74-4; dimethylaluminum 2,4,6-trimethylphenoxide, 96930-15-3; dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide, 86803-85-2; *trans*-1-ethyl-4-*tert*-butylcyclohexanol, 25143-76-4; *cis*-1-ethyl-4-*tert*-butylcyclohexanol, 17328-78-8; *trans*-1-butyl-4-*tert*-butylcyclohexanol, 79928-59-9; *cis*-1-butyl-4-*tert*-butylcyclohexanol, 79928-58-8; *trans*-1-allyl-4-*tert*-butylcyclohexanol, 42437-23-0; *cis*-1-allyl-4-*tert*-butylcyclohexanol, 42437-24-1; *trans*-1,2-dimethylcyclohexanol, 19879-12-0; *cis*-1,2-dimethylcyclohexanol, 19879-11-9; *cis*-1,3-dimethylcyclohexanol, 15466-94-1; *trans*-1,3-dimethylcyclohexanol, 15466-93-0; *cis*-1-butyl-3-methylcyclohexanol, 96930-11-9; *trans*-1-butyl-3-methylcyclohexanol, 96930-12-0; *cis*-1-allyl-3-butylcyclohexanol, 96930-13-1; *trans*-1-allyl-3-butylcyclohexanol, 96930-14-2; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; 2,4,6-tri-*tert*-butylphenol, 732-26-3; phenol, 108-95-2; trimethylaluminum, 75-24-3; MeLi, 917-54-4; EtMgBr, 925-90-6; BuMgBr, 693-03-8; CH₂=CHCH₂MgBr, 1730-25-2; MeMgI, 917-64-6; BuC≡CMgBr, 32359-01-6.

## Cyano Complexes of Trivalent Nickel in Aqueous Solution

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Oxidation of $Ni^{II}(CN)_4{}^{2-}$ in aqueous solution gives *trans*-diaquatetracyanonickelate(III), which is an excellent precursor for the formation of a new series of nickel(III) complexes. This $Ni^{III}(CN)_4(H_2O)_2{}^-$ complex is moderately stable at low concentrations ($<2 \times 10^{-4}$ M) in acidic solution (11-min $t_{1/2}$ at 25 °C, pH 1–3) but decays rapidly in base (0.5-s $t_{1/2}$ at pH 10). EPR spectra indicate that it is tetragonally elongated with water molecules in the axial positions. Studies with $^{13}CN^-$ confirm that the unpaired electron is in the nickel $d_{z^2}$ orbital, where it is not affected by the $^{13}C$ nuclear spin of the equatorially coordinated cyanides. The $Ni^{III}(CN)_4(H_2O)_2{}^-$ complex undergoes rapid axial substitution with ammonia, imidazole, pyridine, acetonitrile, azide, cyanate, and chloride ions to form bis trans complexes as observed by frozen aqueous EPR. Bipyridyl chelates with nickel(III) to form a mixed cyano complex. Addition of cyanide to the diaqua complex forms $Ni^{III}(CN)_6{}^{3-}$, which gives temperature-dependent EPR spectra in frozen aqueous solution.

The formation of tetracyanonickelate(III) has been reported in the X-ray irradiation of $Ni(CN)_4{}^{2-}$ doped in NaCl crystals[1] and by X-ray irradiation in frozen aqueous solution.[2,3] It also has been observed as a transitory species by pulse radiolysis[4] of $Ni(CN)_4{}^{2-}$. We find that the nickel(III) complex is easily prepared in aqueous solution with a bulk electrolysis column[5,6] or by chemical oxidation.

The cyclic voltammetry gives a formal reduction potential of 1.19 V (vs. NHE) for the $Ni^{III,II}(CN)_4{}^{-,2-}$ couple between pH 2.0 and 7.2. This potential is 0.37 V higher than the value for the $Ni^{III,II}(H_{-2}Aib_3)^{0,-}$ couple[7,8] and 0.16 V higher than for the $Ni^{III,II}(cyclam)^{3+,2+}$ couple.[9,10]

The UV spectrum of $Ni^{III}(CN)_4(H_2O)_2{}^-$ has a peak at 255 nm ($\epsilon$ 1.16 × 10⁴ M⁻¹ cm⁻¹). Mulazzani et al.[4] reported a peak at

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**Table I.** Frozen Aqueous Glass EPR Parameters for Nickel(III) Cyano Complexes

| | $g_\perp{}^a$ | $g_\parallel$ | $A_\perp$ | $A_\parallel$ |
|---|---|---|---|---|
| $Ni^{III}(CN)_4(H_2O)_2{}^-$ | 2.198 | 2.007 | | |
| $Ni^{III}(CN)_4(Cl)_2{}^{3-}$ | 2.161 | 2.008 | $9^b$ | $33.6^b$ |
| $Ni^{III}(CN)_4(NH_3)_2{}^-$ | 2.116 | 2.009 | $18.3^c$ | $24.5^c$ |
| $Ni^{III}(CN)_6{}^{3-}$ (−190 °C) | 2.081 | 2.010 | $92^d$ | $100^d$ |
| $Ni^{III}(CN)_6{}^{3-}$ (−35 °C) | $2.056^e$ | | $37.3^d$ | |

$^a$ Spectra were simulated with $g_{xx} = g_{yy}$.  $^b$ Cl hyperfine splitting.  $^c$ N hyperfine splitting.  $^d$ $^{13}C$ hyperfine splitting.  $^e$ $g_{iso}$.
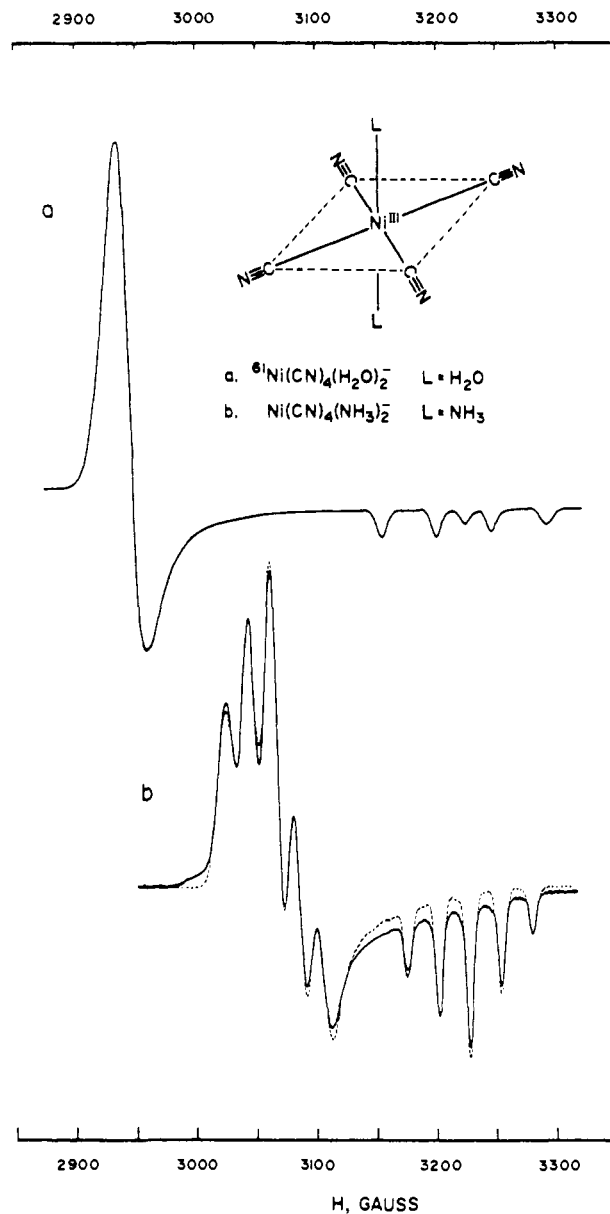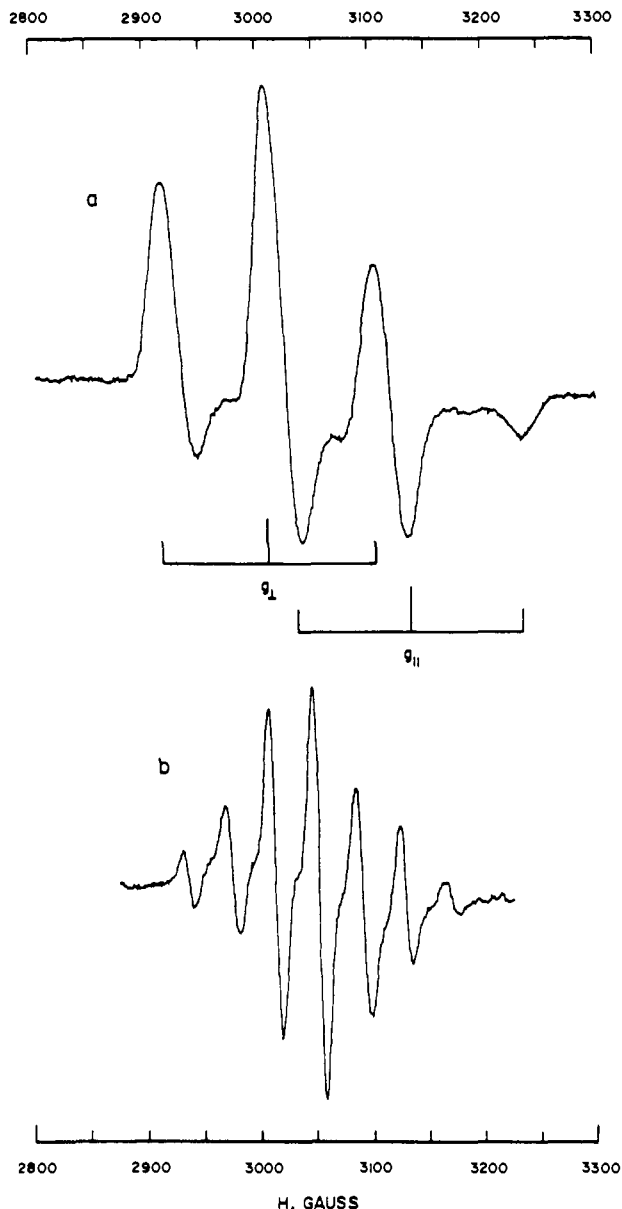


**Figure 1.** Magnetically dilute frozen aqueous solution X-band EPR spectra of tetracyanonickelate(III) complexes at −150 °C: (a) $^{61}Ni^{III}$-$(CN)_4(H_2O)_2{}^-$, 88.8% enriched $^{61}Ni$; the small peak in the center of the $g_\parallel$ region is the $^{58}Ni$ $g_\parallel$ peak. (b) $Ni^{III}(CN)_4(NH_3)_2{}^-$ (from 2.5 × 10⁻² M NH₃ and 1.0 × 10⁻³ M $Ni^{III}(CN)_4(H_2O)_2{}^-$); the dashed line is the computer simulation used to calculate the g values in Table I.

250 nm in pulse radiolysis studies, but they also found a second, more intense peak at 270 nm that we do not observe.

The aqueous room-temperature EPR spectrum of $Ni^{III}(C-N)_4(H_2O)_2{}^-$ is a simple derivative. The $g_{iso}$ value is 2.142, which is smaller than $g_{av}$ values of 2.17–2.20 for nickel(III) peptide complexes[11,12] or 2.157 for the $Ni^{III}(cyclam)(H_2O)_2{}^{3+}$ complex.[13]

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**Figure 2.** Frozen aqueous X-band EPR spectrum of $Ni^{III}(^{13}CN)_6{}^{3-}$ prepared from $1.0 \times 10^{-3}$ M $Ni^{III}(CN)_4(H_2O)_2{}^-$ and $7.4 \times 10^{-2}$ M $^{13}CN^-$; pH 10.5, $\mu = 0.10$ $NaClO_4$: (a) $-190$ °C; (b) $-35$ °C.

which contains the unpaired electron.

The frozen EPR spectrum for $Ni^{III}(CN)_4(NH_3)_2{}^-$ (Figure 1b) shows intense hyperfine splitting in both the $g_{\parallel}$ and $g_{\perp}$ regions due to interaction of the unpaired electron in the $d_{z^2}$ orbital with the two $^{14}N(I = 1)$ nuclei. There is also a characteristic shift of $g_{\perp}$ to smaller values with stronger axial donors (Table I). Aqueous room-temperature EPR shows that the $Ni^{III}(CN)_4(imidazole)_2{}^-$ complex is fully formed with $2.5 \times 10^{-2}$ M imidazole added to $1.0 \times 10^{-3}$ M $Ni^{III}(CN)_4(H_2O)_2{}^-$. This indicates that the overall stability constant for this complex is greater than $1.6 \times 10^5$ $M^{-2}$.

Although the $Ni^{III}(CN)_4(H_2O)_2{}^-$ complex is a strong oxidizing agent, it coordinates excess $CN^-$ to form $Ni^{III}(CN)_6{}^{3-}$ rather than rapidly oxidizing cyanide ion. Hexacyanonickelate(III) gives an anisotropic EPR spectrum at $-190$ °C, with $g_{\perp} = 2.081$ and $g_{\parallel} = 2.010$ (Table I). At $-35$ °C the frozen spectrum collapses to an isotropic signal, $g_{iso} = 2.056$. Addition of excess $^{13}CN^-$ ($7.4 \times 10^{-2}$ M) to $Ni^{III}(CN)_4(H_2O)_2{}^-$ ($1.0 \times 10^{-3}$ M) followed by a rapid freeze gives an anisotropic spectrum at $-190$ °C with 1:2:1 triplets in the $g_{\perp}$ and $g_{\parallel}$ regions (Figure 2a). This corresponds to two "EPR active" axial $^{13}CN^-$ in a tetragonally elongated geometry. Once again the equatorial $^{13}CN^-$ are "EPR silent". Figure 2b gives the frozen EPR spectrum of $Ni^{III}(^{13}CN)_6{}^{3-}$ at $-35$ °C. A rapid exchange of cyanide ions occurs and this seven-line spectrum, with intensity ratios of 1:6:15:20:15:6:1, corresponds to six equivalent $^{13}CN^-$ bonded to nickel(III). The change between Figure 2 parts a and b is reversible with temperature. This is an example of dynamic Jahn–Teller distortion,[17] where the six cyanides become equivalent, even in the frozen medium at $-35$ °C, due to vibrational interchange.

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## Stereospecific Synthesis of the Bicyclo[2.2.2] Portion of Granaticin: Synthesis of Sarubicin A

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The naphthoquinone antibiotic granaticin (1)[1] and the benzoquinone antibiotic sarubicin A (2)[2] have in common the 2-oxabicyclo[2.2.2] ring system, derived from glucose.[3] As part of our effort toward a synthesis of granticin, we report here the stereospecific synthesis of compound 3, which comprises key features of granaticin (1) and constitutes a formal synthesis of sarubicin A (2).[4] The general strategy is outlined in Scheme I. The key stages are (1) adding a formyl unit (or equivalent) to tetralone 4 trans to the hydroxyl, (2) diastereoselective addition of a methyl nucleophile to the aldehyde carbonyl in 5, and (3) closing the 2-oxabicyclo[2.2.2] ring from 6a.

The successful tactics are presented in Scheme II. The known[4] bromotetralone 7 was converted to the silyl enol ether (lithium diisopropylamide, $t$-BuMe$_2$SiCl, THF/HMPA, $-78$ to 20 °C).

The frozen EPR spectrum of $Ni^{III}(CN)_4(H_2O)_2{}^-$ is similar to the spectra of nickel(III) peptide complexes where $g_{xx} \approx g_{yy} > g_{zz}$, and a tetragonally elongated geometry is assigned.[11,14] The $g$ values (Table I) agree with those obtained by $\gamma$-irradiation of $Ni(CN)_4{}^{2-}$ in frozen aqueous solution.[3] Isotopically enriched $^{61}Ni$ ($I = {}^3/_2$) shows a quartet splitting in the $g_{\parallel}$ region (Figure 1a), but there is no observable splitting in the $g_{\perp}$ region. The axial spin coupling constant is 43.2 G. Thus, the unpaired electron is associated primarily with the nickel atom. This spin coupling constant is roughly twice the value for nickel(III) in biological molecules.[15,16]

Solution and frozen EPR spectra of the $^{13}C$ ($I = {}^1/_2$) (99% enriched) cyanide complex $Ni^{III}(^{13}CN)_4(H_2O)_2{}^-$ are identical with the spectra for the $^{12}C$ cyanide complex. The lack of $^{13}C$ splitting from equatorial cyanides indicates that there is little interaction between their sp donor orbitals and the nickel(III) $d_{z^2}$ orbital,

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