Mono- and Trinuclear Nickel(II) Complexes with Sulfur-Containing Oxime Ligands: Uncommon Templated Coupling of Oxime with Nitrile

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4,7-Dithiadecane-2,9-dione dioxime forms both violet and purple-black nickel(II) complexes with unexpected structural properties, quite unlike the square-planar chelates formed by its dithiaundecane homologue. Their perchlorate salts were isolated and examined crystallographically. The lilac product [Ni{(Dtox)(CH₃CNH)₂}]-(ClO₄)₂ entails a bis(iminoether) ligand formed by coupling of the dioxime with two moles of acetonitrile. The purple-black complex results from further ligand deprotonation, to yield trinuclear, antiferromagnetic [Ni₃(Dtox)-(DtoxH)₂](ClO₄)₂·CH₃CN, which maintains its structure in solution. The first one-electron electrochemical oxidation step is relatively facile for the trimer, yielding a $Ni_2^{II}Ni^{III}$ complex, whereas for [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂ a transient Ni(I) species is accessible. Comment is made on those properties (coordination number, donor type, core charge) of nickel(II) coordination spheres that affect the accessibility of the corresponding nickel(I) and nickel(III) forms. [Ni₃(Dtox)(DtoxH)₂](ClO₄)₂·CH₃CN crystallizes in the monoclinic space group $P2_1/n$, with cell parameters $a = 12.295(2)$ Å, $b = 17.360(2)$ Å, $c = 20.764(2)$ Å, $\alpha = 90°$, $\beta = 94.080(10)°$, $\gamma = 90°$, $V = 4420.7(6)$ Å³, Z = 4. [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂ crystallizes in the rhombohedral space group $R\bar{3}$, with cell parameters $a = 32.954(2)$ Å, $b = 32.954(2)$ Å, $c = 13.477(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, Z = 18.

Introduction

We present here a study of two nickel complexes with the new dithioether-dioxime ligand 4,7-dithiadecane-2,9-dione dioxime, DtoxH₂. Its homologue 3,9-dimethyl-4,8-dithiaundecane-2,10-dione dioxime (DtdoH₂) described previously[1] forms a planar nickel(II) complex of the type Ni(Dtdo)ClO₄. Nickel-(II) complexes with some other polydentate thioether-oxime ligands have been reported.[2−7] The aim of this work was to examine the structural, spectral, and redox properties of the new nickel complexes and to compare these characteristics with those of nickel(II) complexes with the analogous ligands (DtdoH₂,

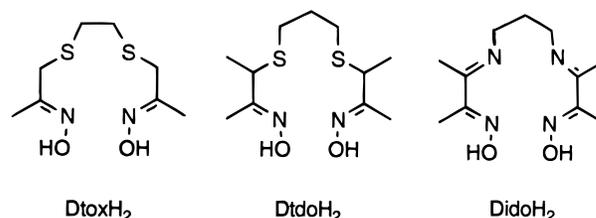**Figure 1.** Ligands treated in this paper.

DidoH₂, Figure 1) described in the literature. In this paper, for convenience, we modify the prior abbreviations for these two ligands[1,2,4] because of their potential ability form dianions, though of all their known metal complexes entail their mono-anionic forms. We have focused on sulfur-containing oximes because of their potential ability to stabilize both low oxidation states due to their "soft" sulfur donors and high oxidation states owing to their "hard" anionic oximate. We were curious about the consequences of such a juxtaposition and also wanted to examine the effects of the length of the carbon chain between the sulfur donors for the new ligand DtoxH⁻ in comparison with Ni(DtdoH)⁺ and Ni(DidoH)⁺. It was not obvious that the DtoxH⁻ ion would readily engird the metal ion to form a pseudomacrocycle like DtdoH⁻, because of the potential structural tensions associated with the shorter carbon chain. If such equatorial coordination occurred, then we expected that the resulting pseudomacrocycle's chemistry might be quantitatively distinct from that of Ni(DtdoH)⁺. DtoxH⁻ clearly may coordinate as a tetradentate N₂S₂ ligand, but precedent exists for such dioxime ligands also utilizing the oximate oxygens as

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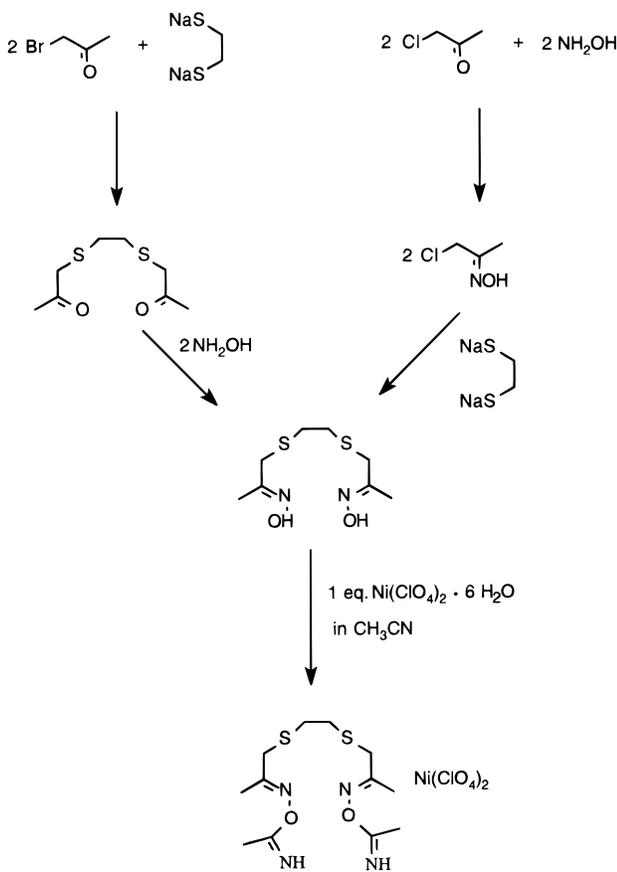† National Academy of Sciences of the Ukraine.
‡ Drexel University.
§ Howard University.
⊥ Memorial University.

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(6) Luneav, D.; Oshio, H.; Okawa, H.; Koikawa, M.; Kida, S. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 2212.
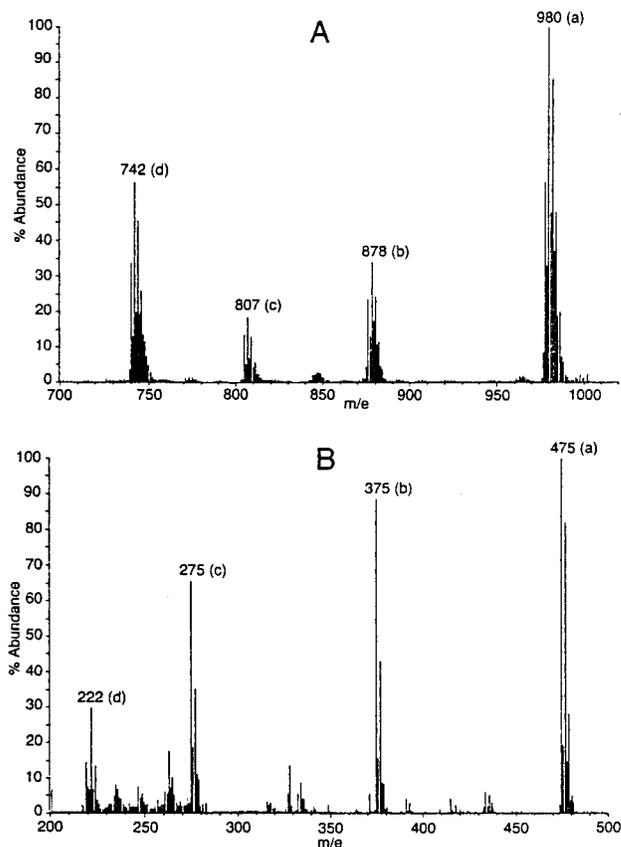(7) Costes, J.-P.; Dahan, F.; Dopvis, A.; Laurent, J.-P. *J. Chem. Soc., Dalton Trans.* **1998,** 1307.

Scheme 1. DtoxH$_2$ Synthesis and Ni^{2+}-Induced Coupling with Acetonitrile

Figure 2. FAB-MS of complexes. (A) Purple-black trimer: (a) [M(ClO$_4$)]$^+$, (b) M$^+$, (c) [M − C$_3$H$_5$NO]$^+$, (d) [M − C$_5$H$_{10}$NSO]$^+$, where M is [Ni$_3$(C$_{24}$H$_{47}$N$_6$S$_6$O$_6$)]. (B) Lilac acetonitrile adduct: (a) [M(ClO$_4$)]$^+$, (b) M$^+$, (c) [M − C$_4$H$_8$N$_2$O]$^+$, (d) [M − C$_7$H$_{13}$N$_3$O]$^+$, where M is [Ni(C$_{12}$H$_{22}$N$_4$S$_2$O$_2$)].

donor atoms to form oligonuclear compounds.[6,7] The attendant magnetic exchange interactions have recently also drawn some attention.[8,9]

Results and Discussion

Synthesis. The ligand was prepared according to Scheme 1 using two alternative routes. In route (i), the order of combining the reagents is quite critical, the desired product being obtained only when the disodium salt of ethanedithiol is added to the bromoacetone (Scheme 1). An analogous situation pertained for the synthesis of H$_2$Dtdo,[1] which may signal interference from some cyclic thioacetal formation. To circumvent this, an alternative synthesis of DtoxH$_2$ was also performed by condensing 3-chloro-2-propanone oxime with 1,2-ethanedithiol. As in the case of [Ni(DtdoH)]$^+$, the precursory diketone is not robust with respect to storage at ambient temperature.

Two different nickel(II) complexes were obtained by combination of the dioxime ligand DtoxH$_2$ with nickel(II) perchlorate in CH$_3$CN. Lilac prisms were obtained in the absence of added base, while base addition yielded a purplish-black product. Only the latter could be isolated when alcohol solvents were used for the synthesis. Although elemental analyses at least indicated that Ni(II) and the Dtox unit were present in a 1:1 ratio in these two compounds, they and several other lines of evidence (ultimately including the X-ray crystal structures) showed that neither is a simple pseudomacrocyclic complex of the type Ni(DtoxH)(ClO$_4$).

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Mass Spectra of Complexes. Peaks for compositions such as NiDtoxH$^+$ or NiDtoxClO$_4$$^+$ were not immediately apparent in the FABS mass spectra (Figure 2) of either the lilac or the purple-black nickel chelates of the dioxime ligand. The lilac complex, however, displays an intense peak at m/e = 475, corresponding to ^{35}ClO$_4$$^-$-adduced [^{58}Ni{(Dtox)(CH$_3$CNH)$_2$}]$^{2+}$, though the corresponding desolvated ions expected, such as [Ni{(Dtox)(CH$_3$CNH)}](ClO$_4$)$^+$ or [Ni(DtoxH$_2$)](ClO$_4$)$^+$, were observed weakly or not at all. In contrast, the purple-black product displayed an intense ion at m/e = 980, attributed to the trinuclear formulation Ni$_3$(Dtox)(DtoxH)$_2$(ClO$_4$)$^+$ (the calibration precision at masses higher than 900 is ±0.03%). Both spectra also contained peaks of ions formed as the result of C−S bond cleavage.

Structure of [Ni$_3$(Dtox)(DtoxH)$_2$](ClO$_4$)$_2$·CH$_3$CN. The purple-black trimer (Figure 3) entails three dioxime ligands, from which four of the six protons have been removed, so that only two perchlorates are required for electrostatic balance. The DtoxH$^-$ moieties are folded so that in each one both of the oximinopropyl arms are perpendicular to the central S−C−C−S units. The nickels(II) all display *trans*-N$_2$, *cis*-O$_2$, *cis*-S$_2$ pseudo-octahedral coordination and form an isosceles triangular arrangement. The triangle's base has the longer dimension, with Ni(1)−Ni(3) = 3.83 Å and the other two Ni−Ni(2) sides 3.18 Å. In each of DtoxH$^-$(1) and DtoxH$^-$(3), one of the two oxime-O's (O[1a] or O[1b]) is deprotonated and links each respective Ni(Dtox) moiety to the other two nickels: O(1a) of Ni(1) thus bridges between Ni(2) and Ni(3). Simultaneously, two oximate-O's (O[1c] and O[2c]) of the doubly deprotonated Dtox^{2-} coordinate to Ni(1) and Ni(3), respectively, while the last two
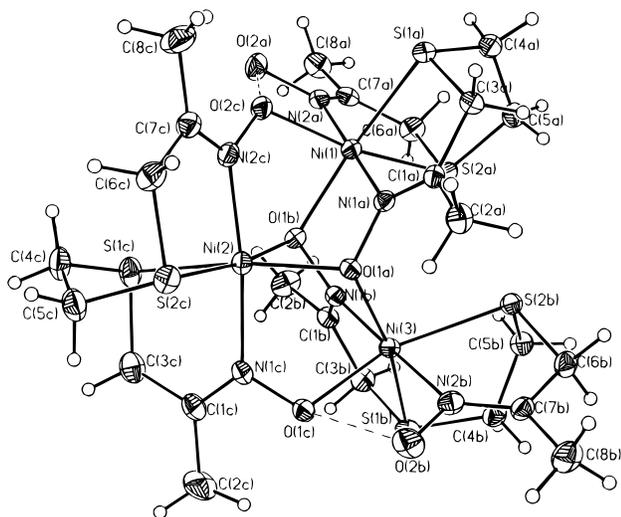
Figure 3. ORTEP projection of [Ni₃(Dtox)(DtoxH)₂](ClO₄)₂·CH₃CN (only cation shown). Thermal ellipsoids are drawn at the 20% probability level for clarity. The hydrogen atoms are shown as spheres of arbitrary size.

Table 1. Crystallographic Data

	[Ni₃(Dtox)(DtoxH)₂-(ClO₄)₂]·CH₃CN	[Ni(Dtox)(CH₃CNH)₂](ClO₄)₂
formula	$C_{26}H_{47}Cl_2N_7O_{14}Ni_3S_6$	$C_{12}H_{22}Cl_2N_4O_{10}NiS_2$
fw	1121.1	576.06
space group	$P2_1/n$	$R\bar{3}$
a, Å	12.295(2)	32.954(2)
b, Å	17.360(2)	32.954(2)
c, Å	20.764(2)	13.477(2)
α, deg	90	90
β, deg	94.080(10)	90
γ, deg	90	120
V, Å³	4420.7(6)	12675(2)
Z	4	18
ρ_{calc}, g cm⁻³	1.684	1.358
$F(000)$	2312	5328
μ, mm⁻¹	1.735	1.072
λ (Mo Kα), Å	0.71073	0.71073
T, K	293(2)	293(2)
R;[a] R_w[b]	0.0508; 0.1028	0.0615; 0.1218

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

oxime-O's of the DtoxH⁻ moieties (O[2a], O[2b]) are H-bonded to these coordinated O[nc]. The coordination octahedra are slightly irregular, with several angles departing from right angles by 10° or so, as exemplified in Figure 3 by N(1b)−Ni(3)−S(2b) at 100.05°. At the same time, the Ni(3)−S(2b) bond is the longest one, at 2.47 Å, the others varying down to 2.41 Å (S[1a]), though S(1c) and S(2c) are both 2.44 Å from Ni(2). Crystal and structural data for [Ni₃(Dtox)(DtoxH)₂])ClO₄)₂·CH₃-CN are given in Tables 1 and 2.

Structure of [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂. The structure (Figure 4) of the lilac monomer again reveals how the reactivity of Ni(DtoxH)⁺ is quite different from that of Ni(DtdoH)⁺. While the latter is monomeric, square planar, and inert toward CH₃-CN, its homologous DtoxH⁻ complex has reacted with solvent CH₃CN by coupling covalently to the nitrile. Indeed, each oxime group has added across the C≡N bond of a CH₃CN molecule to yield an iminoether, R−O−(C=NH)CH₃. Consequently, in what is now a linear hexadentate 2,5,12,15-tetramethyl-1,4,13,16-tetraaza-3,14-dioxa-7,10-dithiahexadeca-1,4,12,15-tetraene ligand, the two new imine nitrogens have become coordinated cis to the nickel(II). As in the trimer, the remaining N₂S₂ coordination is trans with respect to N donors and cis with respect to S atoms,

and the oximinopropyl arms are again folded away from the central S−C−C−S unit (Figure 4). This folding is a critical feature of these molecules, and we advance that it is one of the causes for formation both of the trimer and of the bis(iminoether) by destabilization of the square planar macrocyclic alternative. Incorporation of relatively larger thioether donors into the framework of a multidentate N,O donor ligand limits the ability of the chelating agent to fold its terminal arms so as to engird the metal ion equatorially.[10,11] In Ni(DtdoH)⁺, this constraint is alleviated by the presence of the additional C-atom in the trimethylene linkage between the thioether sulfurs, so that the oxime-N's and −O's remain in the NiSS plane, ultimately reinforced by the O's being H-bonded together into a quasi-macrocycle. However, in Ni(DtoxH)⁺, such an arrangement would lead to unfavorable compression of the Ni−S bonds, enlargement of the CSC angles, and elongation of the (S)C−C(S) and Ni−N bonds. These stresses are relieved by folding of the tetradentate ligand at its sulfurs, so that the oxime-O's are now trans. The immediate consequences are that (i) a face of the metal ion is now bared for coordination by two more cis donors and (ii) the reactivity of the oximes is no longer masked by their engagement in an O−H−O hydrogen bond system. Some mechanical stress does persist in the ultimate structure, as the N(1) and N(4) are somewhat pulled away from one another, so that the angles N(2)−Ni−N(4) and N(1)−Ni−N(3) are enlarged (102−103°), while angles such as N(3)−Ni−N(4) and N(1)−Ni−N(2) are accordingly reduced (77°). Crystal and structural data for [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂ are given in Tables 1 and 3.

Covalent Addition of 4,7-Dithiadecane-2,9-dione Dioxime to Acetonitrile in the Nickel(II) Complex. We found that the oxime/nitrile coupling reported here does not occur in the absence of the metal: after an acetonitrile solution of free ligand had been stirred for several days, unchanged ligand was obtained in quantitative yield. On the other hand, the reversible nature of the nickel-mediated coupling is confirmed by the fact that the purple-black trinuclear complex may be obtained from the lilac monononuclear [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂ by treatment of the latter with sodium acetate.

Metal ions are known to activate a wide range of coordinated ligands, making them able to attack various substrates, including nitriles.[12−17] This coordinated oxime/nitrile addition reaction has been observed in a few previous cases: for a palladium(II) system[15] and by Grigg et al.[12] in the case of a dioxovanadium(V) complex, the last apparently also involving reversibility. Attack of coordinated nitrile by oxime was proposed in the last instance, although there is little in the way of mechanistic

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ni₃(Dtox)(DtoxH)₂](ClO₄)₂·CH₃CN

Bond Lengths

Ni(1)−O(2C)	2.007(4)	Ni(1)−N(1A)	2.038(4)
Ni(1)−N(2A)	2.046(5)	Ni(1)−O(1B)	2.058(4)
Ni(1)−S(1A)	2.409(2)	Ni(1)−S(2A)	2.450(2)
Ni(2)−N(2C)	2.029(5)	Ni(2)−N(1C)	2.035(5)
Ni(2)−O(1B)	2.061(4)	Ni(2)−O(1A)	2.091(3)
Ni(2)−S(2C)	2.436(2)	Ni(2)−S(1C)	2.440(2)
Ni(3)−O(1C)	2.019(4)	Ni(3)−N(1B)	2.038(4)
Ni(3)−N(2B)	2.045(5)	Ni(3)−O(1A)	2.065(3)
Ni(3)−S(1B)	2.450(2)	Ni(3)−S(2B)	2.469(2)
N(2C)−O(2C)	1.369(6)	O(1A)−N(1A)	1.391(5)
N(1A)−C(1A)	1.276(6)	C(3A)−S(1A)	1.822(6)
S(1A)−C(4A)	1.799(6)	S(2A)−C(6A)	1.818(6)
C(7A)−N(2A)	1.270(7)	N(2A)−O(2A)	1.396(6)
O(1B)−N(1B)	1.394(5)	N(1B)−C(1B)	1.272(7)
N(1S)−C(1S)	1.114(12)	O(1A)−N(1A)	1.391(5)
C(3B)−S(1B)	1.805(6)	S(1B)−C(4B)	1.793(6)
C(5B)−S(2B)	1.807(6)	S(2B)−C(6B)	1.811(6)
C(7B)−N(2B)	1.261(7)	N(2B)−O(2B)	1.390(6)
O(1C)−N(1C)	1.360(6)	N(1C)−C(1C)	1.275(7)
C(3C)−S(1C)	1.824(7)	S(1C)−C(4C)	1.803(7)
C(5C)−S(2C)	1.821(7)	S(2C)−C(6C)	1.805(6)
C(7C)−N(2C)	1.277(7)		

Bond Angles

O(2C)−Ni(l)−N(lA)	94.3(2)	O(2C)−Ni(l)−N(2A)	84.0(2)
O(2C)−Ni(l)−O(lB)	88.7(2)	N(lA)−Ni(l)−O(lB)	87.2(2)
N(2A)−Ni(l)−O(lB)	93.9(2)	O(2C)−Ni(l)−S(lA)	90.70(12)
N(lA)−Ni(l)−S(lA)	81.79(13)	N(2A)−Ni(l)−S(lA)	97.00(13)
N(lA)−Ni(l)−S(2A)	102.10(12)	N(2A)−Ni(l)−S(2A)	79.48(14)
O(1B)−Ni(l)−S(2A)	95.96(10)	S(lA)−Ni(l)−S(2A)	87.72(6)
N(2C)−Ni(2)−O(lB)	91.8(2)	N(lC)−Ni(2)−O(lB)	94.8(2)
N(2C)−Ni(2)−O(lA)	94.6(2)	N(lC)−Ni(2)−O(lA)	90.3(2)
O(1B)−Ni(2)−O(lA)	82.13(14)	N(2C)−Ni(2)−S(2C)	81.38(14)
N(lC)−Ni(2)−S(2C)	91.94(13)	O(lA)−Ni(2)−S(2C)	99.83(11)
N(2C)−Ni(2)−S(lC)	94.40(14)	N(lC)−Ni(2)−S(lC)	81.36(14)
O(1B)−Ni(2)−S(lC)	91.13(11)	S(2C)−Ni(2)−S(lC)	87.91(6)
O(lC)−Ni(3)−N(lB)	94.8(2)	O(lC)−Ni(3)−N(2B)	86.4(2)
O(lC)−Ni(3)−O(lA)	85.73(14)	N(lB)−Ni(3)−O(lA)	87.8(2)
N(2B)−Ni(3)−O(lA)	91.9(2)	O(lC)−Ni(3)−S(lB)	88.32(12)
N(lB)−Ni(3)−S(lB)	81.61(13)	N(2B)−Ni(3)−S(lB)	98.78(14)
N(lB)−Ni(3)−S(2B)	100.05(12)	Ni(1)−O(1B)−Ni(2)	101.00(12)
Ni(2)−O(1a)−Ni(3)	99.90(12)		

Torsion Angles

Ni(1)−O(1B)−N(1B)−Ni(3)	69.5(1)	Ni(2)−N(1C)−O(1C)−Ni(3)	−43.0(1)
Ni(2)−N(2C)−O(2C)−Ni(1)	−31.1(1)	Ni(2)−O(1A)−N(1A)−Ni(1)	−32.8(1)
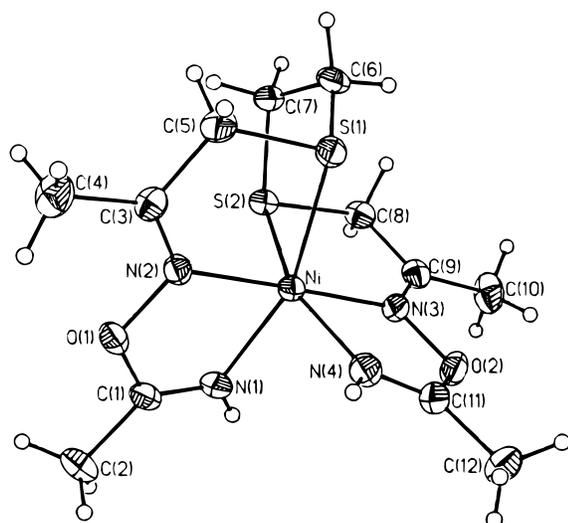
Figure 4. ORTEP projection of [Ni{(Dtox)(CH₃CNH)₂}](ClO₄)₂ (only cation shown). Thermal ellipsoids are drawn at the 20% probability level for clarity. The hydrogen atoms are shown as spheres of arbitrary size.

information in the literature. Inevitably at some stage, there must be attack of the oxime-O on the nitrile carbon atom. However,

it is not clear whether the greater part of the coordinative promotion of this reaction is through N-coordinative polarization of the nitrile or metal-ion assisted deprotonation[15] of oxime to the more nucleophilic oximate. Moreover, the close juxtaposition of the two reacting molecules via their coordination to Ni and the stabilization of the product molecule as a result of its chelation are undoubtedly also significant factors.[16b]

Electronic Spectra. The solution spectrum (Table 4) of the trinuclear complex [Ni₃(Dtox)(DtoxH)₂](ClO₄)₂·CH₃CN displays a broad, intense band at 255 nm which tails to 465 nm and which is absent from the spectrum of the mononuclear compound. This band might be compared with those in the trinuclear Ni(II) complexes with 3-mercaptoethylamine (MeaH) and 2-mercaptopropylamine (MpaH), of composition [Ni₃(Mpa/Mea)₄]²⁺. For the former, with an Ni−Ni distance of 2.7 Å, observable nickel−nickel interaction has been proposed,[17] while in [Ni₃(Mpa)₄]²⁺ ($r_{Ni-Ni} = 3.1$ Å) there is no electronic interaction. The longer Ni−Ni distances in [Ni₃(Dtox)-(DtoxH)₂]²⁺ and the presence of the oximate bridge, along with its energy and bandwidth, lead us to conclude that the 255 nm absorption is a composite of intraligand and/or O → Ni LMCT transitions[6,18] rather than a band involving multiple Ni(II) centers

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Table 3. Selected Bond Lengths (Å) and Angles (deg) in [Ni{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$

Bond Distances			
Ni−N(2)	2.007(4)	Ni−N(3)	2.011(5)
Ni−N(l)	2.028(5)	Ni−N(4)	2.037(6)
Ni−S(l)	2.450(2)	Ni−S(2)	2.451(2)
S(l)−C(6)	1.809(6)	S(l)−C(5)	1.822(6)
S(2)−C(7)	1.814(6)	S(2)−C(8)	1.826(6)
O(1)−C(1)	1.371(7)	O(1)−N(2)	1.418(5)
O(2)−C(11)	1.371(8)	O(2)−N(3)	1.408(6)
N(l)−C(l)	1.243(6)	N(2)−C(3)	1.259(7)
N(3)−C(9)	1.271(7)	N(4)−C(11)	1.247(8)

Bond Angles			
N(2)−Ni−N(3)	178.9(2)	N(2)−Ni−N(1)	76.8(2)
N(3)−Ni−N(1)	102.2(2)	N(2)−Ni−N(4)	102.9(2)
N(3)−Ni−N(4)	76.8(2)	N(l)−Ni−N(4)	92.9(2)
N(2)−Ni−S(1)	79.82(13)	N(3)−Ni−S(1)	101.20(13
N(l)−Ni−S(l)	156.6(2)	N(4)−Ni−S(1)	93.2(2)
N(2)−Ni−S(2)	100.33(14)	N(3)−Ni−S(2)	80.0(2)
N(l)−Ni−S(2)	95.0(2)	N(4)−Ni−S(2)	156.6(2)
S(l)−Ni−S(2)	88.29(6)	C(6)−S(l)−C(5)	102.6(3)
C(6)−S(l)−Ni	100.7(2)	C(5)−S(l)−Ni	97.7(2)
C(7)−S(2)−C(8)	102.9(3)	C(7)−S(2)−Ni	100.7(2)
C(8)−S(2)−Ni	97.4(2)	C(l)−O(l)−N(2)	110.4(4)
C(11)−O(2)−N(3)	111.2(4)	C(l)−N(l)−Ni	116.5(5)
C(3)−N(2)−O(1)	114.2(5)	C(3)−N(2)−Ni	130.3(4)
O(1)−N(2)−Ni	115.4(3)	C(9)−N(3)−0(2)	114.8(5)
C(9)−N(3)−Ni	130.0(4)	O(2)−N(3)−Ni	115.1(4)
C(ll)−N(4)−Ni	116.2(5)	N(l)−C(l)−O(l)	120.3(5)
N(l)−C(l)−C(2)	130.6(7)	O(1)−C(1)−C(2)	109.0(6)
N(2)−C(3)−C(4)	125.5(6)	N(2)−C(3)−C(5)	116.8(5)
C(3)−C(5)−S(1)	114.4(4)	C(7)−C(6)−S(1)	116.1(4)
C(6)−C(7)−S(2)	116.1(4)	C(9)−C(8)−S(2)	115.3(4)
N(3)−C(9)−C(8)	116.6(5)	N(3)−C(9)−C(10)	125.0(7)
N(4)−C(11)−0(2)	120.0(6)	N(4)−C(ll)−C(12)	129.3(8)

Table 4. Characteristic Properties of the Complexes

complex	medium	λ (nm)	ϵ (M^{-1} cm^{-1})	$E_{1/2}{}^{a}$ (V)
[Ni$_3$(Dtox)(DtoxH)$_2$]$^{2+}$	CH$_3$CN	870	80	+0.412
		560	37000	
		255	37000	
[Ni{(Dtox)(CH$_3$CNH)$_2$}]$^{2+}$	CH$_3$CN	826	88	−0.716
		559	29	
[Ni(DtdoH)]$^{+}$	CH$_3$CN	410	800	−1.155^{b}
		320	3200	
[Ni(DidoH)]$^{+}$	CH$_3$CN	405	4300	−1.14^{b}
		380	4600	−1.73

^{a} Vs the nonaqueous Ag^{+}(0.01 M, 0.1 M NEt$_4$ClO$_4$, MeCN)/Ag reference electrode; add 0.536 V for estimate of $E_{1/2}$ vs SHE. ^{b} From refs 1 and 2.

per se. For [Ni{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$, the appearance of the spectrum and its attendant classical spectroscopic parameters (10Dq = 12,100 cm^{-1}, Racah B = 678 cm^{-1})[19] are consistent with the compound's paramagnetic (vide infra) pseudo-octahedral nature. The LMCT band obscures the ^{3}A$_{2g}$ → ^{3}T$_{1g}$ transition in the trinuclear compound, so we can only estimate that 10Dq < 11 000 cm^{-1} for it.[20] The larger 10Dq value for the mononuclear compound results from replacement of oximate O donors by the imino N donors. The differences between the solid state and solution UV−vis spectra are minor, evidencing that [Ni$_3$(Dtox)(DtoxH)$_2$])ClO$_4$)$_2$·CH$_3$CN maintains its trinuclear structure in CH$_3$CN solution. The spectrum is also the same in DMF, though not all anionic oxygen-bridged nickel(II) systems

(19) The Racah B parameter was calculated as (2$\nu_1{}^2$ + $\nu_2{}^2$ − 3$\nu_1\nu_2$)/(15ν_2 − 27ν_1): Cooper, S. R.; Rawle, S. C.; Hartman, J. A. *Inorg. Chem.* **1988**, *27*, 1209.
(20) Rosenfield, S. G.; Wong, M. L. Y.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1987**, *24*, 4119.

are so solvent resistant; [Ni$_3$(2-mercaptopropionate)$_4$]$^{2-}$ apparently falls into a dissociation equilibrium.[20]

IR Spectra. The band at 1620 cm^{-1} in the IR spectrum of [Ni$_3$(Dtox)(DtoxH)$_2$](ClO$_4$)$_2$·CH$_3$CN may be assigned to the oxime C=N group. Two bands in the same region are present in the IR spectrum of [Ni{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$ at 1660 and 1705 cm^{-1}. In the alcohol or amine adducts of [Ni(Apdt)-(CH$_3$CN)]$^{+13}$, the imine C=N stretch is observed at 1640 or 1600 cm^{-1}, respectively, so we assign the band at 1660 cm^{-1} to the imine C=N bond. Coupling of CH$_3$CN with the oxime in [Ni{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$ also results in new N−H stretching bands at 3340 cm^{-1}, not present in the reactants. Again, these data are in good agreement with the 3320 cm^{-1} N−H absorptions in the [Ni(Apdt)(CH$_3$CN)]$^{+}$ alcohol/nitrile adducts. There is no shift of the oxime C=N band at 1620 cm^{-1} in the trinuclear complex in comparison to the free ligand.

Magnetic Properties. Whereas the lilac monomeric [Ni-{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$ is a simple paramagnet, with μ_{eff} = 2.9 μB at 293 K, the trinuclear complex entails magnetically coupled nickels(II).

Magnetic interactions in trinuclear nickel(II) systems were originally modeled in terms of the exchange integral constants J_a (or $J_{1,2} = J_{3,2}$) and J_b (or $J_{1,3}$) by Ginsberg et al.:[21]
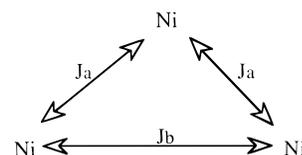
in relationship to the Hamiltonian:

$$\mathcal{H} = -2J_{1,2}[(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3)] - 2J_{3,1}(\hat{S}_3 \cdot \hat{S}_1) \quad (1)$$

yielding, for the molar susceptibility of the trimer:

$$\chi_m = \frac{2g^2 N\beta^2}{3kT} \cdot \frac{N}{D} \quad (2)$$

where g, N, β, k, and T have their usual meanings and

$$N = 42e^{(4J_a+2J_b)/kT} + 15e^{(2J_b-2J_a)/kT} + 15e^{(2J_a-2J_b)/kT} + 3e^{(2J_b-6J_a)/kT} + 3e^{(-2J_a-2J_b)/kT} + 3e^{-4J_b/kT}$$

$$D = 7e^{(4J_a+2J_b)/kT} + 5e^{(2J_b-2J_a)/kT} + 5e^{(2J_a-2J_b)/kT} + 3e^{(2J_b-6J_a)/kT} + 3e^{(-2J_a-2J_b)/kT} + 3e^{-4J_b/kT} + e^{(-4J_a-2J_b)/kT}$$

The same magnetically isosceles treatment has subsequently been applied in the literature explicitly to geometrically triangular $S = 1$ ion arrangements, including triangular $S = 1$ vanadium(III)[22] as well as other nickel(II) systems. More recently published work on trinickel(II)[23,24,25b] includes a term (zJ') for intertrimer exchange, uses a different model, and relates to a Hamiltonian differing from that of the prior work with respect to the definition of J:[21]

$$\mathcal{H} = -J_{1,2}[(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3)] - J_{3,1}(\hat{S}_3 \cdot \hat{S}_1) \quad (3)$$

(21) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1968**, *7*, 932; χ_A is given as (2$g^2 N\beta$ N)/(27k^2TD) or (2$g^2 N\beta^2N$)/(36kTD), which we presume is due to typographical error.
(22) Castro, S. L.; Streib, W. E.; Christou, G. *Inorg. Chem.* **1996**, *35*, 4462.
(23) Escuer, A.; Vicente, R.; Kumar, S. B.; Solans, X.; Font-Bardia, M.; Caneschi, A. *Inorg. Chem.* **1996**, *35*, 3094.
(24) Escuer, A.; Castro, I.; Mautner, F.; El Fallah, M. S.; Vicente, R. *Inorg. Chem.* **1997**, *36*, 4633.
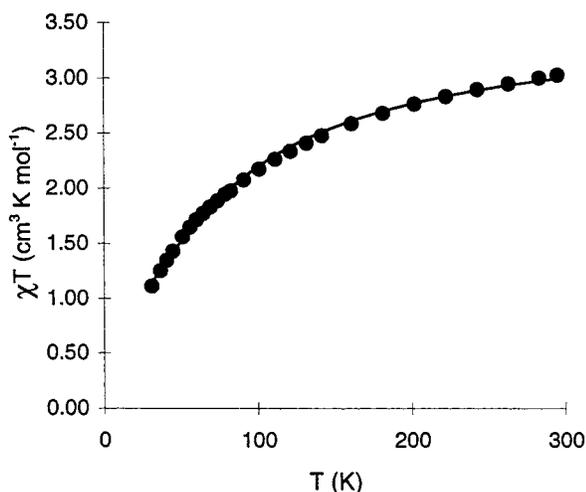
Figure 5. $\chi_m T$ *vs* T plot (per mole of trimer) for [Ni$_3$(Dtox)(DtoxH)$_2$]-(ClO$_4$)$_2$·CH$_3$CN.

The zero-field splitting in the nickel(II) ions is not taken into account in any of the published $S = 1$ models (a nontrivial task for oligonuclear systems[25a]).

We have estimated the coupling in the trimeric unit, in relationship to the corresponding molar susceptibility of the trimer as given by the Ginsberg model. The decrease in χT at lower temperature (Figure 5) relative to the corresponding simple paramagnet value (3.0 for $g = 2$ for a trinickel molecule) is clearly indicative of a dominant antiferromagnetic interaction within the trimer. Indeed, fitting of the data to the above expressions from eqs 1 and 2 results in estimates of -14.4 ± 0.6 and -7.6 ± 1.1 cm^{-1} for J_a and J_b, respectively. All three individual interactions being antiferromagnetic in nature is a situation having precedent in other $S = 1$ ion trimers.[22–24] The attendant g estimate (2.166 ± 0.006) matches expectation for $S = 1$ Ni(II),[27] while use of eq 3 yields J values that are essentially just double these above. The moderate couplings are consistent with their mediation by the two types of oximate bridges. First, Ni(2) is linked directly to each of Ni(1) and Ni(3) by a single-atom oximate-O bridge: the larger-than-90° bridge angles are consonant with the Ni–Ni coupling being antiferromagnetic.[26] Second, the four other bridges that link Ni(1) to Ni(2) and Ni-(3) and additionally Ni(3) to Ni(2) and Ni(1) are two-atom N–O linkages with a smaller contribution to the net coupling expected, as is observed for the Ni(2)–Ni(3) value (J_b).

Electrochemistry. In CH$_3$CN, the complex Ni$_3$(Dtox)-(DtoxH)$_2$$^{2+}$ is electroactive in the potential range -1 to $+1$ V vs the nonaqueous Ag$^+$/Ag reference electrode (Table 4). Cyclic voltammetry reveals a reversible oxidation at $E_{1/2} = +0.412$ V ($i_{p,c}/i_{p,a} = 1.0$) consistent with an $n = 1$ process and a rather low D value[28,29] of 4.6×10^{-6} cm^2 s^{-1} for this fairly large

diameter trinickel molecule. One might note that alternative assignments such as $n = 2$ do not lead to credible values for D. Another oxidation at higher potential ($+1.152$ V) is not Nernstian ($\Delta E_p = 160$ mV at $v = 100$ mV s^{-1}). The potential for Ni$^{3+/2+}$ in Ni$_3$(Dtox)(DtoxH)$_2$$^{2+}$ is similar to those found for the nickel(II) complexes of Dadtdo and Dadtpo[5] ($+0.33$ V, $+0.37$ V vs SCE, respectively, in water). The Ni(I) forms are unstable: there is a quite irreversible reduction with $E_{p,c} = -0.285$ V ($v = 100$ mV s^{-1}) having an anodic stripping counterpart peak at -0.065 V. No dependence of $E_{1/2}$ on Ni$_3$-(Dtox)(DtoxH)$_2$$^{2+}$ concentration between 2 and 5 mM was found, indicating that no dissociation of the compound or its oxidation product occurs in this concentration range.

A perusal of literature (available in the Supporting Information) involving electrochemical results for S/N-ligated Ni(II) oxidation and reduction reveals the influences of various ligand properties on the electrochemical potentials for generation of Ni(I) and Ni(III) species. Although we are not as yet able to codify these influences to the extent that has been possible for Cu$^{2+/+}$ or Ru$^{3+/2+}$ couples,[30,31] we advance certain coordination features, for three of which, the consequences for the Ni$^{3+/2+}$ and Ni$^{2+/+}$ couples parallel those for Cu$^{2+/+}$.

(1) Core charge is the dominant variable with respect to stabilizing Ni(III) relative to Ni(II). For example, with a core charge of -2, a complex such as [Ni(Pdc)$_2$]$^{2-}$ has an $E_{1/2}$ of around -100 mV.[32] This steps upward by about 350–400 mV for each unit increment in charge, reaching around $+1.4$ V for a core charge of $+2$, as in [Ni(9-ane-S$_3$)$_2$]$^{2+}$.[33] Core charge appears a less critical consideration for Ni(I) generation from Ni(II) than for Ni(III) generation, and also less so than in Cu-(II)/Cu(I) chemistry, where it has a substantial effect.[34,35]

(2) In regard to stabilizing Ni(I) relative to Ni(II), the introduction of S or P donors into the coordination sphere is much more influential than that of N or O donors, [Ni(Ph$_2$P·CH$_2$·CH$_2$·SEt)$_2$]$^{2+}$ serving as a good example of an unusually positive Ni$^{II/I}$ $E_{1/2}$.[36] This is rationalizable in terms of the HSAB principle,[37] with nickel(I) being markedly "soft". Conversely, S donors for example are ineffective at stabilizing Ni(III) relative to Ni(II).

(3) As in copper chemistry again, aliphatic N donors tend to stabilize the higher and aromatic N donors the lower oxidation states, though this is thermodynamically a lesser factor than (1) and (2) above. Thus, aliphatic-N bound to nickel(II) lowers the potential for generation of nickel(III), while unsaturated-N may be employed for stabilization of Ni(I).

(4) The coordination number of the Ni(II) reactant seems to have little bearing on the ease or difficulty of generating the corresponding Ni(I) species. However, most known Ni(III) complexes appear to be low-spin octahedral,[38–40] so that coordination number of the precursory Ni(II) molecule acquires

(25) (a) Mohanta, S.; Nanda, K. K.; Werner, R.; Haase, W.; Mukherjee, A. K.; Dutta, S. K.; Nag, K. *Inorg. Chem.* **1997**, *36*, 4656. (b) Although some apparently erroneous equations[23] were later adjusted,[24] these still seem incorrect as explicitly presented and should instead be: $\chi_{m3} = (g^2 N\beta^2/kT)\cdot(U/L)$, where $U = 6 + 6e^{(2J_a-2J_b)/kT} + 30e^{2J_a/kT} + 6e^{(3J_a-3J_b)/kT} + 30e^{(4J_a-J_b)/kT} + 84e^{5J_a/kT}$ and $L = 3 + e^{(J_a-2J_b)/kT} + 3e^{(2J_a-2J_b)/kT} + 5e^{2J_a/kT} + 3e^{(3J_a-3J_b)/kT} + 5e^{(4J_a-2J_b)/kT} + 7e^{5J_a/kT}$ as D is often considerably greater than zJ'[26] it seems not entirely appropriate to include only the latter within these existing models.

(26) Nanda, K. K.; Addison, A. W.; Paterson, N.; Sinn, E.; Thompson, L. K.; Sakaguchi, U. *Inorg. Chem.* **1998**, *37*, 1028.

(27) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill Book Co.: New York, 1972.

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

(29) $D\eta \approx 3 \times 10^{-7} (\rho/m))^{1/3}$, where the molecular mass m is in amu and the other quantities (diffusion coefficient D, absolute viscosity η, and effective molecular density ρ) are in cgsu.[26] Values for ρ of ca. 1.5 g cm^{-3} appear to be appropriate for many transition metal complexes.

(30) Addison, A. W. *Inorg. Chim. Acta* **1989,** *162*, 217.

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

(32) Krüger, H.-J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955; H$_2$-pdc = pyridine-2,6-bis(thiocarboxylic acid); we define core charge as the sum of the formal charges on the metal and the donor atoms.

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(37) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

relevance. Indeed, the majority of reported potentials for Ni(II) → Ni(III) involve hexacoordinate Ni(II).

The irreversible reduction of Ni$_3$(Dtox)(DtoxH)$_2$$^{2+}$ stands in contrast to that of Ni(DtdoH)$^+$, which occurs reversibly at -1.155 V.[1] The former complex lacks the delocalization associated with square-planar nickel(II), which is related to criterion 2 above. On the other hand, the oxidation of [Ni$_3$-(Dtox)(DtoxH)$_2$]$^{2+}$ is reversible, which was not observed in the case of Ni(DtdoH)$^+$ or Ni(DidoH)$^+$. As noted above, stabilization of Ni(III) in [Ni$_3$(Dtox)(DtoxH)$_2$]$^{3+}$ is effected partly by the greater anionicity of the donor environment compared to Ni(DtdoH)$^+$ or Ni(DidoH)$^+$ or their NiN$_4$ analogues. [Ni-{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$ displays a quasireversible wave at $E_{1/2} = -0.716$ V, which we attribute to a Ni$^{2+/+}$ redox process. Again, however, the Ni(I) product does not possess long-term stability under these experimental conditions.

Conclusions

4,7-Dithiadecane-2,9-dione dioxime forms nickel complexes with uncommon structural properties. In comparison with the prior trimethylene-dithioether chelates, decreasing the oligomethylene linkage between the two thioether sulfur donors has a marked influence on the outcome of the connected equilibria for complex deprotonation, self-association, quazimacrocyclization, and reaction with nitrile. A straightforward mononuclear low-spin nickel(II) chelate does not readily form. Among possible Ni–Ni interactions in [Ni$_3$(Dtox)(DtoxH)$_2$](ClO$_4$)$_2$, only antiferromagnetic exchange interactions may be firmly identified. The differences in donor atom type and in coordination number are the main reasons for variations in $E_{1/2}$ among [Ni$_3$-(Dtox)(DtoxH)$_2$],$^{2+}$ [Ni{(Dtox)(CH$_3$CNH)$_2$}]$^{2+}$, and the complexes with homologous N$_2$S$_2$ and analogous N$_4$ ligands.

Experimental Section

Materials. Commercially available reagents (from Aldrich and UkrReaChim) were used without further purification. Bromoacetone was prepared as described[41] and used immediately after distillation. Acetonitrile for electrochemistry was distilled off P$_4$O$_{10}$ under N$_2$.

Physical measurements. IR spectra were recorded on a Carl Zeiss-Jena Specord-75 and electronic spectra on a Carl Zeiss-Jena Specord M40 spectrophotometer, diffuse reflectance spectra in the solid-state being obtained from BaSO$_4$ matrixes. Variable-temperature magnetic susceptibility data were collected in the range 35–300 K using an Oxford Instruments superconducting Faraday magnetic susceptibility system incorporating a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed. Susceptibility data were corrected for diamagnetism using Pascal's constants, and HgCo(NCS)$_4$ was used as a calibration standard. Data were analyzed using SAS Institute's JMP 3.1 or MathSoft's MathCad Plus least-squares procedures on a Macintosh 603e platform. Elemental microanalyses were performed on a Carlo Erba 1106 microanalyzer or by Robertson Microanalytical Laboratories (Madison, NJ). Electrochemical data were obtained using a Bioanalytical Systems BAS-100 Electrochemical Analyzer, vs the nonaqueous Ag$^+$/Ag reference electrode; solutions were deoxygenated by bubbling with N$_2$. FABS-mass spectra were obtained from a ZABHF instrument.

Structure Analyses. For X-ray diffraction, a suitable crystal mounted on a glass fiber with epoxy cement and attached to a goniometer head was transferred to a Siemens P4S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7103$ Å). Cell constants and

orientation matrixes were obtained by least-squares refinement of setting angles of 25 randomly selected reflections. Accurate cell constants and improved orientation matrixes were obtained from the least-squares refinement of setting angles of the 50 strongest reflections found in the thin shell between 12.0 and 13.0° in θ. The collected data sets were analyzed for intense high χ (above 80°) reflections over a range of 2θ values, which were then scanned to provide the basis for empirical absorption corrections.

For [Ni$_3$(Dtox)(DtoxH)$_2$](ClO$_4$)$_2$·CH$_3$CN a total of 8173 reflections were collected ($0 \leq h \leq 14$, $-20 \leq k \leq 0$, $-24 \leq m \leq 24$) in the range of 2.03° to 25.00° with 7785 being unique ($R_{int} = 2.13\%$). The empirically derived transmission coefficient ranged from 0.67 to 0.82. The perchlorates were disordered and were modeled by idealizing the fragments to tetrahedral geometry and then refining the O occupancies so that they summed to unity.

For Ni[{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$, a total of 6460 reflections were collected ($0 \leq h \leq 40$, $-42 \leq k \leq 0$, $0 \leq m \leq 15$) in the range of 2.298° to 27.50° with 6087 being unique ($R_{int} = 3.52\%$). The empirically derived transmission coefficient ranged from 0.64 to 0.83.

The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 to R values.[42] Hydrogens were included in structure factor calculations in calculated positions and refined using a riding model.

Syntheses (See Scheme 1). *Warning! Although neither Ni$_3$(Dtox)-(DtoxH)$_2$(ClO$_4$)$_2$·CH$_3$CN nor Ni[{(Dtox)(CH$_3$CNH)$_2$}](ClO$_4$)$_2$ has yet proved to be mechanically sensitive, such perchlorates are potentially explosive and should be handled with due caution.*

4,7-Dithiadecane-2,9-dione. The synthesis was performed under Ar. To 1.47 g (64 mmol) of Na metal and 0.12 g (3 mmol) of NaBH$_4$ in 96% ethanol (110 mL) were added 3.00 g (32 mmol) of 1,2-ethanedithiol, and the solution was stirred for 0.5 h under reflux. The resulting white suspension of sodium ethanedithiolate was added over 1 h to a solution of 8.77 g (64 mmol) of bromoacetone in 96% ethanol (65 mL) at 40 °C. After the solution was stirred for 0.5 h, the ethanol was removed (rotary evaporator), the product was extracted with diethyl ether (3 × 15 mL), the extract was dried with Na$_2$SO$_4$, and the ether was rotary evaporated off. The product (5.58 g, 85%), a yellowish liquid with a mildly pungent odor, darkens on standing for a few days at room temperature and was thus used immediately without further purification.

4,7-Dithiadecane-2,9-dione Dioxime. A 5.85 g (27 mmol) portion of the above diketone was added to a filtered solution generated from 3.76 g (54 mmol) of hydroxylamine hydrochloride and NaOH (2.16 g, 54 mmol) in 70 mL of 75% ethanol. After several hours of stirring, the white needles of dioxime formed were filtered off and recrystallized from 80% ethanol. Yield: 5.10 g (80%). Mp: 131.5 °C. Anal. Calcd for C$_8$H$_{16}$N$_2$O$_2$S$_2$: C, 40.7; H, 6.83; N, 11.9. Found: C, 40.1; H, 7.13; N, 11.6. ^{1}H NMR (CD$_3$OD): s 1.82 (6H); s 2.52 (4H); s 3.4 (4H) (the methylene multiplets are unresolved). IR (KBr), cm^{-1}: 2920, 1620, 1410, 1365, 1273, 1205, 1170, 1130, 1015, 870, 820, 680, 630.

Alternatively, the ligand can be prepared by the reaction of 3-chloro-2-propanone oxime with 1,2-ethanedithiol according to the procedure used for the dithioether-dione synthesis; after all the ether was removed the white solid was recrystallized from 80% ethanol (56% yield).

3-Chloro-2-propanone Oxime. A 46.3 g (0.50 mol) portion of chloroacetone in diethyl ether (50 mL) was cooled to 0 °C in a salt/ice bath. A solution of 34.7 g (0.5 mol) of hydroxylamine hydrochloride in 30 mL of H$_2$O was added slowly with stirring. A saturated aqueous solution of 69 g of K$_2$CO$_3$ was gradually added over 40 min. The mixture was stirred for an additional 2 h. The product was extracted with diethyl ether (3 × 25 mL), the extract was dried over Na$_2$SO$_4$, and the ether was removed via rotary evaporation. The pale yellow liquid product (48 g, 90%) was used without further purification due to its lachrymatory nature. MS: 107 ([M$^+$], 26), 71 ([MH$^+$ − Cl], 48).

[Ni$_3$(Dtox)(DtoxH)$_2$](ClO$_4$)$_2$·CH$_3$CN. A 0.100 g (0.423 mmol) portion of 4,7-dithiadecane-2,9-dione dioxime was added to a solution of 0.155 g (0.423 mmol) of Ni(ClO$_4$)$_2$·6H$_2$O in 10 mL of 96% ethanol under reflux. A solution of 0.077 g (0.564 mmol) NaAcO·3H$_2$O in 5

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(41) *Synthesis of Organic Compounds;* Adams, R., Gilman, G., Eds.; GHTI: Moscow, 1932; pp 298−301.

(42) *SHELXTL*, Version 5.030; Siemens Analytical X-ray Instruments; Madison, WI, 1994.

mL of 70% ethanol was added to the resulting dark-blue solution, which was stirred under reflux for 15 min. The solution's color changed to gray-blue and a gray precipitate formed; recrystallization of this from CH_3CN by vapor-phase diffusion of ether led to the formation of purple-black crystals of $[Ni_3(Dtox)(DtoxH)_2](ClO_4)_2 \cdot CH_3CN$, which were filtered off and air-dried. Yield: 0.16 g (35%). Anal. Calcd. for $C_{26}H_{47}$-$Cl_2N_7Ni_3O_{14}S_6$: C, 27.9; H, 4.24; N, 8.78; Ni, 15.6. Found: C, 27.8; H, 4.50; N, 8.65; Ni, 15.3. IR spectrum (KBr), cm^{-1}: 2920, 1620, 1420, 1370, 1210, 1090, 725, 665, 625. This complex is soluble in CH_3CN but insoluble in ethanol. Use of Na_2CO_3 instead of NaOAc (1:1 molar ratio) followed by the same crystallization procedure gave the same product, while reducing the amount of NaOAc to 1 equiv gave a lower yield.

Ni[{(Dtox)(CH₃CNH)₂}](ClO₄)₂. A 0.100 g (0.423 mmol) portion of 4,7-dithiadecane-2,9-dione dioxime was added to a solution of Ni-$(ClO_4)_2 \cdot 6H_2O$ (0.155 g, 0.423 mmol) in 10 mL of 96% ethanol under reflux, and the solution was then allowed to stand at room temperature for several days. The resulting precipitate was recrystallized from CH_3-CN (ether vapor diffusion) to give violet needles of Ni[{(Dtox)(CH₃-CNH)₂}](ClO₄)₂, which were air-dried (0.096 g, 40%). Anal. Calcd for $C_{12}H_{22}Cl_2N_4NiO_{10}S_2$: C, 25.1; H, 3.86; N, 9.76; Ni, 10.1. Found:

C, 25.4; H, 4.05; N, 9.76; Ni, 10.1. IR spectrum (KBr), cm^{-1}: 3340, 2970, 1705, 1660, 1435, 1390, 1350, 1090, 965, 885, 820, 640, 550. The compound is sparingly soluble in CH_3CN and insoluble in ethanol.

Reaction of Ni[{(Dtox)(CH₃CNH)₂}](ClO₄)₂ with NaAcO·3H₂O. NaAcO·3H₂O (0.012 g, 0.085 mmol) in 3 mL of 96% ethanol was added to a solution of Ni[{(Dtox)(CH₃CNH)₂}](ClO₄)₂ (0.050 g, 0.087 mmol) in 4 mL of ethanol−CH_3CN mixture (3:1). The solution's color immediately changed from violet to gray-blue, and after partial evaporation of the solvent, purple-black crystals were formed, evidenced by the IR, MS, and analytical data to be Ni₃(Dtox)(DtoxH)₂(ClO₄)₂·CH₃-CN.

Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, least-squares planes, views of unit cell contents and a summary of literature data for $Ni^{III}/Ni^{II}/Ni^{I}$ potentials. This material is available free of charge via the Internet at http://pubs.acs.org.

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