polyhedral {CH} group, for similar geometries are observed in the electronically similar complexes $(C_5H_5)_2NiCoCB_7H_8$, $(C_5H_5)_2Co_2C_2B_6H_8$,[6] $(CoC_2B_7H_9)_2^-$,[12] $C_2B_8H_{10}$,[13] and $B_{10}H_{10}^{2-}$.[14] Within experimental errors, all equivalent bond distances are the same in this series of compounds.[15]

Although it is impossible to discern between the cobalt and nickel atoms, it is interesting that the metal–metal distance is significantly shorter than is the Co–Co distance in $(C_5H_5)_2Co_2C_2B_6H_8$. It should be noted that "tropical"[12] bond distances in bicapped square antiprisms are generally found to be longer than "equatorial" bond distances, thus diminishing the significance of this observation.

The cyclopentadienyl rings, while exhibiting the large librational motion typical in compounds of this type studied at room temperature, exhibit D_{5h} symmetry, as expected. The metal–carbon distances to the cyclopentadienyl rings are again equal within experimental error, further establishing the positional disorder of the metals.

Acknowledgment. We thank Dr. C. G. Salentine for providing the sample. We also thank the Office of Naval Research for partial support of this work and the UCLA Campus Computing Network for computer time.

Registry No. 2,3-(η-C_5H_5)$_2$-(2,3)-NiCo-10-CB_7H_8, 57483-40-6.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Section of Chemistry,
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$[(C_6H_5)_4As]_2[Ni(Se_2C{=}C(CN)_2)_3]$, a New Ni(IV) Chelate with an Unsaturated 1,1-Diselenolate Ligand

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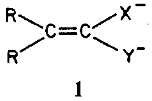
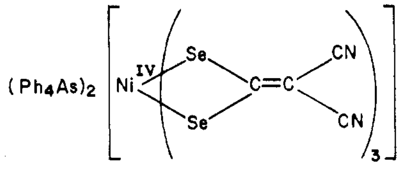
Usually chelates with selenium donor atoms are more difficult to prepare than the analogous sulfur compounds.[1] We report the preparation of the Ni(IV) tris chelate of isomaleonitrilediselenolate which was isolated as the tetraphenylarsonium salt. Curiously, the corresponding sulfur chelate could not be prepared applying the same conditions. Considerable work has been devoted to the stabilization of high formal oxidation states of transition-metal ions by unsaturated sulfur or selenium donor ligands like 1,2-dichalcogenolenes[2] or dichalcogenocarbamates.[3] It is noteworthy, however, that only two examples are known up to now with a 1,1-disubstituted ethylene dichalcogenolate (**1**). Coucouvanis and co-workers prepared the Cu(III) bis chelate $[Cu(ded)_2]^-$ and the Fe(IV) tris chelate $[Fe(ded)_3]^{2-}$ (R = $COOC_2H_5$; X = Y = S).[4,5] However, the isolation of Ni species with high formal oxidation states was unsuccessful. Obviously, substitution of the sulfur donor atoms by selenium facilitates the oxidation and enables the isolation of the Ni(IV) complex $(Ph_4As)_2[Ni(i\text{-mns})_3]$[6] (**2**) with R = CN and X = Y = Se.



1

X = Y = S; Se
X = S; Y = Se



2

Experimental Section

Physical Measurements. Electronic spectra were recorded on a Specord spectrophotometer (VEB Carl Zeiss, Jena). Infrared spectra from 400 to 3500 cm^{-1} in KBr were recorded using a UR 20 spectrometer (VEB Carl Zeiss, Jena). Molar conductivities were measured at 10^{-4} M in CH_3NO_2 (20 °C) using a conductivity bridge Type LM 301 (VEB Hydromat Bannewitz).

The X-band ESR spectra were recorded on a Varian E 112 spectrometer.

Voltammetric measurements were made in acetonitrile solution on a Radiometer (Copenhagen) PO 4 instrument. The concentration of the supporting electrolyte ($NaClO_4$) was 10^{-1} M. A rotating Pt electrode (1500 rpm) was used.

Preparation of the Complexes. $(n\text{-Bu}_4N)_2[Ni(i\text{-mns})_2]$.[6] $K_2Se_2C{=}C(CN)_2$,[7] 3.12 g (0.01 mol), was dissolved in 30 mL of methanol. Dropwise addition of a solution of $NiCl_2{\cdot}6H_2O$, 1.188 g (0.005 mol), in 20 mL of methanol, yields a red-brown complex solution to which tetra-*n*-butylammonium bromide, 3.3 g (0.01 mol), dissolved in 20 mL of methanol, was added. A red precipitate was obtained and filtered. The complex salt could be recrystallized by dissolving in acetone, adding 2-propanol, and reducing the volume by evaporation. Yield 60%; mp 198 °C; Λ_M 189 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd: C, 47.49; H, 7.17; N, 8.31; Se, 31.22. Found: C, 48.31; H, 7.07; N, 8.02; Se, 31.30. Electronic spectrum in acetonitrile solution (ν_{max} in cm^{-1} × 10^3, log ϵ in parentheses): 16.3 (2.96), 20.1 (4.14), 21.7 (3.89 sh), 26.9 (4.57), 31.9 (4.39), 33.5 (4.42).

$(Ph_4As)_2[Ni(i\text{-mns})_2]$. This compound was prepared according to above using tetraphenylarsonium chloride. It could be recrystallized from acetonitrile/2-propanol in about 50% yield; mp 220–222 °C;

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Table I. Assignment of the Spin-Allowed Transitions in $[Ni(i\text{-mns})_3]^{2-}$ and $[Co(i\text{-mns})_3]^{3-}$ and Comparison with $[Ni(Bu_2dsc)_3]^+$ and $Co(Bu_2dsc)_3$

Compd	ν_1 [a]	ν_2 [a]	Δ [a]	B [b]	β_{35} [c]
$(Ph_4As)_2[Ni(i\text{-mns})_3]$	16.1	21.2	16.9	359	0.29
$(Ph_4As)_3[Co(i\text{-mns})_3]$	14.6	21.8	15.1	559	0.51
$[Ni(Bu_2dsc)_3]Br$ [d]	16.6	19.0	17.1	158	0.13
$Co(Bu_2dsc)_3$ [d]	14.4	18.6	15.1	292	0.26

[a] In cm^{-1} × 10^3. [b] In K. [c] Calculated with B = 1100 and 1250 K for the gaseous Co^{3+} and Ni^{4+} ions, respectively.[11] [d] Values from ref 12.

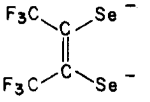
Λ_M = 169 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd: C, 52.00; H, 3.12; N, 4.33. Found: C, 51.33; H, 3.27; N, 4.18.

$(Ph_4As)_2[Ni(i\text{-mns})_3]$. $(Bu_4N)_2[Ni(i\text{-mns})_2]$, 1.011 g (0.001 mol), was dissolved in 100 mL of acetonitrile. Dropwise addition of a solution of iodine, 0.189 g (0.0013 mol), dissolved in 50 mL of acetonitrile, changed the color from red-brown to intense green. The solvent was removed by vacuum evaporation. A black slurry was obtained. This residue was dissolved in 50 mL of acetone followed by addition of 1.2 g of Ph_4AsCl (0.0029 mol), dissolved in 50 mL of 2-propanol. On removal of the acetone using a water pump, black needles were precipitated. This procedure was repeated and the compound was recrystallized again in the same way without adding Ph_4AsCl. Yield 0.77 g (76% based on the ligand); mp 195–197 °C; Λ_M = 144 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd: C, 47.18; H, 2.64; N, 5.52; Se, 31.02. Found: C, 47.35; H, 2.79; N, 5.31; Se, 31.45. Electronic spectrum in acetonitrile solution (ν_{max} in cm^{-1} × 10^3, log ϵ in parentheses): 16.1 (3.57), 21.2 (4.15), 26.7 (4.89), 33.4 (4.29 sh).

$(Ph_4As)_3[Co(i\text{-mns})_3]$. This compound was prepared similar to the method of Jensen and Krishnan.[8] It could not be recrystallized. Electronic spectrum in acetone solution (ν_{max} in cm^{-1} × 10^3, log ϵ in parentheses): 14.6 (2.98), 21.8 (4.33), 27.1 (4.77), 31.0 (4.54 sh).

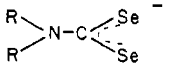
Results and Discussion

The ligand i-mns^{2-} turns out to be the third example of unsaturated ligands, containing selenium donor atoms exclusively, which can stabilize transition-metal ions in high formal oxidation states. The diselenolene ligand (**3a**) forms bis complexes only with Ni(II), Ni(III), and Ni(IV).[1] Tris complexes are known with V, Mo, or W; $Mo(tfs)_3$ has a trigonal-prismatic coordination geometry.[9] From the dialkyldiselenocarbamates (**3b**), Ni(II) bis chelates and Ni(IV) tris chelates are known.[4] Besides differences in the charge, the complexes of i-mns^{2-} (**3c**) seem to have similar properties. Because of the similarity of the visible spectra of $[Ni(i\text{-mns})_3]^{2-}$ and of the isoelectronic $[Co(i\text{-mns})_3]^{3-}$ with those of $[Ni(Bu_2dsc)_3]^+$ and $Co(Bu_2dsc)_3$, similar molecular structures can be assumed. In $[Ni(Bu_2dsc)_3]Br$, the quadrivalent nickel ion is octahedrally coordinated by six selenium atoms.[10] Assuming a related coordination geometry for the low-spin complexes $[Ni(i\text{-mns})_3]^{2-}$ and $[Co(i\text{-mns})_3]^{3-}$, the ligand field splitting energy Δ and the Racah parameter B can be calculated, Table I,[13] from the two lowest absorption bands between 14 and 22 cm^{-1} × 10^3. The values for Δ are practically the same for i-mns^{2-} and R_2dsc^- complexes and suggest the same spectrochemical position for both ligand types.[14] On the other hand, the values for B and, therefore, β_{35} are not as low as for the diselenocarbamato complexes indicating a lower covalency for the metal–ligand bands of the i-mns^{2-} complexes.



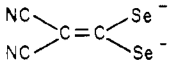
3a

tfs^{2-}



3b

R_2dsc^-



3c

i-mns^{2-}

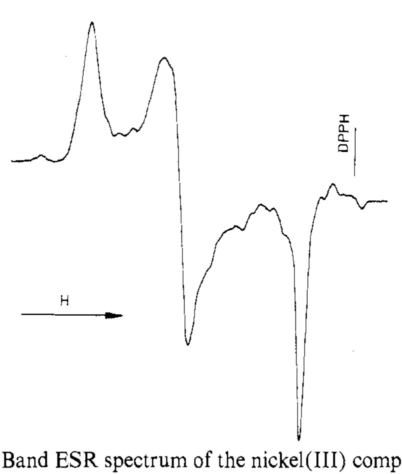


Figure 1. X-Band ESR spectrum of the nickel(III) complex recorded immediately after oxidation of $[Ni(i\text{-mns})_2]^{2-}$ by iodine in acetonitrile (T 120 K).

The infrared frequencies are collected in Table II. Most remarkable is the increase of the frequency for the perturbed C=C stretching mode for the complex ion $[Ni(i\text{-mns})_3]^{2-}$ compared to the bis complexes $[Ni(i\text{-mns})_2]^{2-}$. This increase of the double-bond character and the increase of the frequency for the C≡N stretching mode indicate that the electron density is less extensively delocalized onto the ligands in the Ni(IV) compound.

Voltammetric measurements show for the Ni(II) complex a one-electron oxidation step, the half-wave potential of which is 0.14 V (acetonitrile solution; supporting electrolyte 0.1 M sodium perchlorate; rotating Pt electrode vs. SCE). The existence of a reactive Ni(III) chelate was manifested by ESR: cautious oxidation of $[Ni(i\text{-mns})_2]^{2-}$ with iodine in acetonitrile results in an olive green solution from which a well-resolved ESR spectrum immediately taken after oxidation at T = 100 K has been obtained (Figure 1). It should be noted that the same spectrum was observed for an equimolar mixture of $[Ni(i\text{-mns})_2]^{2-}$ and $[Ni(i\text{-mns})_3]^{2-}$. The spectrum shows rhombic symmetry; the following principal values of the **g** tensor were derived: g_1 = 2.045 ± 0.003, g_2 = 2.149 ± 0.003, and g_3 = 2.232 ± 0.003. ^{61}Ni hyperfine splitting could not be observed due to the low natural abundance of ^{61}Ni. There are some weak satellite lines which are difficult to classify and are possibly caused by hyperfine interactions with the Se donor atoms of the ligands. The pronounced g anisotropy and the fact that none of the g values has been found near the free-electron g value are consistent with a distorted planar structure of the Ni(III) complex and can be explained with a σ-type ground state molecular orbital for the unpaired electron which contains the metal d_{xy} orbital. Most of the nickel(III) dichalcogeno–ligand complexes investigated hitherto have a π ground state to which the metal contributes its d_{yz} orbital.[16-18]

Table II. Representative Vibrational Spectra[a]

	Tentative assign[b]				
Compd	ν(C≡N)	ν(C=C)	$\nu(CSe_2)$, ν(C–CN)	δ(C–C–Se)	$\delta(CSe_2)$, δ(CCN), $\omega(C{=}CSe_2)$
$(Bu_4N)_2[Ni(i\text{-mns})_2]$	2200 s	1390 s	850 m, 855 m	610 w	440 w
$(Ph_4As)_2[Ni(i\text{-mns})_2]$	2200 s	1395 s	850 m, 855 m	610 w	440 w
$(Ph_4As)_2[Ni(i\text{-mns})_3]$	2210 s	1420 s	850 m, 855 m	605 w	435 w
$(Ph_4As)_3[Co(i\text{-mns})_3]$	2190 s	1380 s	860 m, 855 m	600 w	445 w

[a] Frequencies in cm^{-1}: s, strong; m, medium; w, weak. [b] See ref 15.

The similarity of the $[Ni(i\text{-mns})_3]^{2-}$ chelate with the nickel(IV) dichalcogenocarbamates leads to the question concerning analogies in the photosensitivity of both systems.[19,20] Solutions of $[Ni(i\text{-mns})_3]^{2-}$ are found to be fairly stable. The absorptivity of the first band (16.1×10^3 cm^{-1}) decreases only to about 4% in the dark and to about 30% at laboratory light within 3 weeks (acetonic solution; $c = 10^{-3}$ M). However, treatment of this solution with strong visible light (1000-W projection lamp) results in the disappearance of the intense green color leaving the red-brown Ni(II) species. After removal of the light source, the green color reappears. Repeated color changes of the solution with visible light have a clear discernible effect upon the intensity of the green color. Though there are analogies to the photobleaching of the $[Ni(S_2CNR_2)_3]^+$ complexes, the fatigue of the photochromism of the *i*-mns system is faster than that of the former.[20] The mechanism of the photochromic behavior of the latter is not known up to now.

Registry No. $(n\text{-}Bu_4N)_2[Ni(i\text{-mns})_2]$, 65701-74-8; $(Ph_4As)_2[Ni(i\text{-mns})_2]$, 65701-75-9; $(Ph_4As)_2[Ni(i\text{-mns})_3]$, 65701-73-7; $(Ph_4As)_3[Co(i\text{-mns})_3]$, 27902-48-3.

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Electron Spin Resonance Spectra of Copper(II) Bipyridyl Complexes

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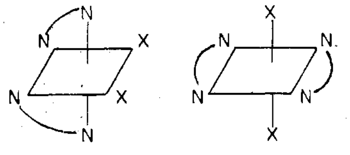
Complexes of copper(II) with 2,2′-bipyridyl (bpy) have been studied by the ESR method.[1-4] The ESR spectral parameters of the mono (I), bis (II), and tris (III) complexes have been reported and are summarized in Table I. Bis(bipyridyl)copper(II) can exist as the cis or trans isomer. There are conflicting reports in the literature with respect to the stability of the bis(bipyridyl)copper(II) species.[1-10] The ESR spectral parameters for transition-metal complexes depend on the nature of the ligands and their geometric arrangements,[11] and for a variety of complexes the ESR parameters of cis and trans isomers are different.[9,11]



cis trans

During the investigation of ethanol–water solutions (40%, 60%) containing copper(II) bipyridyl complexes with a bipyridyl:copper ratio of 2.0, Noack and Gordon[1] simultaneously observed two different spectra, $g_{\parallel} = 2.285 \pm 0.010$, $A_{\parallel} = (165.4 \pm 2.0) \times 10^{-4}$ cm^{-1} and $g_{\parallel} = 2.227 \pm 0.010$, $A_{\parallel} = (128.9 \pm 2.0) \times 10^{-4}$ cm^{-1}, which were ascribed to the trans isomer and the cis isomer as is noted in Table I.

Later, Walker and Siegel[2] repeated some of the latter experiments with the pure ^{63}Cu isotope and concluded that the two series of lines observed by Noack and Gordon were due to the complexes of $Cu(bpy)^{2+}$ and $Cu(bpy)_3{}^{2+}$, which resulted from disproportionation of $Cu(bpy)_2{}^{2+}$. The authors suggested that under such conditions the spectrum with $g_{\parallel} = 2.227$ and $A_{\parallel} = 128.9 \times 10^{-4}$ cm^{-1}, previously assigned to the cis isomer of bis(bipyridyl)copper(II), was absent. According to Walker and Siegel, the predominant geometric isomer of $Cu(bpy)_2{}^{2+}$ in the range of its coexistence with mono- and tris(bipyridyl) complexes must have spectral parameters similar to, although not fully identical with, those of $Cu(bpy)_3{}^{2+}$.

In frozen methanol–chloroform solutions Rehorek and Thomas[3] observed the ESR signal for the copper(II) bipyridyl complex and reported the appropriate ESR parameters. Despite the suggestion of Walker and Siegel,[2] the authors[3] considered the existence of bis(bipyridyl)copper(II) as a real fact although they did not observe the cis spectrum II (Table I). In 1971, McKenzie[9] suggested that the two spectra observed by Noack and Gordon could be due to bis(bipyridyl)copper(II) complexes containing different numbers of solvent molecules.

In our study of the interaction between components of the copper(II)-catalyzed oxidation of hydroquinone (H_2Q) with hydrogen peroxide in the presence of bipyridyl in borate buffers, we observed a complex with $g_{\parallel} = 2.222 \pm 0.005$ and $A_{\parallel} = (129 \pm 3) \times 10^{-4}$ cm^{-1} (II_1) as is shown in Figure 1a and 1b and Table I. In the pH range of 7.0–8.2, and in the presence of all of the reaction components, with an ~20-fold excess of bipyridyl, only the complex II_1 is observed. It is necessary to note in this context that complex II_1 could be observed only by using precooled reagents at approximately 5 °C.

The ESR spectral parameters we observed in the catalytic system containing mixed bipyridylcopper(II) complexes, within the limits of experimental error, are the same as those reported by Noack and Gordon for the *cis*-bis(bipyridyl)copper(II) species. In this connection the existence of the *cis*-bis(bipyridyl)copper(II) complex is interesting, in that it appears to play an important role in the general mechanism for the catalytic oxidation[12] of hydroquinone with H_2O_2 in the presence of such activators as pyridine and 2,2′-bipyridyl. A number of our other experimental results which will be published in detail elsewhere permit us to suggest that H_2O_2 and H_2Q also enter the coordination sphere of the bis(bipyridyl)copper(II) species during the catalytic process.

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