CaH_2$ was used as the eluent. Preparative adsorption chromatography was performed with an Altex model 110A pump connected to a 2.5 × 45 cm glass column packed with silica gel (60–200 mesh, Baker) using dichloromethane as the eluent. Thin-layer chromatography (TLC) was carried out using silica gel coated sheets containing a fluorescent indicator (Baker) with dichloromethane as the eluent. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer. The $^1H$ NMR spectra were obtained on a Varian EM-390 (90 MHz), UCB 200 (200 MHz), or UCB 250 (250 MHz) spectrometers. The $^{13}C\{^1H\}$ NMR spectra were measured at 25.14 MHz with a Nicolet NTC-TT-23 spectrometer or at 62.89 MHz on the UCB 250. The $^{19}F$ NMR spectra were recorded on a Varian EM-390 (84.67 MHz) or UCB 180 (169.34 MHz) instruments. The $^1H$ NMR spectroscopic simulations were obtained on a Nicolet 1280 computer using the Nicolet ITRCAL (LAOCN3-based) iterative program. Mass spectra were obtained on an AEI-MS-12 or on an AEI-MS-9 instrument fitted with a field desorption source. Elemental analyses were carried out at the University of California, Berkeley.

### *Syntheses*

#### *4,5-Octanedione Dioxime*

A mixture of 4,5-octanedione (7.8 g, 5.5 × $10^{-2}$ mol), hydroxylamine hydrochloride (8.5 g, 0.12 mol), ethanol (45 ml), and pyridine (30 ml) was placed in a beaker and became homogeneous upon stirring and heating. The solution was refluxed for several minutes. The solvent was then removed under reduced pressure, and the resulting white solid washed with water (100 ml). Recrystallization from ethanol-benzene gave 5.3 g (56% yield) of the dioxime (m.p. 179–181 °C).

#### *3,4-Hexanedione Dioxime*

The procedure used to prepare this dioxime was similar to the one used to prepare the 4,5-octanedione dioxime.

#### *Bis[(4,5-octanedione dioximato)(1-)-N,N'] nickel(II),* 2a

A mixture of 4,5-octanedione dioxime (4.7 g, 27 mmol), sodium hydroxide (1.2 g, 30 mmol), and methanol (100 ml) was placed in a 250 ml round-bottomed flask. After stirring to dissolve the solids, a solution of $NiCl_2 \cdot 6H_2O$ (3.2 g, 13 mmol) in methanol (80 ml) was slowly transferred to the unstirred solution of the dioxime. Long red needles of the product began to form shortly after the start of the addition. After the addition was complete, the mixture was stirred for several minutes and placed in an ice bath. The mixture was filtered cold, and the crystals were washed with cold methanol, water, cold methanol, and finally diethyl ether. The yield was 5.0 g (96%). Several recrystallizations from methanol and then dichloromethane-hexane gave the pure complex *2a*. *Anal.* Calcd for $C_{16}H_{30}N_4NiO_4$: C, 47.91; H, 7.54; N, 13.97. Found: C, 47.94; H, 7.61; N, 13.98%.

#### *Bis[(3,4-hexanedione dioximato)(1-)-N,N'] nickel(II),* 2b

The procedure used to prepare *2b* was analogous to that used for compound *2a*. *Anal.* Calcd for $C_{12}H_{22}N_4NiO_4$: C, 41.77; H, 6.43; N, 16.24. Found: C, 41.89; H, 6.38; N, 16.32%.

#### *Mixture of Compounds* 2a, 2b *and* 2e *as well as* 2b, 2c *and* 2d

These two mixtures were prepared in a method similar to that used for compound *2a* except that a 1:1 molar mixture of the two different $\alpha$-dioximes (4,5-octanedione dioxime and 3,4-hexanedione dioxime or 3,4-hexanedione dioxime and 2,3-butanedione dioxime) was used instead of only 4,5-octanedione dioxime. The resulting precipitates were used after rinsing and drying. The presence of all three complexes in each mixture was ascertained by the observation of three resolved spots on TLC.

### *(2,2-Difluoro-5,6,12,13-tetrapropyl-2-bora-9-hydro-4,7,11,14-tetraaza-1,3,8,10-tetraoxacyclotetradeca-4,6,11,13-tetraenido,N,N′,N″,N‴)nickel(II),* 3a

A solution of $BF_3 \cdot Et_2O$ (0.20 g, 1.3 mmol) in dichloromethane (25 ml) was added slowly to a solution containing complex *2a* (0.56 g, 1.4 mmol) in dichloromethane (25 ml). The resulting solution was boiled for several minutes, and the solvent subsequently removed under reduced pressure. The resulting orange solid was recrystallized several times from acetone. *Anal.* Calcd for $C_{16}H_{29}BF_2N_4NiO_4$: C, 42.80; H, 6.51; N, 12.48. Found: C, 42.96; H, 6.51; N, 12.60%.

### *(2,2-Difluoro-5,6,12,13-tetraethyl-2-bora-9-hydro-4,7,11,14-tetraaza-1,3,8,10-tetraoxacyclotetradeca-4,6,11,13-tetraenido,N,N′,N″,N‴)nickel(II),* 3b

The method used to synthesize compound *3b* was analogous to that of compound *3a* except that the solvent used for recrystallization was hexane-acetone. *Anal.* Calcd for $C_{12}H_{21}BF_2N_4NiO_4$: C, 36.69; H, 5.39; N, 14.26. Found: C, 37.14; H, 5.46; N, 14.18%.

### *(2,2,9,9-Tetrafluoro-5,6,12,13-tetraethyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N′,N″,N‴)nickel(II),* 4b

Boron trifluoride etherate (1.8 g, 13 mmol) was added slowly over a period of ~5 minutes to a dichloromethane solution (25 ml) of compound *2b* (1.1 g, 3.2 mmol). The solution was refluxed for several minutes. The resulting small, yellow needles were filtered cold and rinsed with diethyl ether. Recrystallization of compound *4b* from THF–ethyl acetate and then acetone yielded 0.45 g (32%). *Anal.* Calcd. for $C_{12}H_{20}B_2F_4N_4NiO_4$: C, 32.71; H, 4.57; N, 12.71. Found: C, 33.11; H, 4.56; N, 12.85%.

### *(2,2,9,9-Tetrafluoro-5,6,12,13-tetrapropyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N′,N″,N‴)nickel(II),* 4a

The synthesis of compound *4a* was similar to that of compound *4b* except that the product was not recrystallized (yield 64%). *Anal.* Calcd for $C_{16}H_{28}B_2F_4N_4NiO_4$: C, 38.69; H, 5.68; N, 11.28. Found: C, 38.51; H, 5.57; N, 11.17%.

### *Mixture of* 4b, 4c, *and* 4d

The procedure used to synthesize the mixture of compounds *4b, 4c* and *4d* was similar to the one used for compound *4b* except that a mixture of compounds *2b, 2c,* and *2d* was used instead of only compound *2b*. The resulting mixture of *4b, 4c,* and *4d* was not recrystallized and was used after rinsing with diethyl ether. All three compounds were shown to be present in the mixture by TLC, which produced three resolved spots.

### *(2,2,9,9-Tetrabutyl-5,6,12,13-tetrapropyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N′,N″,N‴)nickel(II),* 5

Tri-*n*-butylborane (3.9 ml of a 1 *M* solution in THF, 3.9 mmol) was added to a benzene solution (30 ml) of compound *2a* (0.71 g, 1.8 mmol), and the resulting solution was refluxed for 3 hours. The solvent was removed under reduced pressure to give a red oil. The crude material was passed through the gel permeation column, and the middle fraction (after removal of solvent under reduced pressure) was recrystallized three times from methanol. *Anal.* Calcd for $C_{32}H_{64}B_2N_4NiO_4$: C, 59.20; H, 9.94; N, 8.63. Found: C, 59.08; H, 9.80; N, 8.74%.

### cis- *and* trans-*(2,9-Difluoro-2,9-diphenyl-5,6,12,13-tetraethyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N′,N″,N‴)nickel(II),* 6b

Phenyldifluoroborane (2.2 g, 17 mmol) was added to a chloroform solution (100 ml) containing compound *2b* (2.9 g, 8.4 mmol). The resulting yellow solution was stirred for several minutes, and the chloroform was removed under reduced pressure to give a yellow solid. The solid was recrystallized four times by dissolving it in refluxing THF, adding 8–10 volumes of refluxing ethanol, and allowing it to cool undisturbed. The resulting yellow flakes were filtered and dried *in vacuo*. *Anal.* Calcd for $C_{24}H_{30}B_2F_2N_4NiO_4$: C, 51.77; H, 5.43; N, 10.06. Found: C, 51.80; H, 5.51; N, 10.09%; mass spectrum *m/e* 556 (parent), 479 (base).

### cis- *and* trans-*(2,9-Difluoro-2,9-diphenyl-5,6,12,13-tetrapropyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N′,N″,N‴) nickel(II),* 6a

The *cis* and *trans* isomers of compound *6a* were prepared in a method analogous to the one used to prepare the *cis* and *trans* isomers of compound *6b* except that the crude reaction mixture was first purified using gel permeation chromatography. The middle fraction was saved, and recrystallization from dichloromethane–hexane yielded the mixture of isomers. *Anal.* Calcd. for $C_{28}H_{38}B_2F_2N_4NiO_4$:

C, 54.87; H, 6.25; N, 9.14. Found: C, 54.85; H, 6.22; N, 9.16%.

### cis- *and* trans*-(2,9-Difluoro-2,9-dibutyl-5,6,12,13-tetraethyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N, N',N'',N''')nickel(II),* 7

The procedure used to prepare the *cis* and *trans* isomers of compound *7* was analogous to that used to prepare the *cis* and *trans* isomers of compound *6b* except recrystallization was from chloroform–hexane. *Anal.* Calcd. for $C_{20}H_{38}B_2F_2N_4NiO_4$: C, 46.48; H, 7.41; N, 10.84. Found: C, 46.25; H, 7.21; N, 10.88%.

### *(2-Phenyl-2,9,9-trifluoro-5,6,12,13-tetrapropyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-2,9-diboracyclotetradeca-4,6,11,13-tetraenido-N,N',N'',-N''')-nickel(II),* 8

Phenyldifluoroborane (0.11 g, 0.9 mmol) was added to a chloroform solution (50 ml) of compound *3a* (0.29 g, 0.65 mmol) and was stirred for 10 min. The chloroform was removed under reduced pressure to yield a yellow solid. The yellow solid was chromatographed on the gel permeation column, the middle fraction was collected, and the solvent was removed. The solid was precipitated several times from dichloromethane by adding hexane. *Anal.* Calcd for $C_{22}H_{33}B_2F_3N_4NiO_4$: C, 47.62; H, 5.99; N, 10.10. Found: C, 47.28; H, 5.99, N, 10.15%; mass spectrum *m/e* 554 (parent), 477 (base).

### *1,4-Butanediylbis(difluoroborane),* 10

A mixture of 1,4-phenylenebis(dichloroborane) (0.37 g, 1.5 mmol) and $TiF_4$ (0.37 g, 3.0 mmol) was placed in a sublimer in the drybox. Acetone and dry ice were placed in the cold finger condenser. The sublimer, under 1 atm of nitrogen, was gradually heated in a water bath. Reaction began to occur at 65–70 °C as indicated by the formation of long (up to 3 cm), colorless needles of the product. The product was collected under a nitrogen atmosphere in a glovebag. The yield was variable and ranged from 30–70% (m.p. 74–77 °C). The compound was unstable and was used the same day it was prepared. *Anal.* Calcd for $C_6H_4B_2F_4$: C, 41.49; H, 2.32. Found: C, 41.55; H, 2.49%.

### *1,4-Butanediylbis(difluoroborane),* 10

The method used to synthesize compound *10* was similar to that used for butyldifluoroborane except that 1,4-butanediboronic acid was used instead of butylboronic acid [10]. The yield of the liquid 1,4-butane-diylbis(difluoroborane) was variable but ranged from 10–20%.

### *Dimer* 1a

A chloroform solution (250 ml) of 1,4-phenylenebis(difluoroborane) (0.59 g, 3.4 mmol) was added slowly over a period of one hour by cannula to a flask containing a chloroform solution (250 ml) of compound *2a* (5.6 g, 14 mmol) and $Na_2CO_3$ (~1.5 g). The resulting reaction mixture was extracted with dilute aqueous $Na_2CO_3$, the chloroform layer separated, and the chloroform removed under reduced pressure. Gel chromatography of the resulting red solid yielded four resolved bands. The second band was identified as dimer *1a*. The yield of the orange-red dimer *1a*, based on the limiting reagent, 1,4-phenylenebis(difluoroborane), was ~70%. Mass spectrum *m/e* 935 (parent), 935 (base).

### *Dimer* 1b

Dimer *1b* was prepared in a manner analogous to *1a* using 1,4-butanediylbis(difluoroborane) as the linking reagent. The yield of the orange–red dimer *1b* based on 1,4-butanediylbis(difluoroborane), was also ~70%.

### *Dimer* 1c, *Method A.*

A chloroform solution (17 ml) of 1,4-phenylenebis(difluoroborane) (0.097 g, 0.56 mmol) was added over a period of 8 minutes by cannula to a 250 ml Schlenk flask containing a vigorously-stirred chloroform solution (100 ml) of the monomeric compound, *3a* (0.50 g, 1.1 mmol) and $Na_2CO_3$ (~1.5 g). The reaction mixture was stirred for an additional 1.5 hours, and then filtered to remove the $Na_2CO_3$. The supernatant was concentrated under reduced pressure, and the residual yellow-orange solid was chromatographed to give three resolved bands. The second band was identified as dimer *1c*. The dimer was chromatographed a second time, precipitated twice from a dichloromethane solution with hexane, and dried *in vacuo*. *Anal.* Calcd for $C_{38}H_{60}B_4F_6N_8Ni_2O_8$: C, 44.24; H, 5.86; N, 10.86. Found: C, 44.57; H, 5.87; N, 10.72%.

### *Dimer* 1c, *Method B*

A THF solution (1.7 ml) of $BF_3 \cdot Et_2O$ ($6.4 \times 10^{-3}$ g, $4.5 \times 10^{-5}$ mol) was slowly added over a period of 5 minutes to a solution of dimer *1a* (0.020 g, $2.1 \times 10^{-5}$ mol) in THF (5 ml). The solution was stirred for 15 minutes, and the solvent was removed under reduced pressure. The resulting solid was chromatographed to give three bands, the second of which was identified as dimer *1c*. The yield was 52% based on *1a*.

### *Dimer* 1d

Dimer *1d* was prepared by Method A in a procedure analogous to that given for the preparation of dimer *1c*. *Anal.* Calcd. for $C_{36}H_{64}B_4F_6N_8Ni_2O_8$: C, 42.74; H, 6.38; N, 11.08. Found: C, 42.88; H, 6.31; N, 11.07%; mass spectrum *m/e* 1012 (parent), 477 (base).

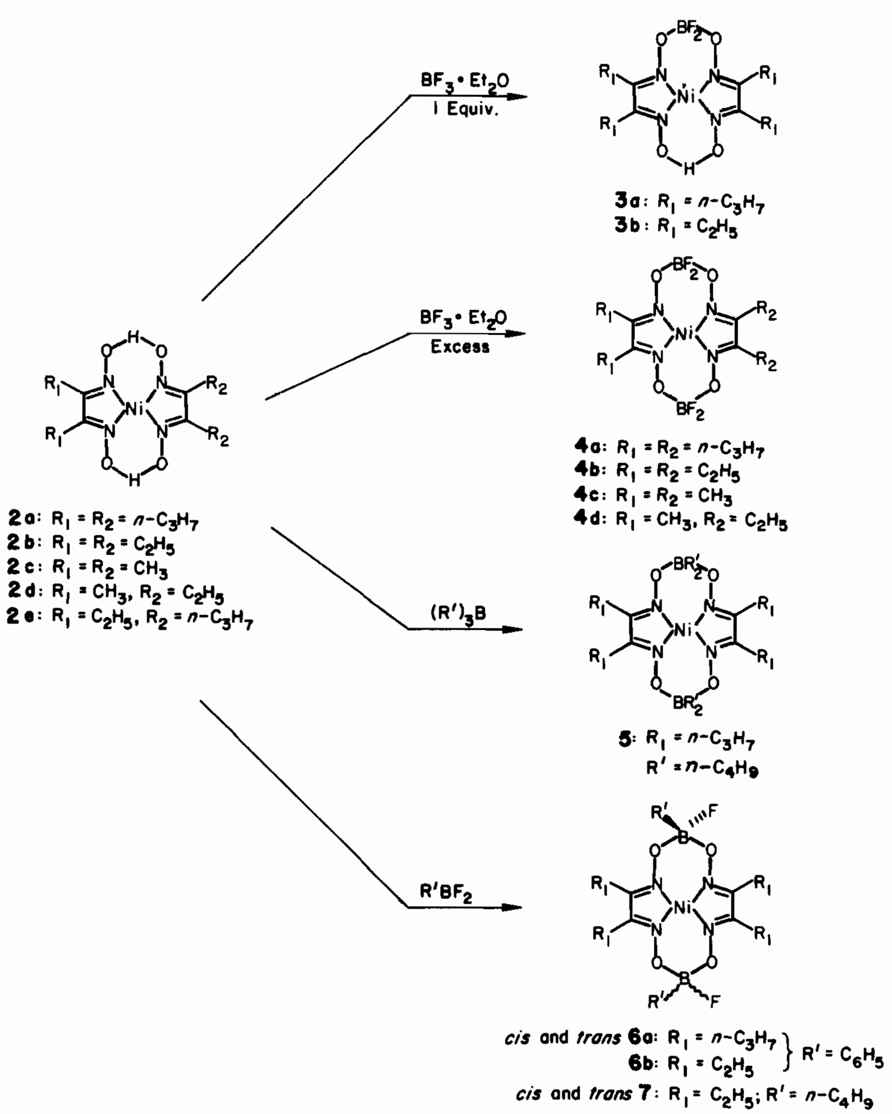

Fig. 2. Schematic diagram showing the synthesis of the mononuclear complexes *2* through *7*.

## Results and Discussion

### *Synthetic Aspects*

### *Mononuclear Complexes*

The mononuclear complexes, *2* through *8* (Figs. 2 and 3) were prepared for three reasons: (1) to test the feasibility of preparing the binuclear compounds (*i.e.* to help select the proper reaction conditions and to help in the identification and characterization of the binuclear compounds once formed and isolated), (2) to examine the stability of the boron bridged bis(α-dioximato)nickel(II) complexes under various conditions, and (3) to be used as precursors for the binuclear compounds. The mononuclear complexes were obtained in yields which ranged from 35–60% based on the limiting reagent. The compounds range in color from red to yellow with the hydrogen bridged compounds being red, the $BF_2$

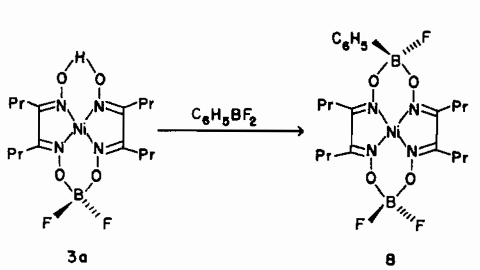

Fig. 3. Equation showing the synthesis of complex *8* from complex *3a*.

compounds yellow, and the BFR bridged compounds orange to yellow. The geometric isomers of compounds *6a, 6b,* and *7* (the two isomers arise from having the two fluorines on the same side of the molecular plane — designated *cis* or on opposite sides — designated *trans*) were detected by TLC. The two isomers of compound *6b* were separated by adsorption chromatography. (The first isomer eluted from the column is designated *6b* (1) and the second *6b* (2).)

### *Binuclear Complexes*

The binuclear compounds *1a* and *1b* were obtained in high yields (~70%) at moderate dilution (~$10^{-2}$ *M*) with the monomeric complex *2a* present in fourfold molar excess over the organobis(difluoroborane) linking reagent. Dimers *1a* and *1b* were isolated from their respective reaction mixtures by gel permeation chromatography and were completely resolved from other products. The first band from the column probably consisted of polymeric species, the second one was dimer *1a* or *1b*, and the last band was unreaced *2a.* The binuclear complexes *1a* and *1b* could not be obtained in an analytically pure form, but they were obtained in sufficient purity for spectral identification and characterization. Both dimers *1a* and *1b* decompose slowly in solution to give a mixture of polymeric material and the monomer *2a.* This decomposition apparently occurs by exchange of the –R–B–F bridges for hydrogen bridges.

To eliminate the instability of dimers *1a* and *1b*, we decided to synthesize dimers *1c* and *1d*, which have the bridging H replaced by $BF_2$. Dimer *1c* was prepared by two methods. Method A involves linking two bis(α-dioximato)nickel(II) complexes together first (forming dimer *1a*) followed by addition of a stoichiometric amount of $BF_3 \cdot Et_2O$. Whereas Method B involves first bridging the bis(α-dioximato)nickel(II) complex by a single $BF_2$ (forming monomer *3a*) and then linking two compound *3a* units together with 1,4-phenylenebis-(difluoroborane).

Dimers *1c* and *1d* were also isolated from their reaction mixture using gel permeation chromatography with yields of ~50%. Three bands were obtained from the column: band one was polymeric species, band two was dimer *1c* or *1d*, and band three was monomeric species. Identification of some of the component monomeric species by $^1$H- and $^{19}$F-NMR shows evidence of B–C bond cleavage during the dimer forming reactions. This may be the reason why dimers *1c* and *1d* are obtained in significantly lower yields than dimers *1a* and *1b.*

Attempts have been made to synthesize binuclear compounds containing two linking units connecting the two bis(α-dioximato)nickel(II) complexes together. These binuclear complexes would be held together in a permanent cofacial arrangement unlike dimers *1a–d* which can rotate about the B–C bonds. The reactions were performed under conditions of moderate dilution ($10^{-3}$ *M*) by slowly adding a solution containing the linking reagent (compound *9* or *10*) to a solution containing dimer *1a* or *1b.* Gel permeation chromatography of the resulting reaction mixtures gave only one large band. The band in each case was collected in several fractions and analyzed by $^1$H- and $^{19}$F-NMR. The spectral properties of these materials were similar to those of the polymeric materials produced in the syntheses of dimers *1a* and *1b.* When the individual fractions were chromatographed a second time, only one large band (similar to the original but fainter) was produced regardless of whether the fraction chromatographed was from the first or the last part of the original band. Since the column separates compounds on the basis of molecular size, it can be concluded that the compounds in the reaction mixture were changing their size by polymerizing and cleaving. Therefore any dilinked dimers formed probably rearrange to form more stable polymeric species. (Evidence of the lability of the –R–B–F unit has been presented above.) Attempts to isolate the di-linked dimers using adsorption chromatography with silica, alumina, and reverse-phase materials also produced only streaks.

### *$^1$H NMR*

The $^1$H NMR spectra (Table I) are diagnostic for the various compounds in this study. The hydrogen that bridges the oxygens is strongly deshielded and its resonance in these compounds appears at *ca.* δ 17.7. In phenyldifluoroborane, butyldifluoroborane, and compounds *9* and *10*, the proton resonances of the phenyl and butyl protons shift upfield upon changing the geometry at boron from trigonal to tetrahedral. Bridging boron groups cause the resonances of the ethyl and propyl groups to shift downfield relative to those in compounds *2b* and *2a* respectively. The effect can be as large as 0.15 ppm for the methylene group adjacent to the imine carbon. Compounds with two types of bridging groups (BFR or $BF_2$ at one end and H at the other, *e.g.* compounds *1a, 1b, 3a,* and *3b*) have two types of ethyl or propyl groups which give rise to overlapping resonances in the $^1$H NMR.

At low magnetic field strengths (90 MHz) the compounds *1c, 1d, 6, 7* and *8* give rise to simple spectra for the substituents on the α-dioxime (*i.e.* $A_2X_3$-like for ethyl substituted α-dioximes and $A_2M_2X_3$-like for the propyl substituted α-dioximes). However, at higher field strengths (200 or 250 MHz) the spectra become more complicated due to the stereochemical inequivalence of the two protons on the methylene groups. This gives rise to an $ABX_3$ spin system for both isomers of *6b* and *7*, an $ABMNX_3$ spin system for both isomers of *6a*, and two overlapping $ABMNX_3$ spin

TABLE 1. $^1$H NMR Spectral Data.[a]

| | |
|---|---|
| *1a*[b] | 0.99(t, 12H, *J* = 7), 1.59(septet, 8H, *J* = 7), 2.49(q, 8H, *J* = 7), 7.54(s, 2H), 17.8(s, 1H) |
| *1b*[b] | 0.5(br s, 2H), 0.97(t, 12H, *J* = 7), 1.5(m, 10H), 2.43(q, 8H, *J* = 7), 17.8(s, 1H) |
| *1c*[b] | 1.03(t, 6H, *J* = 7)[f], 1.62(sextet, 4H, *J* = 7), 2.57(t, 4H, *J* = 7), 7.54(s, 1H) |
| *1d*[b] | 0.5(br s, 1H), 1.01(t, 6H, *J* = 7), 1.54(m, 5H), 2.51(br t, 4H, *J* = 7) |
| *2a*[b] | 0.96(t, 6H, *J* = 7), 1.52(sextet, 4H, *J* = 7), 2.42(t, 4H, *J* = 7), 17.8(s, 1H) |
| *2b*[b] | 1.07(t, 6H, *J* = 7), 2.46(q, 4H, *J* = 7), 17.8(s, 1H) |
| *3a*[d] | 1.00(q, 12H, J = 6.9), 1.59(septet, 8H, *J* = 8)[f], 2.47(t, 4H, *J* = 7.8), 2.55(t, 4H, *J* = 7.8), 17.71(s, 1H) |
| *3b*[d] | 1.13(t, 6H, *J* = 7.6), 1.17(t, 6H, *J* = 7.6), 2.53(q, 4H, *J* = 7.6), 2.61(q, 4H, *J* = 7.6), 17.71(s, 1H) |
| *4b*[c] | 1.21(t, 3H, *J* = 7.6), 2.66(q, 2H, *J* = 7.6) |
| *5*[d] | 0.63(t, 2H), 0.88(t, 3H, *J* = 7.1), 0.97(t, 3H, *J* = 7.4), 1.15(quintet, 2H, *J* = 8), 1.32(sextet, 2H, *J* = 7.0), 1.56(m, 2H), 2.48(t, 2H, *J* = 7.6) |
| *6a*[b,e] | 1.01(t, 6H, *J* = 7), 1.60(sextet, 4H, *J* = 7), 2.57(t, 4H, *J* = 7), 7.31(m, 3H), 7.56(m, 2H) |
| *6b*[d,e] | 1.19(t, 6H, *J* = 7.5), 2.63(m, 3H), 7.60(m, 2H) |
| *7*[d,e] | 0.47(m, 2H), 0.89(t, 3H, *J* = 6.5), 1.16(t, 6H, J = 7.5), 1.31(m, 4H), 2.58(m, 4H) |
| *8*[d] | 1.03(q, 12H, *J* = 7.3), 1.63(sextet, 8H, *J* = 7.3), 2.58(m, 8H), 7.32(m, 3H), 7.55(m, 2H) |
| *9*[d] | 8.00(s) |
| *10*[b] | 1.02(br s, 1H), 1.48(br s, 1H) |

[a] Chloroform-*d* solution; expressed in δ units relative to TMS internal standard; *J* given in Hz. [b] 90 MHz spectrum. [c] 200 MHz spectrum. [d] 250 MHz spectrum. [e] Mixture of *cis* and *trans* isomers. [f] Contains further fine structure.

TABLE II. $^{13}C\{^1H\}$ NMR Spectral Data.[a]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *1a*[b] | 162.6 | 154.8 | 138.7 | 28.2 | 27.9 | 19.4 | 19.1 | 14.1 |
| *1b*[b] | 161.8 | 154.7 | 28.1 | 27.7 | 19.3 | 19.0 | 13.9 | |
| *1c*[b] | 163.2 | 162.6 | 130.6 | 28.6 | 19.4 | 14.0 | | |
| *1d*[b] | 163.1 | 161.8 | 28.6 | 28.5 | 27.7 | 19.4 | 14.0 | |
| *2a*[b] | 155.3 | 27.6 | 19.1 | 14.0 | | | | |
| *2b*[b] | 156.1 | 19.0 | 9.8 | | | | | |
| *3a*[c] | 163.6 | 155.0 | 28.2 | 28.0 | 19.4 | 19.1 | 14.1 | 14.0 |
| *3b*[b] | 164.9 | 156.1 | 19.7 | 19.4 | 9.9 | 9.6 | | |
| *5*[c] | 159.1 | 28.1 | 27.8 | 26.4 | 19.2 | 14.3 | 14.1 | |
| *6b*[b,d] | 163.8 | 163.0 | 131.6 | 127.6 | 127.3 | 20.1 | 9.9 | |
| *7*[c,d] | 162.6 | 161.9 | 26.6 | 25.9 | 19.9 | 14.2 | 9.9 | |
| *8*[b] | 162.9 | 162.2 | 131.7 | 127.6 | 127.3 | 28.5 | 19.4 | 14.0 |
| *10*[b] | 24.6 | 13.0(br) | | | | | | |

[a] Chloroform-*d* solution; expressed in δ units relative to chloroform-*d* (δ 77.0). [b] 25.14 MHz spectrum. [c] 62.89 MHz spectrum. [d] Mixture of *cis* and *trans* isomers.

systems for compounds *1c*, *1d*, and *8*. (Compounds *1c*, *1d*, and *8* contain two chemically distinct propyl groups due to the difference in the two bridging boron groups, $BF_2$ and BFR.)

The 250 MHz spectra of isomers *6b*(1) and *6b*(2) along with their simulated spectra based on an $ABX_3$ spin system are shown in Figs. 4 and 5, respectively. The chemical shifts, coupling constants, and RMS error of fit from the simulations are as follows: isomer *6b*(1); $\delta_A = 2.72$, $\delta_B = 2.56$, $\delta_X = 1.19$, $J(AB) = 13.24$ Hz, $J(AX) = 7.62$ Hz, $J(BX) = 7.48$ Hz, RMS error of fit = $3.2 \times 10^{-4}$ ppm; isomer *6b*(2); $\delta_A = 2.68$, $\delta_B = 2.61$, $\delta_X = 1.19$, $J(AB) = 13.51$ Hz, $J(AX) = 7.65$ Hz, $J(BX) = 7.58$ Hz, RMS error of fit = $5.2 \times 10^{-4}$ ppm. The geminal coupling constants, $J(AB)$, for these two isomers are of the order of 13 Hz as compared to other geminal coupling constants for organic compounds of 0–20 Hz [12].

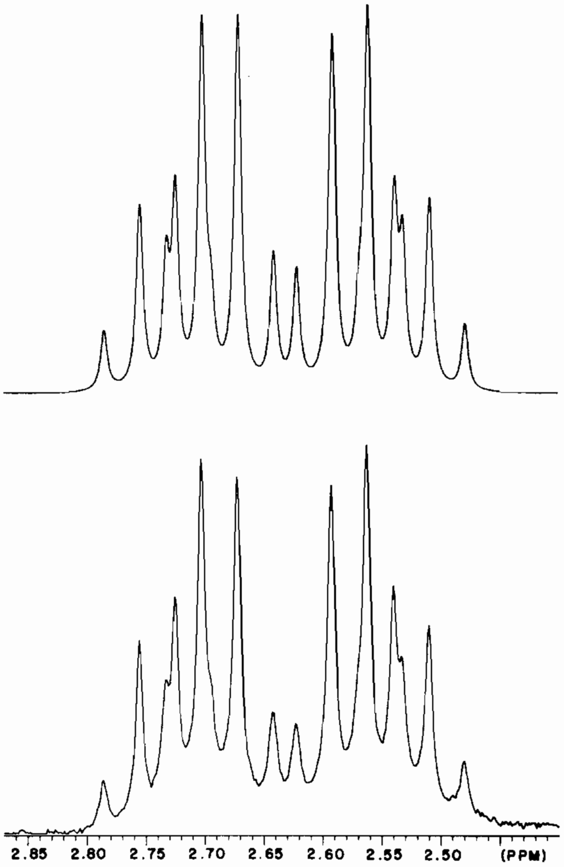

Fig. 4. Comparison of the observed (bottom) and simulated (top) $^1$H NMR spectra (250 MHz) of isomer *6b* (1). The simulated spectrum was generated using an $ABX_3$ model.

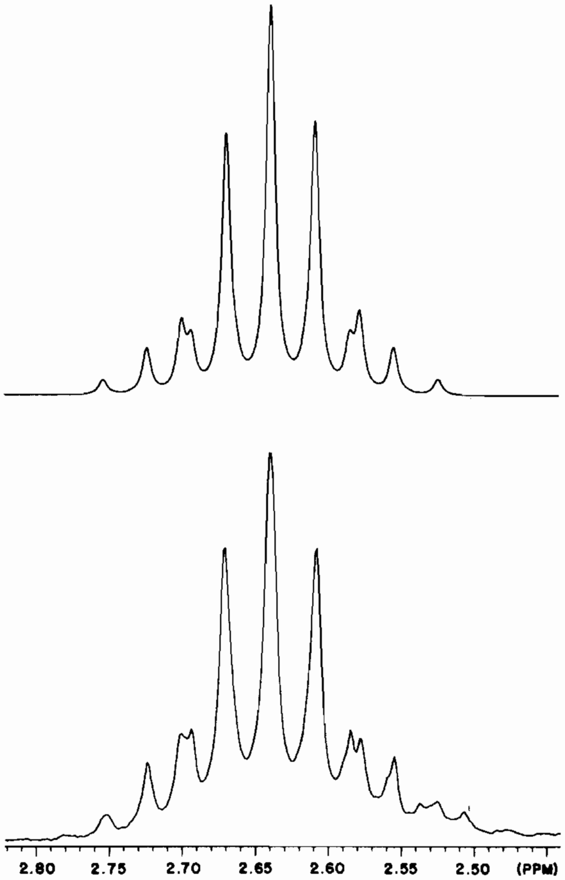

Fig. 5. Comparison of the observed (bottom) and simulated (top) $^1$H NMR spectra (250 MHz) of isomer *6b* (2). The simulated spectrum was generated using an $ABX_3$ model.

### $^{13}C\{^1H\}$ *NMR*

Similar trends are observed in the $^{13}C\{^1H\}$ NMR spectra as those observed in the $^1$H NMR spectra for the various complexes (Table II).

The resonances of the imine carbons, which lie in the region of δ 155–165, shift downfield as much as 8.8 ppm on going from compounds with hydrogen bridges to boron-group bridges. Compounds with two types of bridging groups (BFR or $BF_2$ at one end and H at the other, *e.g.* compounds *1a, 1b, 3a,* and *3b, or* BFR at one end and $BF_2$ at the other, *e.g. 1c, 1d,* and *8*) have two types of imine carbons with a chemical shift difference of up to 1.3 ppm. The mixtures of the isomers of compounds *6b* and *7* contain two resonances for the imine carbon separated by *ca.* 0.7 ppm. Since the four imine carbons in each isomer are chemically equivalent, each imine carbon resonance must be due to only one isomer. The carbon-13 resonances of the methylene and methyl groups of these complexes occur at δ 14–28, and the resonances of the phenylene carbons occur at δ 130–139. The carbon attached to the boron atom is only observable in the trigonal boron compound, 1,4-butanediylbis(difluoroborane), *10* (at δ 13) and is very broad. This resonance is absent in all the nickel complexes containing B–R groups; an effect probably due to partially relaxed scalar coupling between boron and carbon caused by the quadrupolar boron nucleus interacting with the electric field gradient generated by its unsymmetrical ligand field [13].

### $^{19}F$ *NMR*

The $^{19}$F NMR spectra of these compounds show several trends that assist in their identification and characterization (Table III). The chemical shift of fluorine on tetrahedral boron is upfield from that of fluorine on trigonal boron compounds by as much as 75 ppm. The $^{19}$F NMR line widths vary from 15–60 Hz for the nickel complexes (Table III) as compared to 2–5 Hz for the (1,3-diketonato)boron difluorides and related compounds [14]. The broad resonances obtained for the nickel complexes further support the hypothesis that the electronic environment

TABLE III. $^{19}$F NMR Spectral Data.[a]

| | Chemical Shifts[a] | | | Line Width[d] |
|---|---|---|---|---|
| *1a* | −149.6(s) | | | 25 |
| *1b* | −151.6(s) | | | 34 |
| *1c* | −149.0(s, 1F) | −151.9(d, 1F, $^{2}J_{\mathrm{FF}} = 53$) | −155.8(d, 1F, $^{2}J_{\mathrm{FF}} = 53$) | 27[e] |
| *1d* | −149.4(s, 1F) | −152.4(d, 1F, $^{2}J_{\mathrm{FF}} = 57$) | −155.8(d, 1F, $^{2}J_{\mathrm{FF}} = 57$) | 30[e] |
| *3a* | −154.3(q, $J_{\mathrm{BF}} = 4.8$) | | | 20 |
| *3b* | −154.6(q, $J_{\mathrm{BF}} = 5.5$) | | | 23 |
| *4b* | −153.6(s) | | | 15 |
| *6a*[b] | −149.3(s) | −150.9(s) | | 48 |
| *6b*[b] | −149.8(s) | −151.9(s) | | 46 |
| *7*[b] | −148.8(s) | −152.0(s) | | 60 |
| *8* | −149.4(s, 1F) | −151.6(d, 1F, $^{2}J_{\mathrm{FF}} = 56$) | −155.9(d, 1F, $^{2}J_{\mathrm{FF}} = 56$) | 57[e] |
| *9* | −87.5(m)[c] | | | |
| *10* | −75.0(q, $J_{\mathrm{BF}} = 75$) | | | |

[a] Chloroform-*d* solution; 84.67 MHz; expressed in δ units relative to hexafluorobenzene internal standard (δ −162.9); *J* given in Hz. [b] Mixture of *cis* and *trans* isomers. [c] Expressed in δ units relative to trifluoroacetic acid external standard (δ −76.5). [d] Full width at half maximum; given Hz. [e] Singlet only.

around boron is not symmetrical, giving rise to quadrupolar broadening effects in the attached nuclei.

The mixtures of the *cis* and *trans* isomers for the compounds *6a, 6b,* and *7* give rise to two broadened resonances separated by ~2 ppm. The isolated isomers of compound *6b* each have only one resonance as is expected for the two chemically equivalent fluorines in each isomer. Isomers *6b*(1) and *6b*(2) have chemical shifts of δ −151.9 and −149.8, respectively. Unfortunately, even though the two isomers *6b*(1) and *6b*(2) have significantly different $^{1}$H- and $^{19}$F-NMR spectra, we are unable to assign them as *cis* or *trans*. The $^{19}$F NMR spectra of the compounds *1a, 1b, 4b, 6a, 6b,* and *7* are singlets whereas the $^{19}$F NMR spectra of the compounds *1c, 1d* (see Fig. 6), and *8* display a singlet and two doublets due to the chemical inequivalence of the three fluorines. The two geminal fluorines have $^{2}J_{\mathrm{FBF}}$ on the order of 55 Hz. The $^{19}$F NMR spectra of the polymeric species from the first band from gel permeation chromatography were recorded and were similar to each other, regardless of whether the species were formed from the reactions which produced mono-linked dimers or di-linked dimers. The $^{19}$F NMR spectra of the polymeric species consisted of two singlets, similar in chemicals shifts and broadness to the spectra of the mixture of isomers of compounds *6a, 6b,* and *7*. This suggests that the polymers are made up of –R–BF bridged bis(α-dioximato)nickel(II) units containing fluorines both *cis* and *trans* to one another.

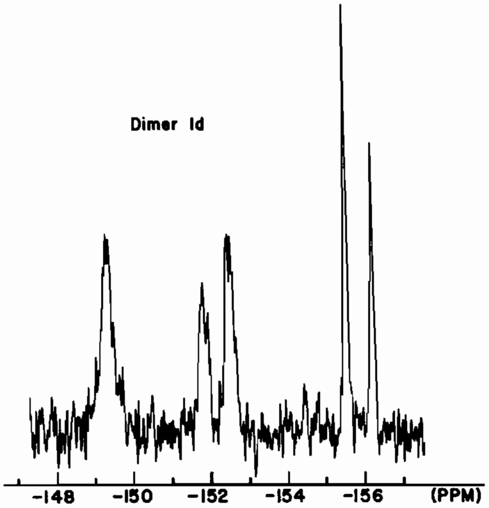

Fig. 6. The $^{19}$F NMR spectrum (84.67 MHz) of the binuclear complex *1d* showing the three chemically distinct types of fluorines and the geminal coupling of two of the fluorines ($^{2}J_{\mathrm{FBF}} = 57$ Hz).

### *Infrared*

The C=N stretching region can be used to distinguish between di-hydrogen bridged compounds (*2a* and *2b*), one-boron bridged compounds (*1a, 1b, 3a,* and *3b*), and di-boron bridged compounds (*4a, 4b, 5, 6a, 6b, 7,* and *8*) (Table IV). The C=N stretching frequency increases by up to 60 cm$^{-1}$ on going

TABLE IV. Infrared Spectral Data in the Region 1480–1620 cm$^{-1}$.[a]

| | | |
|---|---|---|
| *1a* | 1585 | 1500 |
| *1b* | 1580 | 1500 |
| *1c* | 1605 | |
| *1d* | 1605 | |
| *2a* | 1545 | |
| *2b* | 1550 | |
| *3a* | 1595 | 1505 |
| *3b* | 1595 | 1505 |
| *4a* | 1615 | |
| *4b* | 1615 | |
| *5* | 1585 | |
| *6a*[b] | 1600, 1610 | |
| *6b*[b] | 1600 | |
| *7*[b] | 1610 | |
| *8* | 1610 | |

[a] KBr pellet; cm$^{-1}$. [b] Mixture of *cis* and *trans* isomers.

from di-hydrogen bridged to one-boron bridged to di-boron compounds.

There is a peak at ~1500 cm$^{-1}$ that is characteristic only of the complexes containing one bridging boron group such as *1a, 1b, 3a* and *3b* (Table IV). This apparently arises from the change in symmetry of the molecules from $D_{2h}$ for the di-hydrogen bridged and di-boron bridged complexes to $C_{2v}$ for the mono-boron bridged complexes (Point group symmetries are idealized and ignore the inequivalence of the substituents on boron and the non-planar conformations with regard to the boron center.) If only the four C=N groups are considered, then for the $D_{2h}$ symmetry, two IR-allowed transitions of the $B_{2u}$ and $B_{3u}$ type and two Raman-allowed transitions of the $A_g$ and $B_{1g}$ type would be expected. For the $C_{2v}$ case there are two $A_1$ and two $B_1$ transitions which are both IR- and Raman-allowed. Therefore, it is likely that the band at *ca.* 1500 cm$^{-1}$ observed in the mono-boron-bridged complexes is only a Raman-allowed transition for the di-hydrogen bridged and di-boron bridged compounds, and the change in symmetry allows the transition to be IR-allowed in the mono-boron bridged compounds. Further evidence to support this comes from two recent reports in the literature. Nishida and coworkers observed a band at 1510 cm$^{-1}$ in the resonance Raman spectrum of bis(α-dioximato)nickel(II) [15] which is absent in the IR spectrum [16]. Gagné and coworkers have reported the IR spectra of several closely related tetraimine macrocyclic compounds of both $D_{2h}$ and $C_{2v}$ symmetry, and they observed one band due to the C=N group for $D_{2h}$ and two bands for $C_{2v}$ type compounds [17].

The ν(C–H) of the ethyl and propyl groups occur at approximately the same frequencies (*i.e.* ~2880, 2940, and 2975 cm$^{-1}$). The ν(C–H) of the phenyl hydrogens are weak and occur at ~3010, 3055, and 3075 cm$^{-1}$ for compounds *6a, 6b,* and *8* and only one peak at 3060 cm$^{-1}$ for the dimers *1a* and *1c*. The ν(C–H) of the linking butyl group for dimers *1b* and *1d* appears at 2930 cm$^{-1}$. However, the ν(C–H) for the butyl groups of the mononuclear compounds *5* and *7* are complicated because they overlap with the C–H stretches of the ethyl and propyl groups. All the nickel complexes except compounds *2a* and *2b* have a strong broad band at ~1010 cm$^{-1}$ which has been assigned to the B–F stretch based on the work of Schrauzer [5a] and the work of Brown and Bladon [14].

### *Hydrolytic Stability*

Schrauzer [5a] has reported that compound *4c,* which contains two $BF_2$ bridges, is stable not only to dilute but also concentrated hydrochloric acid. However, the compounds containing BF(R) bridges in place of $BF_2$ bridges are unstable in dilute hydrochloric acid and generally decompose within one day. Compound *6b* was decomposed by hydrochloric acid, and the resulting products were analyzed. Phenylboronic acid and compound *2b* were identified by their $^1$H NMR and IR spectra after separation from the product mixture. The rest of the product (a white solid) was unidentified but did not consist in any detectable proportion of either 3,4-hexanedione dioxime or boric acid as might be expected from extensive hydrolysis [18]. The stability of both compounds *6b* and *7* was determined in chloroform and in THF-water solutions in the presence of several bases ($NaHCO_3$, Proton Sponge, or 2,2,6,6-tetramethylpiperidine). The compounds *6b* and *7* are stable under these conditions for at least one month. Some hydrolysis was noticed after several months by the TLC detection of a small amount of compound *2b.* Even after one year in solution, compounds *6b* and *7* were still the major components.

### *Reactivity with $BF_3 \cdot Et_2O$*

All the boron bridged nickel complexes containing BFR bridges (*i.e. 1a–d, 5, 6a–b, 7,* and *8*) react with excess $BF_3 \cdot Et_2O$ to give the di-$BF_2$ bridged compounds (*4a* or *4b*). The rate of this reaction is fast, occurring at room temperature in less than 10 min. (the time necessary to run a TLC experiment or record a $^{19}$F NMR spectrum). Reaction of a stoichiometric amount of $BF_3 \cdot Et_2O$ with a nickel compound containing one BFR bridge and one H bridge (for example Method B, see above) results in the compound containing one BFR bridge and one $BF_2$ bridge. This shows that the attack by $BF_3 \cdot Et_2O$ at the H bridged end *vs.*

the BFR bridged end is more facile, as is expected.

### *Interconversion of Isomers*

Either isolated isomer *6b*(1) *or 6b*(2) can be interconverted to give a mixture of isomers *6b*(1) *and 6b* (2) with a catalytic amount of $BF_3 \cdot Et_2O$ or $BCl_3 \cdot Et_2O$. This interconversion was fast at room temperature and was complete in the time it took to record the $^{19}F$ NMR spectrum or perform an analysis by TLC (~10 min). Isomer *6b*(1) was the minor component (~40%) and isomer *6b*(2) was the major component (~60%) of the equilibrated mixture as determined by the peak areas of the $^{19}F$ NMR spectra. However, interconversion was not observed by the addition of a catalytic amount of $AlCl_3$, $B(n\text{-}C_4H_9)_3$, $(C_6H_5)B(OH)_2$, or aqueous HCl. Furthermore, the addition of an excess amount of $AlCl_3$, $B(n\text{-}C_4H_9)_3$, or aqueous HCl decomposed the isomer *6b*(2) without the formation of any isomer *6b*(1) as determined by TLC.

### *Stability to Ligand Exchange*

We are aware of only one previous study undertaken to examine whether bis(α-dioximato)nickel(II) complexes are stable to ligand exchange [19, 20]. The type of ligand exchange we were interested in studying involves the exchange of only *one* α-dioxime moiety for another between two bis(α-dioximato)-nickel(II) complexes. This ligand exchange process determines how stable these complexes are to ring opening of the macrocycle and eventual exchange of one half of the macrocycle (one α-dioxime moiety) for another. This exchange is expected to be slow or absent for these compounds predominantly because of this macrocyclic effect.

To study this ligand exchange, a solution consisting of a mixture of two different complexes, each one of which contains two identical α-dioxime ligand moieties (*i.e. 2a* and *2b*) was examined. The formation of the compound containing two different α-dioxime ligand moieties (*i.e. 2e*) would indicate that ligand exchange had occurred. Prior to the reaction, an analytical method of separation and identification of the prepared mixture of compounds *2a, 2b,* and *2e* was sought. TLC proved to be a convenient method, and all three compounds were well resolved from one another with the $R_f$ values following the series: *2a* > *2e* > *2b*. The boron bridged bis(α-dioximato)nickel(II) complexes *4b* and *4c* were also tested for ligand exchange and TLC was able to separate the three compounds with the $R_f$ values in the order *4b* > *4d* > *4c*.

*No* ligand exchange was observed for either the di-hydrogen and di-$BF_2$ bridged complexes in neutral media or for the di-$BF_2$ bridged complexes in dilute acidic media. However, the di-hydrogen bridged complexes underwent ligand exchange in the presence of acid. Furthermore, isomer *6b*(2) was kept in solution for several months without any detectable interconversion to isomer *6b*(1) as might be expected if ligand exchange was occurring.

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