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A Nickel(II) Dithia Dioxime Derived Macrocycle

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Introduction

The presence of sulfur-ligated nickel(II) in the active sites of CO-dehydrogenases[2-5] has stimulated interest in nickel(II) complexes with thioether thiols,[6] amino thioethers,[7-11] thioethers,[12-14] and hexadentate thioether imine oximes[15] as possible models. We report here syntheses and properties of nickel(II) complexes with two new tetradentate uninegative dithioether ligands, $Dtdo^-$ and $Thyclops^-$, which are N_2S_2 analogues of the previously described N_4 ligands[16-18] $Dido^-$ and $Cyclops^-$ (Figure 1).

Experimental Section

Reagents and Methods. Synthesis reagents were used as received, except that racemic 3-chloro-2-butanone (Aldrich) was distilled off K_2CO_3 before use and NO was scrubbed with 5 M KOH. Reagents, equipment, and data treatment for electrochemistry were as described previously.[19,20] Other instrumentation included a Finnegan 4500 (MS), Perkin-Elmer 320 (UV-visible), and a GE Omega (300-MHz NMR). X-ray diffraction data were collected on a Siemens R3m/V diffractometer at 296 K.[21] Molecular modeling and NMR simulations were done on Macintosh II platforms, using Chem3D Plus and geNMR/SoftAT software.[22] Elemental microanalyses were performed by Robertson Microanalytical Laboratories (Madison, NJ).

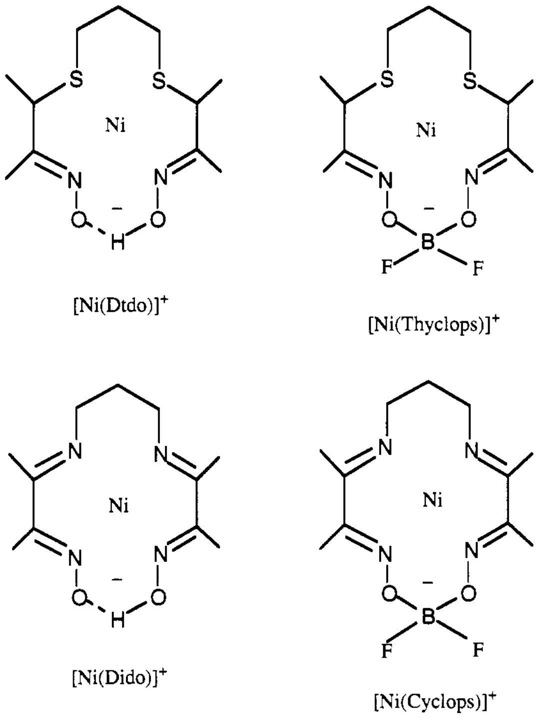
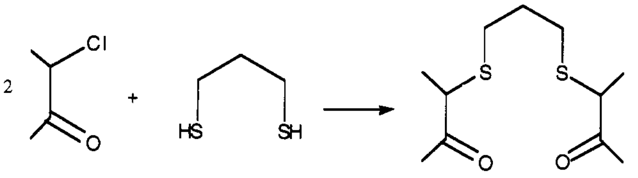

$[Ni(Dtdo)]^+$ $[Ni(Thyclops)]^+$ $[Ni(Dido)]^+$ $[Ni(Cyclops)]^+$

Figure 1. The complexes treated in this paper.

Scheme 1


I

$$(I) + 2\,NH_2OH \longrightarrow DtdoH + 2\,H_2O$$

$$DtdoH + Ni(ClO_4)_2 + NaOAc \longrightarrow [Ni(Dtdo)]ClO_4 + NaClO_4 + HOAc$$

$$[Ni(Dtdo)]^+ + BF_3.NEt_3 \longrightarrow [Ni(Thyclops)]^+ + [HNEt_3]^+F^-$$

Warning! Although neither $[Ni(Dtdo)]ClO_4$ nor $[Ni(Thyclops)]ClO_4$ has yet proved to be mechanically sensitive, such perchlorates are potentially explosive and should be handled with caution.[23]

Results and Discussion

Synthesis. Though conceptually quite straightforward, the Scheme-1 sequence for $[Ni(Dtdo)]ClO_4$ presented practical impediments,[24] originating mainly from the thermal instability of compounds such as the dithia diketone (I). $[Ni(Dtdo)]ClO_4$ may be obtained in a similarly low overall yield (2%) by a one-pot procedure, without isolation of the intermediates. The customarily applied[17,18] ring closure, utilizing excess $BF_3{\cdot}Et_2O$ as both solvent and reactant, or even as stoichiometric reactant, apparently leads here to thioether–carbon bond cleavage, so that, in effect, stoichiometric $BF_3{\cdot}NEt_3$ appears to be the reagent of choice.

Solid-State Structure of $[Ni(Dtdo)]ClO_4$. Crystal data and atomic coordinates for this perchlorate salt are given in Tables 1 and 2, and selected bond distances and angles, in Tables 3 and IV. The unit cell of the complex contains two noninteracting

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(2) Ellefson, W. L.; Whitman, W. B.; Wolfe, R. S. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3707.

(3) Cammack, R.; Patil, D.; Aguirre, R ; Hatchikian, E. C. *FEBS Lett.* **1982**, *142*, 289.

(4) Ragsdale, S. W.; Wood, H. G.; Antholine, W. E. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6811.

(5) Boham, D.; Ludden, P. W. *J. Biol. Chem.* **1987**, *262*, 2980.

(6) Sellmann, D.; Fünfgelder, S.; Pöhlmann, G.; Knoch, P.; Moll, M. *Inorg. Chem.* **1990**, *29*, 4772.

(7) Bouwman, E.; Westheide, C. E.; Driessen, L. W.; Reedijk, J. *Inorg. Chim. Acta* **1989**, *166*, 291.

(8) Ochocki, J.; Chaudhuri, P.; Driessen, W. L.; De Graaf, R. A. G.; Hulsbergen, F. B.; Reedijk, J. *Inorg. Chim. Acta* **1990**, *167*, 15.

(9) Ciampolini, M.; Gelsomini, J.; Nardi, N. *Inorg. Chim. Acta* **1968**, *2*, 343.

(10) Chia, P. S. K.; Livingstone, S. E. *Aust. J. Chem.* **1968**, *20*, 471.

(11) Alberts, A. H.; Lehn, J.-M.; Parker, D. *J. Chem. Soc., Dalton Trans.* **1985**, 2311.

(12) Hartman, J. A. R.; Cooper, S. *Inorg. Chim. Acta* **1986**, *11*, L43.

(13) Sellmann, D.; Neuner, H.-P.; Knoch, F. *Inorg. Chim. Acta* **1990**, *190*, 61.

(14) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

(15) Choudhary, S. B.; Ray, D.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4354

(16) Uhlig, E.; Friedrich, M. Z. *Anorg. Allg. Chem.* **1966**, *343*, 299.

(17) Wicholas, M.; Addison, A. W.; Lau, L. K.-M. *Abstracts of Papers*, 173rd National Meeting of the American Chemical society, New Orleans, LA; American Chemical Society: Washington, DC, 1977; INOR 183.

(18) Addison, A. W.; Watts, B.; Wicholas, M. *Inorg. Chem.* **1984**, *23*, 813.

(19) McDevitt, M. R.; Addison, A. W. *Inorg. Chim. Acta* **1993**, *204*, 141.

(20) Parker, V. D. In *Electroanalytical Chemistry: A Series of Advances, Vol. 14*; Bard, A. J., Ed.; Marcel Dekker Inc.: New York, 1986.

(21) Refinement was performed by direct methods minimizing $\Sigma_w(F_o - F_c)^2$, using the full-matrix least-squares procedure in the Siemens SHELXTL PLUS system, intensities being weighted according to $w^{-1} = \sigma_{F^2} + 0.0013F^2$. Further elaboration is given in the supplementary material.

(22) (a) Chem3D Plus, Cambridge Scientific Computing Inc. (b) geNMR, IvorySoft. (c) SoftAT, Insignia Solutions.

(23) Hawthorne, M. F. *Inorg. Chem.* **1993**, *32* (1), 4A.

(24) The reader bent on carrying out the synthesis is recommended to consult the supplementary material for details.

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Table 1. Crystal Data for [Ni(Dtdo)]ClO$_4$

empirical formula	$C_{11}H_{21}ClN_2NiO_6S_2$
color, habit	orange-red rhomb
crystal size	0.32 × 0.22 × 0.18 mm^3
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 7.200(2)$ Å
	$b = 10.318(3)$ Å
	$c = 13.119(4)$ Å
	$\alpha = 70.14(2)°$
	$\beta = 77.18(2)°$
	$\gamma = 89.88(2)°$
V	891.0(4) Å^3
Z	2
fw	435.6
density (calcd)	1.623 Mg/m^3
abs coeff	1.501 mm^{-1}
F(000)	452
R	5.22%
R_w	5.93%

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2 × 10) for [Ni(Dtdo)]ClO$_4$[a]

atom	$0^4x/a$	$10^4y/b$	$10^4z/c$	U(eq)[b]
Ni	3351(1)	115(1)	1596(1)	36(1)
Cl	4155(2)	2650(1)	3377(1)	52(1)
S(1)	1278(2)	-1314(1)	2946(1)	44(1)
S(2)	1175(2)	1393(1)	979(1)	44(1)
O(1)	6940(4)	-1043(4)	1512(3)	51(1)
O(2)	6929(4)	1138(3)	62(3)	53(1)
N(1)	5148(5)	-1120(4)	2153(3)	40(1)
N(2)	5097(5)	1446(4)	388(3)	40(1)
C(1)	4773(6)	-2088(4)	3138(3)	43(2)
C(2)	2828(7)	-2150(5)	3867(4)	50(2)
C(3)	-112(8)	-324(7)	3719(5)	57(2)
C(4)	-1372(8)	606(7)	3052(5)	63(2)
C(5)	-333(8)	1841(6)	2112(5)	61(2)
C(6)	2636(7)	3005(5)	193(4)	52(2)
C(7)	4652(7)	2647(5)	-162(4)	45(2)
C(8)	6173(9)	-3056(7)	3553(6)	58(2)
C(9)	1986(10)	-3598(8)	4605(6)	79(3)
C(10)	1781(11)	3878(8)	-754(6)	74(3)
C(11)	6087(11)	3676(8)	-1072(6)	68(3)
O(3)	4570(9)	2620(7)	2312(4)	127(3)
O(4)	4053(8)	1338(6)	4170(6)	147(3)
O(5)	5640(9)	3441(7)	3430(6)	142(4)
O(6)	2431(8)	3241(6)	3599(5)	125(3)

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Principal Bond Lengths (Å)[a] in [Ni(Dtdo)]ClO$_4$

Ni–S(1)	2.145(1)	Ni–S(2)	2.163(1)
Ni–N(1)	1.900(4)	Ni–N(2)	1.903(3)
Cl–O(3)	1.374(6)	Cl–O(4)	1.389(5)
Cl–O(5)	1.374(8)	Cl–O(6)	1.398(6)
S(1)–C(2)	1.826(5)	S(1)–C(3)	1.823(7)
S(2)–C(5)	1.830(7)	S(2)–C(6)	1.815(5)
O(1)–N(1)	1.361(4)	O(2)–N(2)	1.366(5)
N(1)–C(1)	1.308(5)	N(2)–C(7)	1.285(5)
C(1)–C(2)	1.498(6)	C(1)–C(8)	1.477(8)
C(2)–C(9)	1.516(8)	C(3)–C(4)	1.512(8)
C(4)–C(5)	1.494(7)	C(6)–C(7)	1.509(7)
C(6)–C(10)	1.520(9)	C(7)–C(11)	1.489(7)
Ni–O(3)	3.222(3)		

[a] Parentheses contain estimated standard deviations in the least significant digit.

molecules, each square-planar nickel(II) being bound (Figure 2) by two oxim(at)e nitrogens and two thioether sulfurs from Dtdo$^-$. The NiN$_2$S$_2$ plane is not exactly flat though, as the SS and NN halves are twisted by 12° with respect to each other. The Ni–S(thioether) distances are in the range observed previously by Sellmann *et al.* for other low-spin tetra- and pentacoordinate nickel(II) thiolate/thioether complexes.[6] The Ni–N(oxime) bonds are expected to be slightly longer than those in the [Ni(Cyclops)]$^+$ cation because of the greater size of the two thioether donors in the Dtdo$^-$ structure. The closest Ni–O(perchlorate) distance (Table 3) is a nonbonded one; its value is close to those described in the literature for $S = 0$ nickel(II) complexes with tetraaza macrocyclic ligands,[25] though the perchlorate oxygen does appear to be sitting in an electrostatic potential well generated by the metal ion.[26] An H-bond links the two oximate oxygen atoms to yield a quasi-macrocyclic structure, as is often the case in Ni(II) complexes with bi- or quadridentate oximes.[27] The ligand possesses a chair conformation, with the trimethylene unit and the oxime oxygens on opposite sides of the central NiN2S2 plane. The nonsymmetrically substituted carbon in the racemic chlorobutanone reactant appears as C(2) and C(6) in the product, the racemic nature being carried through intramolecularly, inasmuch as C(2) and C(6) are stereogenic in opposite senses. The crystallographically defined macrocycle thus has the C(9) and C(10) methyl groups in positions mutually cis with respect

Table 4. Bond Angles (deg)[a] in the [Ni(Dtdo)]$^+$ Cation

S(1)–Ni–S(2)	92.3(1)	S(1)–Ni–N(1)	84.7(1)
S(2)–Ni–N(1)	175.9(1)	S(1)–Ni–N(2)	177.2(1)
S(2)–Ni–N(2)	85.0(1)	N(1)–Ni–N(2)	98.0(1)
Ni–S(1)–C(2)	99.7(1)	Ni–S(1)–C(3)	107.3(2)
C(2)–S(1)–C(3)	101.5(3)	Ni–S(2)–C(5)	109.5(2)
Ni–S(2)–C(6)	99.2(2)	C(5)–S(2)–C(6)	101.1(3)
Ni–N(1)–O(1)	120.2(2)	Ni–N(1)–C(1)	123.9(3)
O(1)–N(1)–C(1)	115.9(4)	Ni–N(2)–O(2)	119.8(2)
Ni–N(2)–C(7)	123.6(3)	O(2)–N(2)–C(7)	116.7(3)
N(1)–C(1)–C(2)	116.3(4)	N(1)–C(1)–C(8)	123.3(4)
S(1)–C(2)–C(9)	110.3(4)	S(1)–C(2)–C(1)	106.9(3)
S(1)–C(3)–C(4)	111.6(5)	C(3)–C(4)–C(5)	114.7(5)
S(2)–C(5)–C(4)	112.9(5)	S(2)–C(6)–C(7)	107.5(3)
S(2)–C(6)–C(10)	110.5(4)	N(2)–C(7)–C(11)	121.7(5)
N(2)–C(7)–C(6)	117.2(3)		

[a] Parentheses contain estimated standard deviations in the least significant digit.

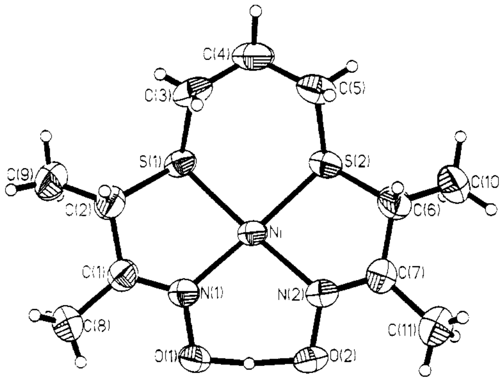

Figure 2. ORTEP representation of the structure of the [Ni(Dtdo)]$^+$ cation, showing the atomic numbering scheme for the non-hydrogen atoms.

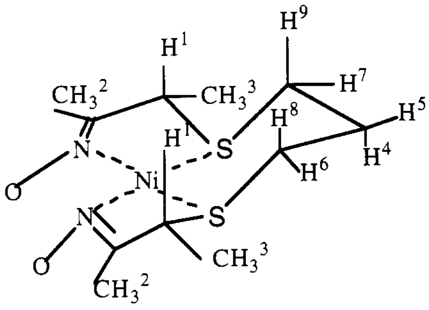

Figure 3. Relative spatial orientations of the protons in [Ni(Dtdo)]$^+$.

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(25) Suh, M. P.; Kang, S.-G.; Goedken, V. L.; Park, S.-H. *Inorg. Chem.* **1991**, *30*, 365.

(26) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 3645.

(27) Murmann, R. K.; Vassian, E. G. *Coord. Chem. Rev.* **1990**, *105*, 1.

Table 5. ^{1}H NMR Data and H–C–H Torsion Angles for [Ni(Dtdo)]ClO$_4$ in CD$_3$NO$_2$

proton type[a]	integral	shift (ppm)	*J* (Hz)
H1	2	4.05	$^3J_2 = 7.4$ (quartet) $^4J_2 = 1.2$ (quartet)
H2	6	2.10	$^4J_1 = 1.2$ (doublet)
H3	6	1.66	$^3J_1 = 7.4$ (doublet)
H4	1	1.80	$^2J_5 = -16.8$ (doublet) $^3J_{8,9} = 10.3$ (triplet) $^3J_{6,7} = 3.4$ (triplet)
H5	1	2.93	$^2J_4 = -16.8$ (doublet) $^3J_{6,7} = 4.9$ (triplet) $^3J_{8,9} = 2.0$ (triplet)
H6, H7	2	3.32	$^2J_{8,9} = -11.9$ (doublet) $^3J_5 = 4.9$ (doublet) $^3J_4 = 3.4$ (doublet)
H8, H9	2	3.37	$^2J_{6,7} = -11.9$ (doublet) $^3J_4 = 10.3$ (doublet) $^3J_5 = 2.0$ (doublet)

		coupling (Hz)	
torsion	angle (deg)[b]	calcd	obsd
4--6; 4--7	65.9	3.19	3.4
4--8; 4--9	165.0	8.58	10.3
5--6; 5--7	52.9	2.81	4.9
5--8; 5--9	76.3	1.74	2.0

[a] See Figure 3 for H-numbering. [b] Torsion angles were determined from the backbone positions as found in the X-ray structure, using the calculated (and minimized) proton positions.

to the NiN$_2$S$_2$ plane; the alternative trans isomers would be associated with C(2) and C(6) displaying the same of either of the alternative stereochemistries. Modeling of [Ni(Thyclops)]$^+$ indicated the chair conformer to again be less sterically encumbered than the boat form. In [Ni(Cyclops)I]^0, the axially bound iodide domes the NiN$_4$ plane and presumably influences the approximately 1:1 conformer distribution[28] as a result.

Spectroscopic Properties. The 1H NMR data for [Ni(Dtdo)]ClO$_4$ (Table 5) confirm persistence of the low-spin $^1A_1$ ground state of the nickel(II) in MeNO$_2$ solution. The protons on the S–ethylene–N bridges are of three different types, according to their attachment points and spatial orientations (Figure 3); their assignment is straightforwardly based on intensities and coupling constants. The shifts and couplings for the protons in the propylene linkage were well-determined via the simulation. Protons 6–9 form a strongly coupled set[29] and entail pairs which have the same chemical shift (6, 7 and 8, 9). The good correlation between the calculated and measured couplings reinforces the assignment of the protons in the structure to the specific shifts in the NMR.

The electronic spectra of the two thioether complexes in acetonitrile and nitromethane are very similar (Table 6), each containing a broad, intense band in the 410-nm region, of the type assigned previously to an MLCT transition.[30] In *N,N*-dimethylformamide solution though, [Ni(Dtdo)]$^+$ displays an electronic spectrum typical of high-spin nickel(II), but not due to Ni(DMF)$_x^{2+}$, thus indicating formation of $S = 1$ [Ni(Dtdo)(DMF)$_2$]$^+$.

Redox Chemistry. (a) [Ni(Dtdo)]$^+$. At both platinum and mercury electrodes, [Ni(Dtdo)]$^+$ showed only a single (reversible) reduction in MeCN, with $E_{1/2} = -1.15$ V. This process is assigned to formation of the Ni(I) complex from [Ni(Dtdo)]$^+$, and this is consistent with the derived $D\eta$ value of 1.8×10^{-8} g cm s^{-2}, typical of a coordination compound of this molecular size.[31] No dependence of the $E_{1/2}$ on concentration was found over a 10-fold range, nor was formation of any other stable Ni(III) or Ni(0) species[15,32] observed between +1.2 and −2.5 V. Impregnation of the MeCN solution of [Ni(Dtdo)]$^+$ with CO shifted the reduction wave anodically by 88 mV, which betokens binding of CO to nickel(I). The anodic peak, though, broadened considerably, with i_{pa} remaining diminished even at quite high scan rates ($i_{pa}/i_{pc} = 0.27$, $\Delta E_p = 1030$ mV at $\nu = 20$ V s^{-1}), and such behavior indicates a relatively rapid ($k_f \approx 3 \times 10^2$ s^{-1} [33]) subsequent lysis within the CO–Ni(I) adduct; possible reactions include C–S bond cleavage (or a fast demetalation). Saturation of the [Ni(Dtdo)]$^+$ solution with NO led to an electrochemically irreversible redox process and shifted the reduction wave anodically by 260 mV, similar to the effect of NO on [Ni(Cyclops)]$^+$,[17] the indication being of strong Ni(I)–NO interaction. In these CO/NO adductions, all the various rate processes were in a time régime comparable to or shorter than that of the voltammetry.

Table 6. Characteristic Properties of the Complexes

complex	medium	λ (nm)	ϵ (M^{-1} cm^{-1})	$E_{1/2}$ (V)[a]
[Ni(Dtdo)]$^+$	CH$_3$CN	410	800	−1.155[b]
	CH$_3$CN	320	3200	
	MeNO$_2$	410	830	
	MeNO$_2$	320	3100	
[Ni(Thyclops)]$^+$	CH$_3$CN	410	833	−0.58[c]
	CH$_3$CN	315	4830	−1.285[d]
	MeNO$_2$	410	830	
	MeNO$_2$	310	840	
[Ni(Cyclops)]$^+$	CH$_3$CN	390	4600	−0.925[e]
[Ni(Dido)]$^+$ [e]	CH$_3$CN	405	4300	−1.14
	CH$_3$CN	380	4600	−1.73

[a] *Vs* the nonaqueous Ag$^+$/Ag reference electrode; add 0.545 V for estimate of $E_{1/2}$ *vs* SHE. [b] Peak-to-peak potential separation ΔE_p extrapolates to 65 mV at zero scan rate. [c] $\Delta E_p = 140$ mV at $\upsilon = 50$ mV s^{-1}. [d] $\Delta E_p = 70$ mV at $\upsilon = 50$ mV s^{-1}. [e] From refs 17 and 18.

(b) [Ni(Thyclops)]$^+$. The Faradaic electrochemistry was rather obscured by adsorption processes. A well-defined reversible reduction is seen at $E_{1/2} = -1.285$ V at the Hg electrode. This 135-mV shift down from the value for [Ni(Dtdo)]$^+$ is rather surprising. However, at Pt, there is also a poorly defined voltammetric wave at *ca.* −0.58 V. If this were attributed to the Ni$^{II/I}$ couple, it would indicate replacement of the two imino nitrogens in [Ni(Cyclops)]$^{+/0}$ [18] by thioether donors stabilizes the nickel(I) relative to the nickel(II) state by about 350 mV. Systematization[34,35] of the effects of donor variation on $E_{1/2}$ appears vitiated, however, by the the two precursor oximate complexes actually exhibiting the same $E_{1/2}$.

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Supplementary Material Available: A textual presentation of the experimental details, Figure S1 (an NMR spectrum), Figure S2 (perchlorate interaction and conformation in the complexes), Table S1 (anisotropic displacement coefficients), and Table S2 (hydrogen atom coordinates) (5 pages). Ordering information is given on any current masthead page.

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(28) Anderson, O. P. *Acta Crystallogr.* **1981**, *B37*, 1194.

(29) The six nonequivalent protons in the propylene linkage were assigned by using the Karplus relationships between the H–C–C–H torsion angle and the ^3J coupling constant, in combination with the interpretation of a ^{1}H–^{1}H COSY spectrum to verify the coupling network. The Ni and the central CH$_2$ of the propylene bridge do not lie in a mirror plane in the solid state, but the torsion angles were averaged for the solution NMR, as noted in Table 5, the value for the ^2J coupling on the sp^3-hybridized carbon being taken as −12.4 Hz.

(30) Burdett, J. K.; Williams, P. D. *Inorg. Chem.* **1980**, *19*, 2779.

(31) Addison, A. W.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1984**, *23*, 1957.

(32) Bemtgen, J. M.; Gimpert, H.-R.; von Zelewsky, A. *Inorg. Chem.* **1983**, *22*, 3576.

(33) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(34) Augustin, M. A.; Yandell, J. K.; Addison, A. W.; Karlin, K. D. *Inorg. Chim. Acta* **1981**, *55* (B2), L35.

(35) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.