

Characterization and Crystal Structure of Nickel Complexes of Imine Oximes Containing Tautomerized Enolate Ligands

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The nickel (II) complexes 3-hydroxy-3-penten-2-one oximato-*N,O*(3-methylimino-2-pentanone oximato-*N,N'*)-nickel(II), Ni(pen)(mei); 3-hydroxy-3-penten-2-one oximato-*N,O*(3-ethylimino-2-pentanone oximato-*N,N'*)-nickel(II), Ni(pen)(eti); 4-hydroxy-4-hexen-3-one oximato-*N,O*(4-methylimino-3-hexanone oximato-*N,N'*)-nickel(II), Ni(hex)(mei); and 4-hydroxy-4-hexen-3-one oximato-*N,O*(4-ethylimino-3-hexanone oximato-*N,N'*)-nickel(II), Ni(hex)(eti) have been synthesized from the corresponding alkyldione monoximes and amines and characterized by NMR, IR, MS, and elemental analysis. The latter three complexes have not been previously reported, and the characterization shows their structure to be contrary to that reported for Ni(pen)(mei) in earlier literature. Their formation suggests two separate courses of the alkyldione monoxime: reaction with amine to form the imine and keto/enol tautomerization. The crystal structure of Ni(hex)(eti) has been determined: monoclinic, $P2(1)/n$, $a = 8.2350(1)$ Å, $b = 14.0895(2)$ Å, $c = 13.7965(1)$ Å, $\beta = 95.964(1)^\circ$, with four molecules per unit cell. The reactivity of the complexes is explained based on the crystal structure and ^1H NMR data.

Introduction

It has been long established that complexes of the *vic*-dioximes, such as the classic bis(dimethylglyoximato)nickel(II), Ni(dmg)₂, are bound to the nickel atom through nitrogen and not oxygen atoms. Before the crystal structure of Ni(dmg)₂ was obtained,¹ only chemical evidence to this fact was available. In 1930, a compound was prepared that has been considered evidence for nitrogen bonding.² By reacting isonitroso diethyl ketone (2,3-pentanedione monoxime) with aqueous methylamine in the presence of nickel acetate, one obtains a red crystalline compound, which was given the proposed structure shown in Figure 1a. In later reviews,^{3–5} references to this structure were erroneously reported to have the form shown in Figure 1b. In either structure, the methylimino nitrogen must coordinate, and since the complex has properties similar to those of a dioxime complex, it was concluded that in the dioximates coordination must be through nitrogen. The structure in Figure 1a was deduced based on elemental analysis. Using modern characterization tools (NMR, IR, MS), we prove the correct structure to be of the form shown in Figure 2 (R = R' = CH₃), which a difference elemental analysis alone could not determine. In addition, we report three new compounds of similar structure with possible mechanisms of their production. The crystal structure determination of Ni(hex)(eti) is also included.

Experimental Section

Synthesis. The ligand precursors, 3,4-hexanedione monoxime and 2,3-pentanedione monoxime, were prepared in a method similar to

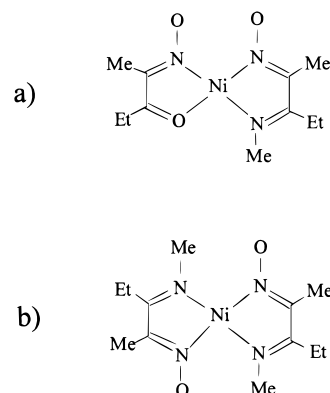


Figure 1. (a) Structure originally assigned by Pfeiffer. (b) Structure in later reviews.

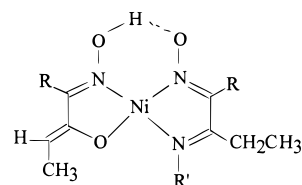


Figure 2. Structure, names, and symbols of the characterized complexes. R = R' = CH₃, Ni(pen)(mei); R = CH₃, R' = C₂H₅, Ni(pen)(eti); R = C₂H₅, R' = CH₃, Ni(hex)(mei); R = R' = C₂H₅, Ni(hex)(eti).

that for the synthesis of dioximes from α -diketones,⁶ except that only 1 equiv of hydroxylamine was used. 3,4-Hexanedione monoxime was prepared by dissolving hydroxylamine hydrochloride (6.08 g, 0.087 mole) in 50 mL of distilled water and cooling it to 0 °C. Potassium hydroxide (4.90 g, 0.087 mol) dissolved in 25 mL of distilled water was added dropwise to this solution until it was slightly basic. An amount of 10 g (0.087 mol) of 3,4-hexanedione (Aldrich) was added

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to the hydroxylamine solution in one portion, and the mixture was stirred overnight. The crude mixture was chilled, filtered, washed with cold water, and allowed to air-dry. Crude yield: 9.77 g (88%). The crude product was then purified by subliming at 50 °C, 0.2 Torr. Final yield: 7.00 g (63%). The procedure for making 2,3-pentanedione monoxime was essentially the same as that for the hexanedione derivative, except that sublimation was carried out at 70 °C/0.2 Torr. Yield: 60%.

Ni(pen)(mei) was prepared in a way similar to Pfeiffer's method² in which a hot solution of nickel(II) acetate tetrahydrate (3.00 g, 12 mmol) in 30 mL of distilled water is stirred with the yellow solution formed from the mixture of 2,3-pentanedione monoxime (3.00 g, 30.3 mmol) in 30 mL of 40% aqueous methylamine (340 mmol). The mixture immediately became grayish-black, with tarry byproducts adhering to the sides of the flask. A fine red-orange suspension forms in this mixture, which was immediately filtered and washed with cold water. The filtrate was set aside, with more product subsequently forming. The crude product was air-dried and recrystallized from hexane. Final yield: 21%. Ni(hex)(mei) was prepared as above using 3,4-hexanedione monoxime (3.00 g, 26.5 mmol). Yield, after recrystallization from hexane: 24%. It was found that by diluting the methylamine solutions with an additional 120 mL of water, the yields could be increased to 40%. Ni(hex)(eti) was prepared as above, except that 30 mL of 33% aqueous ethylamine (200 mmol) was used with the 3,4-hexanedione monoxime (3.00 g, 26.5 mmol). Yield: 40%. Ni(pen)(eti) was prepared as above from 30 mL of 33% ethylamine (200 mmol) and 2,3-pentanedione monoxime (3.00 g, 30.3 mmol). Yield, after recrystallization from hexane: 23%.

Characterization. 2,3-Pentanedione monoxime: IR (KBr, cm^{-1}) 3300 (br, s), 3020 (w), 2920 (w), 2880 (w), 1650 (vs), 1440 (s, br), 1400 (s), 1360 (s), 1350 (s), 1250 (m), 1120 (w), 1095 (m), 1040 (s), 1010 (vs), 910 (m), 795 (m), 770 (m), 730 (m), 695 (m), 610 (w), 570 (w), 515 (w), 450 (w), 410 (w); $^1\text{H NMR}$ (CDCl_3 , ppm, J in Hz) 1.082 (t, 3 H, $J = 7.2$), 1.965 (s, 3 H), 2.775 (q, 2 H, $J = 6.9$), 7.966 (s, 1 H).

3,4-Hexanedione monoxime: IR (KBr, cm^{-1}) 3300 (br, s), 3000 (w), 2960 (m), 2920 (w), 2840 (w), 1650 (vs), 1440 (m), 1395 (s), 1350 (m), 1300 (w), 1215 (s), 1090 (m), 1050 (s), 1005 (m), 980 (s), 960 (s), 890 (s), 780 (w), 735 (w), 700 (w), 670 (sh), 610 (w), 510 (w), 490 (w), 430 (w); $^1\text{H NMR}$ (CDCl_3 , ppm, J in Hz) 1.003 (t, 3 H, $J = 7.5$), 1.070 (t, 3 H, $J = 7.8$), 2.531 (q, 2 H, $J = 7.8$), 2.746 (q, 2 H, $J = 7.5$), 8.15 (s, 1 H).

Mixture of methylamine and 2,3-pentanedione monoxime. $^1\text{H NMR}$ (D_2O , ppm) 0.884 (t, 3 H), 1.630 (s, 3 H), 2.675 (q, 2 H, 2,3-pentanedione monoxime), 2.292 (s, NH_2CH_3).

Ni(pen)(mei), 300.08 g/mol: IR (KBr, cm^{-1}) 3040 (w), 2960 (m), 2900 (m), 2880 (m), 2820 (w), 1750 (br, w), 1600 (m), 1535 (w), 1450 (br, m), 1340 (s), 1285 (w), 1230 (w), 1200 (m), 1140 (s), 1120 (s), 1080 (m), 1070 (sh), 1040 (w), 1000 (m), 960 (m), 920 (m), 825 (w), 805 (w), 740 (m), 700 (w), 660 (w), 600 (m), 515 (w), 500 (m), 480 (m), 450 (m), 440 (m), 410 (m); $^1\text{H NMR}$ (C_6D_6 , ppm, J in Hz) 0.213 (t, 3 H, $J = 7.2$), 1.355 (q, 2 H, $J = 7.8$), 1.465 (s, 3 H), 1.856 (s, 3 H), 2.025 (d, 3 H, $J = 7.2$), 2.639 (s, 3 H), 4.725 (q, 1 H, $J = 6.6$), 16.945 (s, 1 H); MS m/z 300.1, M^+ , r.a. 100. Anal. ($\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_3\text{Ni}$) C, H, N: calcd 43.99, 6.33, 13.99; found 43.32, 6.28, 13.70. mp 148–152 °C.

Ni(pen)(eti), 314.08 g/mol: IR (KBr, cm^{-1}) 3040 (w), 2960 (m), 2940 (w), 2910 (m), 2940 (w), 2400 (br, w), 2280 (w), 1750 (br, w), 1670 (w), 1600 (m), 1540 (w), 1490 (sh), 1470 (m), 1440 (m), 1390 (w), 1340 (s), 1290 (m), 1255 (w), 1200 (w), 1155 (m), 1140 (s), 1120 (s), 1060 (m), 1005 (m), 970 (m), 945 (m), 890 (w), 825 (m), 805 (w), 745 (s), 700 (w), 665 (m), 605 (m), 600 (m), 560 (w), 530 (w), 500 (s), 465 (m), 445 (m), 400 (w). $^1\text{H NMR}$ (C_6D_6 , ppm, J in Hz) 0.281 (t, 3 H, $J = 7.8$), 1.110 (t, 3 H, $J = 7.2$), 1.411 (q, 2 H, $J = 7.2$), 1.461 (s, 3 H), 1.849 (s, 3 H), 1.991 (d, 3 H, $J = 7.5$), 3.041 (q, 2 H, $J = 6.3$), 4.705 (q, 1 H, $J = 7.2$), 16.938 (s, 1 H); MS m/z 314.1, M^+ , r.a. 100. Anal. ($\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_3\text{Ni}$) C, H, N: calcd 45.85, 6.69, 13.37; found 45.64, 6.66, 13.22. mp 115–119 °C.

Ni(hex)(mei), 328.08 g/mol: IR (KBr, cm^{-1}) 3040 (w), 2960 (m), 2920 (w), 2880 (w), 2840 (w), 2820 (w), 1750 (br, w), 1590 (m), 1525 (m), 1445 (sh), 1430 (s), 1375 (s), 1340 (s), 1300 (m), 1280 (m), 1220

(m), 1180 (m), 1130 (m), 1110 (s), 1080 (m), 1055 (m), 1025 (s), 980 (m), 960 (m), 920 (m), 890 (m), 830 (sh), 820 (m), 780 (m), 730 (m), 705 (m), 680 (w), 660 (w), 590 (m), 585 (m), 550 (w), 500 (w), 480 (s), 440 (m), 425 (m), 400 (m); $^1\text{H NMR}$ (C_6D_6 , ppm, J in Hz) 0.270 (t, 3 H, $J = 7.5$), 0.806 (t, 3 H, $J = 7.2$), 1.045 (t, 3 H, $J = 7.5$), 1.397 (q, 2 H, $J = 7.8$), 1.992 (q, 2 H, $J = 7.2$), 2.027 (d, 3 H, $J = 7.2$), 2.378 (q, 2 H, $J = 7.5$), 2.635 (s, 3 H), 4.773 (q, 1 H, $J = 6.9$), 16.839 (s, 1 H); $^{13}\text{C NMR}$ (C_6D_6 , ppm) 9.322, 10.020, 11.113, 11.447, 19.126, 20.112, 21.190, 34.909, 103.111, 154.406, 156.606, 167.214, 175.941; Hetcorr [^1H , ^{13}C], ppm] (0.270, 9.322), (0.806, 10.020), (1.045, 11.447), (1.397, 21.190), (1.992, 11.113), (2.027, 19.126), (2.378, 20.112), (2.635, 34.909), (4.773, 103.111); MS m/z 328.4, M^+ , r.a. 100. Anal. ($\text{C}_{13}\text{H}_{23}\text{N}_3\text{O}_3\text{Ni}$) C, H, N: calcd 47.62, 7.01, 12.81; found 47.50, 7.08, 12.85. mp 123–126 °C.

Ni(hex)(eti), 342.08 g/mol: IR (KBr, cm^{-1}) 3040 (w), 2980 (s), 2960 (s), 2920 (s), 2900 (m), 2860 (m), 2840 (m), 1750 (br, w), 1605 (s), 1580 (w), 1545 (m), 1480 (s), 1450 (s), 1410 (m), 1395 (m), 1380 (s), 1340 (w), 1310 (m), 1295 (m), 1240 (m), 1235 (m), 1180 (m), 1160 (s), 1140 (m), 1120 (s), 1100 (sh), 1070 (m), 1040 (m), 1015 (w), 985 (m), 935 (m), 870 (w), 845 (w), 830 (m), 795 (w), 740 (m), 720 (m), 685 (w), 660 (w), 600 (w), 595 (m), 560 (w), 530 (w), 490 (m), 470 (w), 450 (m), 435 (m), 400 (w); $^1\text{H NMR}$ (C_6D_6 , ppm, J in Hz) 0.377 (t, 3 H, $J = 7.8$), 0.842 (t, 3 H, $J = 7.5$), 1.050 (t, 3 H, $J = 7.2$), 1.126 (t, 3 H, $J = 7.2$), 1.510 (q, 2 H, $J = 7.2$), 1.997 (q, 2 H, $J = 7.2$), 2.021 (d, 3 H, $J = 7.2$), 2.384 (q, 2 H, $J = 7.5$), 3.067 (q, 2 H, 7.5), 4.77 (q, 1 H, $J = 6.9$), 16.853 (s, 1 H); MS m/z 342.1, M^+ , r.a. 100. Anal. ($\text{C}_{14}\text{H}_{25}\text{N}_3\text{O}_3\text{Ni}$) C, H, N: calcd 49.11, 7.31, 12.27; found 49.23, 7.36, 12.33. mp 129 °C.

General. $^1\text{H NMR}$ (300 MHz) and $^{13}\text{C NMR}$ (75 MHz) spectra were recorded on a Varian Gemini-300 spectrometer. The D_2O solution of methylamine was prepared by heating 50 mL of a 40% aqueous solution of methylamine to 90 °C, passing the vapors through a drying tube of CaCl_2 , and bubbling them into 10 mL of D_2O for 1 min. Approximately 3 mL of this was mixed with 3 mg of 2,3-pentanedione monoxime for $^1\text{H NMR}$ analysis. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. The low-resolution mass spectra were obtained on a Finnigan MAT-90 mass spectrometer using chemical ionization. Isobutane was used as the reagent gas, with a source temperature of 250 °C and a source pressure of $(2-10)^{-4}$ Torr. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Crystal Structure Determination for Ni(hex)(eti). The single crystal was obtained by slow cooling of a hot hexane solution: $\text{C}_{14}\text{H}_{25}\text{N}_3\text{O}_3\text{Ni}$, $M_r = 342.08$, monoclinic, $P2_1/n$, $a = 8.2350(1)$ Å, $b = 14.0895(2)$ Å, $c = 13.7965(1)$ Å, $\beta = 95.964(1)^\circ$, $V = 1592.10(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.427$ g cm^{-3} . Data were collected at 173 K on a Siemens SMART Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 7115 reflections. A hemisphere of data (1321 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was $<1\%$). Integration absorption corrections were applied based on indexed measured crystal faces. The structure was solved by the direct methods in SHELXTLS⁷ and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were refined with isotropic thermal parameters and without any constraints. In the final cycle of refinement, 291 parameters were refined using 3145 reflections with $I > 2\sigma(I)$ to yield R1 and wR2 of 3.09% and 6.87%, respectively. Refinement was done using F^2 .

Results and Discussion

Synthesis. Our procedure differed from Pfeiffer's in that we used 40% methylamine as opposed to 33%, resulting in an amine excess of about 10:1. However, using 33% methylamine, the excess is only about half as large. To be certain that this did

(7) Sheldrick, G. *SHELXTLS*; Siemens Analytical Instrumentation: Madison, WI, 1995.

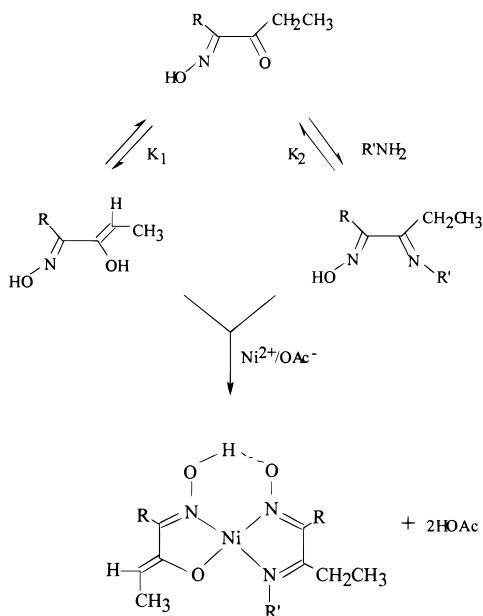


Figure 3. Reaction scheme, showing both courses of the alkyldione monoxime toward complexation.

not vary the product, the preparation of the 2,3-pentanedione monoxime derivative was also performed using 33% methylamine, and a product of exactly the same characteristics as Ni(pen)(mei) was obtained.

In the preparation of these complexes, the imine oxime product of the alkyldione monoxime and amine was not isolated but was reacted in situ with aqueous nickel(II) acetate. If one assumes the imine oxime to be the only species that coordinates, then the structure in Figure 1b is reasonable; however, this structure was never reported by Pfeiffer. Our results show that the imine formation represents only half of the fate of the alkyldione monoxime. Figure 3 shows both courses that the monoxime must take. The monoxime may react reversibly (K₂) with amine forming the imine oxime, but in addition, the keto form of the monoxime must tautomerize (K₁) into the enol form. It is noteworthy that neither of these intermediates have been isolated. Attempts to isolate the imine oxime by evaporating the yellow solution formed on mixing the monoxime and amine resulted in complete reversal, yielding only the unreacted monoxime. Imine formation from ketones may be acid catalyzed,⁸ but this also proved unsuccessful, and equilibrium constants for keto/enol tautomerization are usually very small. To see if any of these species were present before the addition of Ni²⁺, ¹H NMR was carried out on a mixture of 2,3-pentanedione monoxime and methylamine in D₂O. The only peaks observed were a singlet, quartet, and triplet associated with the monoxime and a singlet due to methyl protons on methylamine. The -NH₂ and =N-OH protons undergo D₂O exchange and are not observed. No new peaks indicative of a reaction were present, despite the formation of a yellow solution from colorless reagents. This suggests that either the intermediates are below the detection limit or they are formed only in the presence of Ni²⁺. In the former case, coordination to nickel is irreversible, and precipitation drives these reactions, while in the latter, nickel affords an alternate pathway, promoting the formation of its own ligands. Finally, there is the point of intramolecular hydrogen bonding in the products; no other arrangement will allow for this, be it coordination solely by

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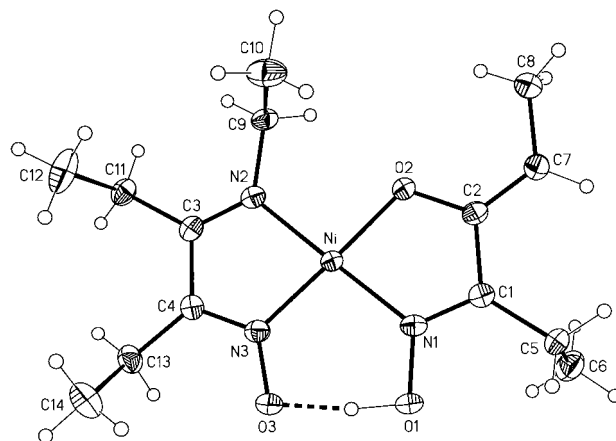


Figure 4. Crystal structure of Ni(hex)(eti).

the imine oxime or the enol, and thermodynamically speaking, it may be a stabilizing factor.

Crystal Structure of Ni(hex)(eti). The structure of the molecule is shown in Figure 4. The nickel atom has a square planar coordination geometry and lies at a distance of 0.015(1) Å from the coordination plane. The O-O distance [2.472(2) Å] is slightly longer than that found in nickel complexes of the *vic*-dioximes,^{1,9,10} with the bridging proton being asymmetrically bound. The O1-H distance is 1.02(3) Å, while the O3-H distance is 1.46(3). Asymmetric hydrogen bonding usually occurs when the O-O distance is greater than 2.5 Å.³ The longer distance in this complex occurs because of the varying lengths of the Ni-N and Ni-O bonds. The Ni-O2 and Ni-N3 bonds are shorter [1.8352(13) and 1.847(2) Å, respectively] than the Ni-N1 and Ni-N2 lengths [1.860(2) and 1.887(2) Å, respectively]. This effectively separates the hydrogen-bridged oxygen atoms more than when all four bonds are nearly the same length as in the *vic*-dioximates (~1.86 Å) and must be a consequence of the oxygen heteroatom in the coordination sphere. Other selected intermolecular distances and angles are shown in Table 1. The complex packs in pairs related by a center of inversion. Short intrapair distances are observed between Ni and N1 [Ni-N1 is 3.488(2) Å and angle N1-Ni-N1 (-x, -y, 2-z) is 102.01(6)°]. The distance between nickel atoms inside a pair is 4.2969(5) Å, and the coordination planes outside of pairs are not parallel to each other. Table 2 gives a summary of the crystal data for Ni(hex)(eti).

IR. The most immediately noticeable feature in the IR spectra of the complexes that supports the structure is the $\nu(\text{C}=\text{H})$, occurring as a medium band [weak in Ni(pen)(mei)] in the characteristic 3050 cm⁻¹ region. Weak bands are also found in this region in the ligand precursors, suggesting that the alkyldione monoximes may exist as oxime enols in the solid state. In the complexes, near 1600 and 1540 cm⁻¹ are a medium and medium/weak band, respectively. In nickel complexes of the *vic*-dioximes, the $\nu(\text{C}=\text{N})$ band occurs¹¹⁻¹³ near 1550 cm⁻¹. So, due to the similarity of our complexes to these, we assign the latter band to $\nu(\text{C}=\text{N})$. The former band is most likely associated with $\delta(\text{C}=\text{C})$. This stretch is normally weak and at lower energy (1690-1635 cm⁻¹) for highly symmetric com-

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(11) Rundle, R.; Parasol, M. *J. Chem. Phys.* **1952**, *20*, 1487-1488.

(12) Blinc, R.; Hadzi, D. *J. Chem. Soc.* **1958**, 4536-4540.

(13) Burger, K.; Ruff, I.; Ruff, F. *J. Inorg. Nucl. Chem.* **1964**, *27*, 179-190.

Table 1. Selected Bond Angles and Distances in Ni(hex)(eti)

bond	angle (deg)	bond	length (Å)
O2–Ni–N3	177.56(6)	Ni–O2	1.8352(13)
O2–Ni–N1	84.15(6)	Ni–N3	1.847(2)
N3–Ni–N1	97.87(7)	Ni–N1	1.860(2)
O2–Ni–N2	95.04(6)	Ni–N2	1.887(2)
N3–Ni–N2	82.93(7)	O1–N1	1.369(2)
N1–Ni–N2	179.06(7)	O1–H1	1.102(3)
N1–O1–H1	100(2)	N1–C1	1.297(2)
C1–N1–O1	117.9(2)	C1–C2	1.472(3)
C1–N1–Ni	117.09(13)	C1–C5	1.498(3)
O1–N1–Ni	124.94(12)	O2–C2	1.341(2)
N1–C1–C2	110.6(2)	N2–C3	1.299(2)
N1–C1–C5	123.1(2)	N2–C9	1.472(2)
C2–C1–C5	126.3(2)	C2–C7	1.345(3)
C2–O2–Ni	113.97(11)	O3–N3	1.316(2)
C3–N2–C9	123.7(2)	O3–H1	1.46(3)
C3–N2–Ni	114.57(13)	N3–C4	1.308(2)
C9–N2–Ni	121.73(12)	C3–C4	1.467(3)
O2–C2–C7	122.6(2)	C3–C11	1.506(3)
O2–C2–C1	114.1(2)	C4–C13	1.507(3)
C7–C2–C1	123.3(2)		
N3–O3–H1	103.0(13)		
C4–N3–O3	119.7(2)		
C4–N3–Ni	117.06(13)		
O3–N3–Ni	123.23(12)		
N2–C3–C4	114.0(2)		
N2–C3–C11	125.7(2)		
C4–C3–C11	120.3(2)		
N3–C4–C3	111.4(2)		
N3–C4–C13	121.0(2)		
C3–C4–C13	127.6(2)		

Table 2. Crystallographic Data for Ni(hex)(eti)^a

chemical formula: C ₁₄ H ₂₅ N ₃ O ₃ Ni	fw: 342.08
<i>a</i> = 8.2350(1) Å, α = 90°	space group: <i>P</i> 2(1)/ <i>n</i>
<i>b</i> = 14.0895(2) Å, β = 95.964(1)°	<i>T</i> = 173(2) K
<i>c</i> = 13.7965(1) Å, γ = 90°	λ = 0.71073 Å
<i>V</i> = 1592.10(3) Å ³	ρ _{calcd} = 1.427 g cm ⁻³
<i>Z</i> = 4	<i>R</i> (<i>F</i> _o ²) = 3.09%
μ = 12.32 cm ⁻¹	<i>R</i> _w (<i>F</i> _o ²) = 6.87%

^a *R* = Σ(|*F*_o| – |*F*_c|)/Σ|*F*_o|. *R*_w = [Σ(*w*(*F*_o² – *F*_c²)²)/Σ(*w*(*F*_o²)²)]^{1/2}. *S* = [Σ(*w*(*F*_o² – *F*_c²)²)/(*n* – *p*)]^{1/2}. *w* = 1/[σ²(*F*_o²) + (0.0370*p*)² + 0.31*p*], *p* = [max(*F*_o², 0) + 2*F*_c²]/3.

pounds but stronger and nearer 1590 cm⁻¹ for asymmetric compounds and compounds containing the C=C–N function,¹⁴ as is the case for our compounds. In the monoxime ligand precursor, the ν(C=N) band is masked by a very strong ν(CO) stretch, which occurs near 1640 cm⁻¹. This band is expectedly missing in the complexes and is replaced by the ν(C=N) band. The strong ν(OH) band in the ligand precursor (3300 cm⁻¹) is apparently shifted to lower energy upon coordination due to hydrogen bridging between oxygen atoms and is not present in this region in the complexes. This has been observed in chelates of the *vic*-dioximes,^{12,15} in which the bridging proton is symmetrically bound; however, at least in the case of Ni(hex)-(eti), the crystal structure shows the hydrogen bond to be asymmetric. A broad, weak band near 1750 cm⁻¹ is observable and is characteristic of δ(OH) for intramolecular hydrogen bonding.¹⁶ The ν(C–H) band near 2900 cm⁻¹ increases, as expected, through the series from Ni(pen)(mei) to Ni(hex)(eti), which contains the most C–H bonds. The region near 1400 cm⁻¹ shows a broad absorption in Ni(pen)(mei), which breaks up into many separate bands on moving through to Ni(hex)-

(eti), characteristic of δ(C–H). The region 1200–400 cm⁻¹ is represented by a host of absorptions. Strong bands near 1050 and 1250 cm⁻¹ are characteristic of the ν(NO) stretch in the *vic*-dioximes;¹¹ however, no distinguishing bands are observable here in our complexes. These bands may be weaker due to the complexes containing fewer N–O groups, and the many unassignable absorptions are undoubtedly complicated by the low symmetry of these molecules.

NMR. The ¹H NMR spectrum of the ligand precursor, 3,4-hexanedione monoxime, was straightforward, giving two sets of triplets (2.73 and 2.54 ppm) and two sets of quartets (1.07 and 1.02 ppm), with the singlet for the oxime proton at 8.15 ppm. In the monoximation of 2,3-pentanedione, isomers were a possibility depending on whether oximation occurred on the carbonyl containing the ethyl group or the methyl group. It was expected that the latter would occur preferentially on steric and electronic grounds, as the carbonyl with the methyl group is a better electrophile for nucleophilic attack by hydroxylamine. Signals associated with a single isomer were obtained and included a triplet and quartet at 1.18 and 2.77 ppm, respectively (ethyl group), a singlet at 1.96 ppm (methyl group), and a singlet at 7.96 ppm (oxime proton). The chemical shifts are consistent with the ethyl group being attached to the carbonyl carbon.¹⁴

The NMR data strongly support the claim that the 2,3-pentanedione monoxime/methylamine derivative prepared as in ref 2 and the other derivatives must have the structure shown in Figure 2. The ¹H NMR spectra of all the complexes are consistent with a structure containing alkyl groups in five separate environments. Deuterated acetone and chloroform were initially used as reference solvents; however, severe overlapping of these signals occurred with subsequent decomposition over time (within hours in acetone and about a day in chloroform), as evidenced by the bright-red solution becoming brown. In deuterated benzene, the compounds are stable indefinitely and all alkyl protons were resolved. The methyl protons on the oxime carbon in Ni(pen)(mei) and Ni(pen)(eti) occur as singlets near 1.46 and 1.85 ppm, the downfield signal likely associated with the deprotonated nitrogen. Ethyl groups in Ni(hex)(mei) and Ni(hex)(eti) result in methylene signals split into quartets by neighboring –CH₃ groups and occur near 1.5 and 1.9 ppm. All of the complexes contain an ethyl group at the imine carbon; for the “pen” derivatives, the methylene quartets are at about 1.3 ppm but at about 2.3 ppm for the “hex” derivatives. Greater deshielding by nitrogen on the methylimino protons gives a singlet further down at 2.63 ppm (“mei” derivatives), while the –CH₂– protons of an ethylimino group give corresponding quartets at 3.05 ppm (“eti” derivatives). The triplets associated with the –CH₃ protons on the ethyl groups are confined to the 0.18–1.15 ppm range for all the derivatives, with ethylimino signals occurring the furthest downfield.

All of the complexes have the same kinds of protons associated with the enolate group. The proton signal is split into a quartet by the neighboring methyl group and occurs at the characteristic frequency of about 4.7 ppm in each case. The methyl group occurs as a doublet at about 2 ppm and overlaps the quartet associated with the ethyl groups on the oxime carbon in Ni(hex)(eti) and Ni(pen)(mei).

The bridging proton is strongly deshielded by the oxygen atoms and occurs as a singlet between 16.83 and 16.94 ppm. In nickel complexes of alkyl-substituted *vic*-dioximes, known to have symmetrical hydrogen bonds,^{1,10} this signal occurs at 17.70 ppm.¹⁷ The lower frequency for our complexes suggests

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that the hydrogen is not symmetrically bonded and is thus deshielded to a lesser extent.

As a further aid in characterizing this novel structure, the ^1H , ^{13}C heteronuclear correlation pulse sequence (Hetcorr) was performed on Ni(hex)(mei). The triplets associated with the ethyl protons correlate to carbon signals occurring around 10 ppm, while the quartets were correlated to carbon signals near 20 ppm, both characteristic for alkyl carbons. The methyl protons on the enolate function also were associated with a carbon signal near 20 ppm, while the proton directly bonded to the enolate carbon was correlated with a carbon signal characteristically at 103 ppm. A carbon signal at 35 ppm (imine carbon) was associated with the protons at 2.6 ppm. As should be the case, four carbon signals between 154 and 176 ppm (= C—O and three C=N's) were not correlated with any protons, and the proton signal at 16.8 ppm (O—H \cdots O) was not correlated to a carbon signal.

Mass Spectra. In each case, the most abundant fragment was the molecular ion. Since the m/z 's, rounded to the nearest whole number, are even in each case and because the complexes contain only elements for which the most abundant atomic mass and valence are both even-numbered or both odd-numbered (H, O, C, Ni), the nitrogens must be present in an odd number.¹⁴ This fact and the very good agreement between the m/z values and calculated molecular weights further supports the assigned structures.

Reactivity with Boranes. In complexes of the *vic*-dioximes, the bridging proton may be replaced in reactions with $\text{BF}_3\cdot\text{Et}_2\text{O}$

or with trialkylboranes forming macrocycles, liberating HF or alkane, respectively.^{17,18} In the BF_2 derivative, the Lewis acidity of the nickel center is thus increased, allowing the attachment of axial ligands. Attempts to carry out these reactions on our complexes in CH_2Cl_2 were unsuccessful, however. This may be explained based on the symmetry of the bridging proton. In the dioximates, the proton is symmetrically bound such that neither O \cdots H bond is as strong as when the bonding is asymmetric and the proton is closer to one oxygen. The crystal structure shows this to be the case in Ni(hex)(eti), and the chemical shifts of the proton signals of the other complexes suggest these also have a proton of lower acidity, thus rendering this location unavailable for further chemistry of this sort.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of Ni(hex)(eti) is available on the Internet only. Access information is given on any current masthead page.

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