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A Novel Mixed Macrocycle Complex of Nickel: Synthesis, Structure, and Redox Chemistry of [$\mathbf{Ni^{II}}$([9]aneN$_3$)([9]aneS$_3$)](ClO$_4$)$_2$·CHCl$_3$ ([9]aneN$_3$ = 1,4,7-Triazacyclononane and [9]aneS$_3$ = 1,4,7-Trithiacyclononane)

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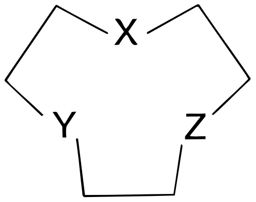
The mixed macrocycle cation, $[\mathrm{Ni([9]aneN_3)([9]aneS_3)}]^{2+}$ (where [9]aneN$_3$ = 1,4,7-triazacyclononane and [9]aneS$_3$ = 1,4,7-trithiacyclononane), has been prepared by stepwise complexation of [9]aneN$_3$ and [9]aneS$_3$, respectively, to Ni(II) cation. The intermediate $[\mathrm{Ni([9]aneN_3)(CH_3NO_2)_3}]^{2+}$ has been isolated and characterized by mass spectrometry and UV−visible spectroscopy. Cyclic voltammetry of $[\mathrm{Ni([9]aneN_3)(CH_3NO_2)_3}]^{2+}$ shows a quasireversible wave for the $\mathrm{Ni^{II/III}}$ couple ($E_{1/2}$ = 0.73V vs $\mathrm{Fc^{+/0}}$), and the Ni(III) species exhibits an axial ESR spectrum ($g_\perp = 2.101$ and $g_\| = 1.985$). The structure of $[\mathrm{Ni([9]aneN_3)([9]aneS_3)](ClO_4)_2 \cdot CHCl_3}$ has been determined. It crystallizes in monoclinic space group $P2_1/c$ with a = 13.3911(8) Å, b = 14.4430(9) Å, c = 13.6116(8) Å, β = 107.2090(10)°, V = 2514.7(3) Å^3, and Z = 4. Of the 15 047 reflections collected, 5765 reflections ($I > 2\sigma(I)$) were used in the refinement to obtain a final $R_w = 0.0278$ and $R_F = 0.0368$. In the cation $[\mathrm{Ni([9]aneN_3)([9]aneS_3)}]^{2+}$, the two macrocycles occupy the trigonal faces of the $\mathrm{Ni^{2+}}$ ion, imposing a distorted octahedral geometry. Cyclic voltammetry of the complex in CH$_3$CN (Pt electrodes, 0.1 M n-Bu$_4$NClO$_4$, 500 mV) shows a quasireversible wave for the $\mathrm{Ni^{II}/Ni^{III}}$ couple ($E_{1/2}$ = 0.86V vs $\mathrm{Fc^{+/0}}$). Chemical oxidation by NOPF$_6$ of the cation $[\mathrm{Ni([9]aneN_3)([9]aneS_3)}]^{2+}$ generates a Ni(III) species that shows axial ESR spectrum with $g_\perp = 2.106$ and $g_\| = 2.063$. No characteristic reduction wave was observed in either CH$_3$CN or CH$_3$NO$_2$ media.

Introduction

The set of cyclononane macrocycles, [9]anesX$_3$ (X = N, O, S, or a combination of these donors) have been used extensively in the complexation of 3d, 4d, and 5d transition metal ions.[1] The unique aspect of these ligands is that they are not sufficiently large enough to incorporate a metal ion in their cavity but, being tridentate, can bind facially to occupy the trigonal faces of an octahedral metal ion. The unusually high formation constants and the kinetic stability of the complexes of these ligands makes feasible the synthesis and study of either the monoligand (ligand/metal 1:1) complex ions,[2] $[\mathrm{M([9]aneX_3)A}_m]^{n+}$ (where A = solvent or anion) or the bis-ligand (ligand/metal 2:1), ions[3] of type $[\mathrm{M([9]aneX_3)_2}]^{n+}$. Complex ions of both these types with a variety of metal ions have been studied.[1]



X = Y = Z = NH, [9]aneN$_3$
X = Y = Z = S, [9]aneS$_3$
X = Y = Z = NR, [9]ane(NR)$_3$
R = Me or iso-Pr

Among these macrocycles, [9]ane(NR)$_3$, where R = Me or iso-Pr, are unique, since they do not form bismacrocyclic complexes, owing to severe steric interactions from the N-alkyl substituents.[4] Hence, they form only complexes of type, $[\mathrm{M([9]ane(NR)_3)(A)}_m]^{n+}$ (A = anion or solvent). Though, monoligand complexes of this type, $[\mathrm{M([9]ane(NR)_3)X_3}]$, are known with some main group and transition metal ions, very few analogues

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of other nonanes, particularly those with mixed donor atoms, have been studied.[5] $[M([9]aneN_3)(solvent)_3]^{n+}$ complexes of several metal ions, including that of Ni(II) described here, are unknown. From the classical coordination chemistry point of view, such mixed solvento complexes present many opportunities to prepare and study the structure, spectroscopy, and redox properties of metal ions that show deviation from perfect octahedral symmetry. We describe here the preparation of the complex cation $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ and its utilization in forming the mixed macrocycle octahedral cation, $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$. The crystal structure, spectroscopic, and redox characteristics of the latter cation are also presented.

Experimental Procedures

Caution. *Perchlorate salts are potentially explosive when heated or dried on filter paper. Sintered glass funnels should be used for filtration, and only small quantities of these complexes should be air-dried under suction. Extreme care should be taken to avoid contact with combustible organic matter and heat.*

The ligand $[9]aneN_3$ was prepared according to literature methods,[6] and $[9]aneS_3$ was purchased from Aldrich Chemical Co.

$[Ni([9]aneN_3)(CH_3NO_2)_3](ClO_4)_2$. To a solution of 1.29 g (0.01 mol) of 1,4,7-triazacyclononane dissolved in 100 mL of 0.5 M $HClO_4$ was added 3.66 g (0.01 mol) of $[Ni(H_2O)_6](ClO_4)_2$ in 25 mL of H_2O under stirring. This mixture was slowly neutralized with solid $NaHCO_3$ until no further effervescence was observed. The resulting blue solution of $[Ni([9]aneN_3)(H_2O)_3]^{2+}$ was concentrated to dryness in a rotary evaporator and was extracted with CH_3NO_2 (5 × 50 mL) until the residue was free of the complex. The CH_3NO_2 extracts were combined together, and 1,4-dioxane was added to precipitate any extracted $NaClO_4$, which was removed by filtration. The resulting solution of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ was used as such for further studies. The existence of this cation was confirmed by UV−visible spectrum and mass spectrometry. UV−visible, λ_{max} in nm (ϵ, $M^{-1}\ cm^{-1}$): $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$, 533 (13.0) compared to 580 (8.0) $[Ni([9]aneN_3)(H_2O)_3]^{2+}$. MS, *m*/*e*, obsd 286 (calcd for $[Ni([9]aneN_3)(ClO_4)]^+$: = 286). Concentration of the solution yielded only a noncrystalline hygroscopic solid due to loss of CH_3NO_2.

$[Ni([9]aneN_3)([9]aneS_3)](ClO_4)_2$. A 5 mL solution (0.028 M) of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ in CH_3NO_2 was titrated with 50 μL aliquots of a 0.1 M solution of $[9]aneS_3$ in the same solvent, the progress of the reaction being monitored from changes in the UV−visible spectrum. The 477 nm isosbestic point was lost after the end point. At the exact equivalence point, the reaction mixture was diluted with Et_2O until the solution was slightly cloudy. Violet crystals of the complex formed within 15 min. The crystals were filtered under suction, washed with ether, and dried under vacuum. Yield: 76.5 mg (100% based on $[9]aneS_3$) Anal. Calcd (found) for $C_{12}H_{25}N_3S_3Cl_2O_8Ni$: C, 25.41 (25.61); H, 4.80 (4.83); N, 7.41 (7.33). MS, *m*/*e* 466.0 (calcd for $[C_{12}H_{25}N_3S_3Ni(ClO_4)]^+$: 466.0), 183.6 (calcd for $[C_{12}H_{25}N_3S_3Ni]^{2+}$: 183.6).

Reagent-quality chemicals (Aldrich Chemical Co) were used as received. Nonaqueous solvents were purified by standard methods.[7] Tetra-*n*-butylammonium perchlorate ($n\text{-}Bu_4NClO_4$) purchased from GFS Chemicals, OH, was used as received. Microanalyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada.

UV−visible spectra were recorded on a Cary 17 dual-beam spectrophotometer. ESR spectra were recorded in an X-band Varian ES-6 spectrometer, at liquid N_2 temperatures with DPPH ($g = 2.0037$) as an external standard. Mass spectra were obtained on a Kratos Concept model 2H mass spectrometer either by FAB (*m*-NBA matrix) or electrospray technique. In all cases, the theoretical isotopic distributions of relevant peaks were calculated and were found to agree with the experimentally observed spectrum.

A three-electrode cell configuration with Pt working electrodes and an Ag wire reference electrode[8] calibrated to the Fc/Fc^+ couple was used in the electrochemical experiments ($T = 25 \pm 0.3$ °C). Cyclic voltammetric experiments were performed using the HeadStart program on a Princeton Applied Research galvanostat/potentiostat model 273 instrument interfaced to an IBM PC. Corrections for liquid junction potentials were not applied. Reversibility of cyclic voltammograms was confirmed as described elsewhere.[9]

Single crystals for X-ray crystallography were obtained by slow diffusion of $CHCl_3$ into a solution of the complex in CH_3NO_2. A suitable single crystal was mounted on a glass fiber, and the diffraction data were collected on a Siemens SMART/CCD diffractometer equipped with an LT-II low-temperature device and corrected for absorption using the SADABS program. SHELXTL[10] was used for the structure solution, and refinement was based on F^2. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically on the basis of corresponding C atoms [$U(H) = 1.2U_{eq}(C)$]. Experimental parameters, fractional coordinates, and anisotropic displacement parameters have been deposited as Supporting Information (CIF format).

Results and Discussion.

Synthetic Aspects. When equimolar volumes of free base, $[9]aneN_3$, were reacted directly with Ni(II) ion, substantial amounts of the octahedral cation, $[Ni([9]aneN_3)_2]^{2+}$, were formed. The procedure described here eliminates this problem and provides $[Ni([9]aneN_3)(H_2O)_3]^{2+}$ exclusively. However, isolation of this cation from $NaClO_4$ proved difficult. The existence in nitromethane of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ (which is not stable in aqueous media) can be inferred from the UV−visible spectrum which is distinctly different from that of $[Ni([9]aneN_3)(H_2O)_3]^{2+}$. In dry CH_3NO_2, $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ is quite stable and can be stored indefinitely. During the preparation of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$, care was taken to handle the aqueous reaction mixture at room temperatures to eliminate any formation of $[Ni([9]ane)_2]^{2+}$. Spectrophotometric titration of $[9]aneS_3$ with $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ yielded the title complex quantitatively.

Description of Structure. The ORTEP diagram of the cation, $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$, is shown in Figure 1. Important bond lengths and angles are presented in Table 1. As expected, the two tridentate ligands occupy the trigonal faces of the octahedral Ni(II) ion. The Ni−N distances 2.103(2), 2.083(2), and 2.097(2) Å observed in this complex are comparable to those found in the $[Ni([9]aneN_3)_2]^{2+}$ ion (2.102, 2.098, and 2.111 Å). However, the Ni−S distances (2.418(5), 2.453(6), and 2.409(5) Å) are slightly longer than the average distance 2.385 Å observed in $[Ni([9]aneS_3)_2]^{2+}$. In particular, a distance of 2.453(6) Å observed for the Ni−S(2) is significantly longer

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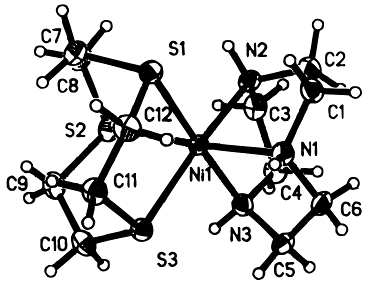

Figure 1. ORTEP diagram of the cation $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$.

Table 1. Important Bond Lengths (Å) and Angles (deg) for $[Ni([9]aneN_3)([9]aneS_3)](ClO_4)_2{\cdot}CHCl_3$

	Bond lengths		
Ni(1)−N(1)	2.103(2)	Ni(1)−S(1)	2.4175(5)
Ni(1)−N(2)	2.083(2)	Ni(1)−S(2)	2.4525(6)
Ni(1)−N(3)	2.097(2)	Ni(1)−S(3)	2.4094(5)
	Bond Angles		
N(2)−Ni(1)−S(1)	96.83(5)	N(3)−Ni(1)−S(3)	92.65(5)
N(1)−Ni(1)−S(1)	93.25(5)	N(1)−Ni(1)−S(3)	96.20(5)
N(1)−Ni(1)−S(2)	175.94(5)	S(1)−Ni(1)−S(2)	86.76(2)
S(3)−Ni(1)−S(1)	87.67(2)	N(3)−Ni(1)−S(1)	176.31(5)
N(2)−Ni(1)−N(3)	82.80(6)	N(2)−Ni(1)−S(2)	93.29(5)
N(2)−Ni(1)−N(1)	82.68(6)	N(3)−Ni(1)−S(2)	96.93(5)
N(3)−Ni(1)−N(1)	83.06(6)	S(3)−Ni(1)−S(2)	87.86(2)
N(2)−Ni(1)−N(3)	175.41(5)		

and thus imparts an axial elongation along this bond. In addition, the natural differences in the lengths of Ni−N and Ni−S bonds that form the trigonal faces of $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ ion also impose a trigonal distortion which is evident in the bond angles. The N−Ni−N bond angles average at 82.7°, a value comparable to those observed in $[Ni([9]aneN_3)_2]^{2+}$ which also exhibits a similar distortion.[11] However, these values are lower than the average value of 88.7° for the S−Ni−S angles observed in the $[Ni([9]aneS_3)_2]^{2+}$ cation.[3b] The N−Ni−S angles at approximately 176° also indicate a small deviation from octahedral geometry. Unlike in $[Ni([9]aneN_3)_2]^{2+}$ and $[Ni([9]aneS_3)_2]^{2+}$ cations, a trigonal twist is observed in the present structure. The planes containing the three nitrogen and three sulfur atoms show a trigonal twist of approximately 3.5°. This again is a reflection of the differences in the relative sizes of N and S donors. Thus, the cation $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ has a geometry that is unique among complexes of $[MA_3B_3]^{n+}$ type. There are also two perchlorate ions and a chloroform molecule per cation present in the unit cell. The crystal is quite stable and did not lose the chloroform molecule over a long period of time.

UV−Visible Spectroscopy. In CH_3NO_2, the $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ ion shows a single broad band at 533 nm (ϵ = 13.0 M^{-1} cm^{-1}) while the $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ ion shows a band at 550 nm (ϵ = 23 M^{-1} cm^{-1}) with a shoulder at 590 nm (ϵ = 15 M^{-1} cm^{-1}). This differs from the single bands observed at 530 nm (ϵ = 28 M^{-1} cm^{-1}) for $[Ni([9]aneS_3)_2]^{2+}$ [3b,12] and at 505 nm (ϵ = 5 M^{-1} cm^{-1}) for the $[Ni([9]aneN_3)_2]^{2+}$ [2c,3a] ions, in the same medium. In aqueous medium, the $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ ion shows relatively strong absorptions at 543 nm (ϵ = 39.4 M^{-1} cm^{-1}), a shoulder at 590 nm (ϵ = 29 M^{-1} cm^{-1}) and a peak at 817 nm (ϵ = 30.1 M^{-1} cm^{-1}). Also, two charge-transfer bands at 222 (ϵ = 9.5 × 10^3 M^{-1} cm^{-1}) and 264 nm (ϵ = 7.1 × 10^3 M^{-1} cm^{-1}) are observed with a shoulder at 325 nm (ϵ = 69 M^{-1} cm^{-1}). Molar extinction coefficients for this complex are significantly larger than those observed for the $[Ni([9]aneX_3)_2]^{2+}$ cations (X = N, S) and reflects the tetragonal distortion that results from the trigonal twist and the resulting elongation of the Ni−S(2) bond as has been confirmed by X-ray structure. The UV−visible spectrum has all the characteristics of an pseudo-octahedral *fac*-N_3S_3 environment. These data may be compared with the Ni(II) complex of the N_3S_3 cage (diaminodiazacapten) prepared previously by Sargeson.[13] In this case, the relevant UV−vis data are (λ_{max} in nm (ϵ in M^{-1} cm^{-1})) 340(70), 520(45), and 810(59). The band at 817 nm in the present mixed ligands complex can be assigned to ${}^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1) and that at 540 to ${}^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2) transitions, respectively. From these data, a *Dq* value of 1224 cm^{-1} is derived for this complex ion compared to 1276 cm^{-1} for $[Ni([9]aneS_3)_2]^{2+}$ and 1250 cm^{-1} for $[Ni([9]aneN_3)_2]^{2+}$. Also, a value of 473 cm^{-1} for the Racah parameter, *B*, calculated using an equation described by Cooper et al.,[14] is lower than those of 680 cm^{-1} for $[Ni([9]aneS_3)_2]^{2+}$ and 853 cm^{-1} for $[Ni([9]aneN_3)_2]^{2+}$.[12] There is the loss of an inversion center in $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ that is found in $[Ni([9]aneN_3)_2]^{2+}$ and $[Ni([9]aneS_3)_2]^{2+}$ cations as a result of the trigonal twist and axial elongation described above.

Electrochemistry. The cyclic voltammetry of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ in CH_3NO_2 showed (n-Bu_4NClO_4, Pt electrodes) a quasireversible wave at $E_{1/2}$ = 0.73 V (vs $Fc^{0/+}$; 100 mV/s, $i_{p,a}/i_{p,c}$ = 0.75) for the $Ni^{2+/3+}$ couple. Even at higher scan rates (500 mV/s) the reversibility of the wave did not improve ($i_{p,a}/i_{p,c}$ = 0.8) significantly. A similar trend was also observed in CH_3CN. The cyclic voltammogram of the $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ cation (CH_3CN, 0.1 M n-Bu_4NClO_4, Pt electrodes) also showed a quasireversible ($i_{p,a}/i_{p,c}$ = 0.88 at 500 mV/s and ΔE_p = 116 mV) wave at 0.86V vs $Fc^{0/+}$. This is significantly different from the values reported for $[Ni([9]aneN_3)_2]^{2+}$ (0.53 V vs Fc/Fc^+)[15] and $[Ni([9]aneS_3)_2]^{2+}$ (0.97 V vs Fc/Fc^+)[12] cations under very similar conditions. While $[Ni([9]aneN_3)_2]^{2+}$ undergoes a metal-based redox process, the quasireversible wave observed at 0.97 V for $[Ni([9]aneS_3)_2]^{2+}$ has been assigned to a ligand-based process.[12] No redox activity was observed for the present complexes in aqueous medium. This behavior is comparable to Sargeson's finding on the Ni(II) complex of the N_3S_3 cage ligand described earlier.[13]

Characterization of the Ni(III) Species. The species $[Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ and $[Ni([9]aneN_3)([9]aneS_3)]^{3+}$ were prepared by oxidation of the corresponding Ni(II) cations in CH_3CN with either NO^+ or ceric ammonium nitrate as oxidant. The bright green solution of $[Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ prepared using ceric ammonium nitrate showed a strong band at 328 nm and was quite stable in the absence of moisture. The ion $[Ni([9]aneN_3)([9]aneS_3)]^{3+}$ prepared with $NOPF_6$ formed a dark orange solution, was ESR active (see below), and exhibited a very weak band at 550 nm and a relatively strong band at 375 nm. It was very sensitive to moisture, decomposing rapidly at room temperature to form the pink solution of the starting Ni(II) complex. However, these orange solutions of Ni(III), when frozen immediately, were quite stable and the metal-centered unpaired electron was confirmed by ESR spectroscopy. The ESR spectra of $[Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ and $[Ni([9]aneN_3)([9]aneS_3)]^{3+}$ in CH_3CN are shown in Figure 2. Both show axial spectra with $g_\perp > g_\parallel$. The ESR spectrum of $[Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ was different from other *fac*-N_6 octahedral systems. For example, in $[Ni([9]aneN_3)_2]^{3+}$ the $g_\parallel$ feature appears as a

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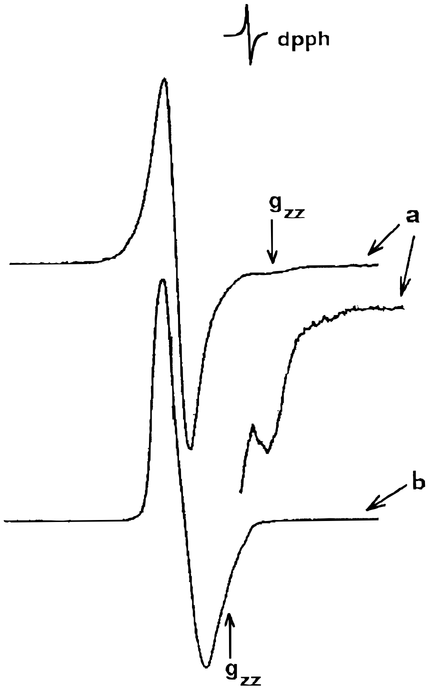

Figure 2. ESR spectra of (a) $[Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ and (b) $[Ni([9]aneN_3)([9]aneS_3)]^{3+}$cations in CH_3CN at 77 K.

shoulder to the $g_\perp$ feature and is hardly noticeable. In comparison, $Ni([9]aneN_3)(CH_3CN)_3]^{3+}$ shows two features that are quite distinct (see Figure 2a) with $g_\perp = 2.101$ and $g_\| = 1.985$, and the $g_\|$ feature was unusually broadened. As a *fac*-N_6 system with one macrocycle and three solvent molecules, this cation lacks the rigidity of $[Ni([9]aneN_3)_2]^{3+}$ and hence, it is probable that the axial elongation observed is due to Jahn–Teller distortion experienced by one of the solvent molecules. This bond may be somewhat longer than the others and subject to dynamic behavior. This is likely to be the cause of an unusually large broadening and features more characteristic of D_{4h} symmetry as observed here. The $[Ni([9]aneN_3)([9]aneS_3)]^{3+}$ cation in CH_3CN ($NOPF_6$) (see Figure 2b) also showed an axial spectrum. However, this was quite similar in characteristics to that of $[Ni([9]aneN_3)_2]^{3+}$. The observed values of $g_\perp = 2.106$ and $g_\| = 2.065$ are clearly indicative of the presence of an unpaired electron on the metal. The fact that the decomposed species can be reoxidized indicates that the complex ion retains its ligands and geometry during the redox cycle.

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Supporting Information Available: Figures of spectrophotometric titration of $[Ni([9]aneN_3)(CH_3NO_2)_3]^{2+}$ with $[9]aneS_3$ and cyclic voltammogram of $[Ni([9]aneN_3)([9]aneS_3)]^{2+}$ are available (2 pages). One X-ray crystallographic file, in CIF format, is also available on the Internet only. Ordering and access information is given on any current masthead page.

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