Oxidation and Reduction of Tetracyanonickelate(II) Ions induced by Ionizing Radiation: An Electron Spin Resonance Study of the $[Ni(CN)_4]^{3-}$, $[Ni(CN)_4]^-$, and $[HNi(CN)_4]^{2-}$ Complexes †

By **Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH
Mohamed M. Aly, Chemistry Department, Assiut University, Assiut, Egypt
Douglas X. West, Department of Chemistry, Illinois State University, Normal-Bloomington, Illinois 61761, U.S.A.

Exposure of salts and aqueous glasses containing tetracyanonickelate(II) ions to ^{60}Co γ-rays at 77 K gives $[Ni(CN)_4]^{3-}$ (d^9) and $[Ni(CN)_4]^-$ (d^7) ions, identified by their g-tensor components, which are markedly dependent upon the medium. For the d^9 complexes this dependence is assigned to interaction with the cyanide ligands, and for the d^7 complexes to interactions in the axial sites. The former ions have a . . . $d^1_{x^2-y^2}$ configuration, and the latter a . . . $d^1_{z^2}$ configuration on nickel. In the potassium salt, and in aqueous glasses containing methanol, d^7 centres are formed whose e.s.r. spectra exhibit large hyperfine coupling to one ^{14}N nucleus. In certain cases, especially for the barium salt, a novel species exhibiting large hyperfine coupling (*ca.* 150 G) to a single proton has been detected. This is identified as the complex $[HNi(CN)_4]^{2-}$.

THE effectiveness of e.s.r. spectroscopy in the study of the electronic structures of transition-metal complexes is now well established.[1] The range of complexes that can be studied in this way has been greatly extended by the use of ionizing radiation, which often provides a simple and effective route to centres with one electron more or less than the diamagnetic complex being irradiated.[2-7] In addition to gaining or losing electrons, various structural changes are often detected. For example, for cyanide complexes one or more CN ligands may bend away from the metal–ligand axis in such a way that slight electron delocalization onto the nitrogen atoms is detected.[3,8,9] In our studies of metal carbonyls,[10] we observed a far more drastic change in the case of electron loss from $[Mn(CO)_5X]$ (X = halide) and $[Mn_2(CO)_{10}]$ complexes. The initially diamagnetic 'd^6' complexes were converted at 77 K into high-spin d^5 complexes which still contained the halide ions. Such major structural changes are unusual.

There have been very few studies of nickel complexes using this technique. In a study of frozen solutions involving Ni^{2+} and a range of ligands, Amano and Fujiwara [11] detected only the d^9 centres, and reported a range of $g_{\parallel}$ and $g_{\perp}$ values for these. Reddy and co-workers [12] used the technique of incorporating $[Ni(CN)_4]^{2-}$ ions into alkali-metal halide lattices followed by exposure to ionizing radiation. Thus their complex was in effect $[Ni(CN)_4Cl_2]^{4-}$. They detected both gain and loss centres, the latter showing strong hyperfine coupling to the two chloride ligands. Similar centres were also studied by Danon and co-workers.[13] These results are compared with ours in Figure 2, below.

EXPERIMENTAL

The salts were prepared by established procedures [14] and their purities were checked by analysis for carbon, nitrogen, nickel, and water. The sample of $K_2[Ni(CN)_4]\cdot 1H_2O$ was prepared from $Ni[CN]_2$ and $K[^{13}CN]$ to give a product that was *ca.* 50% enriched. The product was dried *in vacuo* over P_2O_5 for 3 d.

Samples, as fine powders or in a range of D_2O–CD_3OD solutions, were cooled to 77 K and exposed to ^{60}Co γ-rays for 1—2 h at a dose rate of *ca.* 1.5 Mrad h^{-1}.‡ E.s.r. spectra were recorded on a Varian E-109 spectrometer at 77 K. Spectra were calibrated with a Hewlett–Packard 5246L frequency counter and a Bruker B-H12E field probe, which was standardized with a sample of diphenylpicrylhydrazyl (dpph).

Samples were annealed above 77 K after decanting the liquid nitrogen from the insert Dewar flask, and the spectra were continuously monitored. They were recooled to 77 K whenever significant changes in the spectra were detected. In all cases Q-band spectra were also studied, in order to confirm our analyses and to check the g-value determinations. The Q-band spectrometer was constructed in these laboratories by J. A. Brivati.

RESULTS AND DISCUSSION

In general, two abundant centres were obtained which are assigned to the d^9 and d^7 complexes. (Some typical results are shown in Figure 1.) Other minor centres were also detected. These included $^{\bullet}OH$ radical having normal e.s.r. properties.[15] This result shows that the water molecules involved were not co-ordinated to the nickel ions. These centres are not discussed further.

All salts in the aqueous-methanol glasses gave similar spectra, showing that ion pairing had no significant effect. Yields of the electron-loss centres were greatly reduced relative to the electron-gain centres, in accord with our normal experience. Trapped electron yields were markedly reduced, but $^{\bullet}OH$ and $^{\bullet}CH_2OH$ radicals were formed, as in the absence of the nickel salts.

Electron-gain Complexes.—These were recognised as d^9 complexes with the expected configuration . . . $d^1_{x^2-y^2}$ on the metal by the characteristic form of the g-tensor components, namely $g_{\parallel} > g_{\perp} > 2.00$.[16] The parallel and perpendicular features were unusually broad, the width being greatest for complexes with high values of $g_{\parallel}$. Since $\Delta g_{\parallel}$ (*i.e.* $g_{\parallel} - 2.00$) is so strongly dependent upon the environment of the d^9 complex, we suggest

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† Taken as Unstable Intermediates, Part 188.

‡ Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

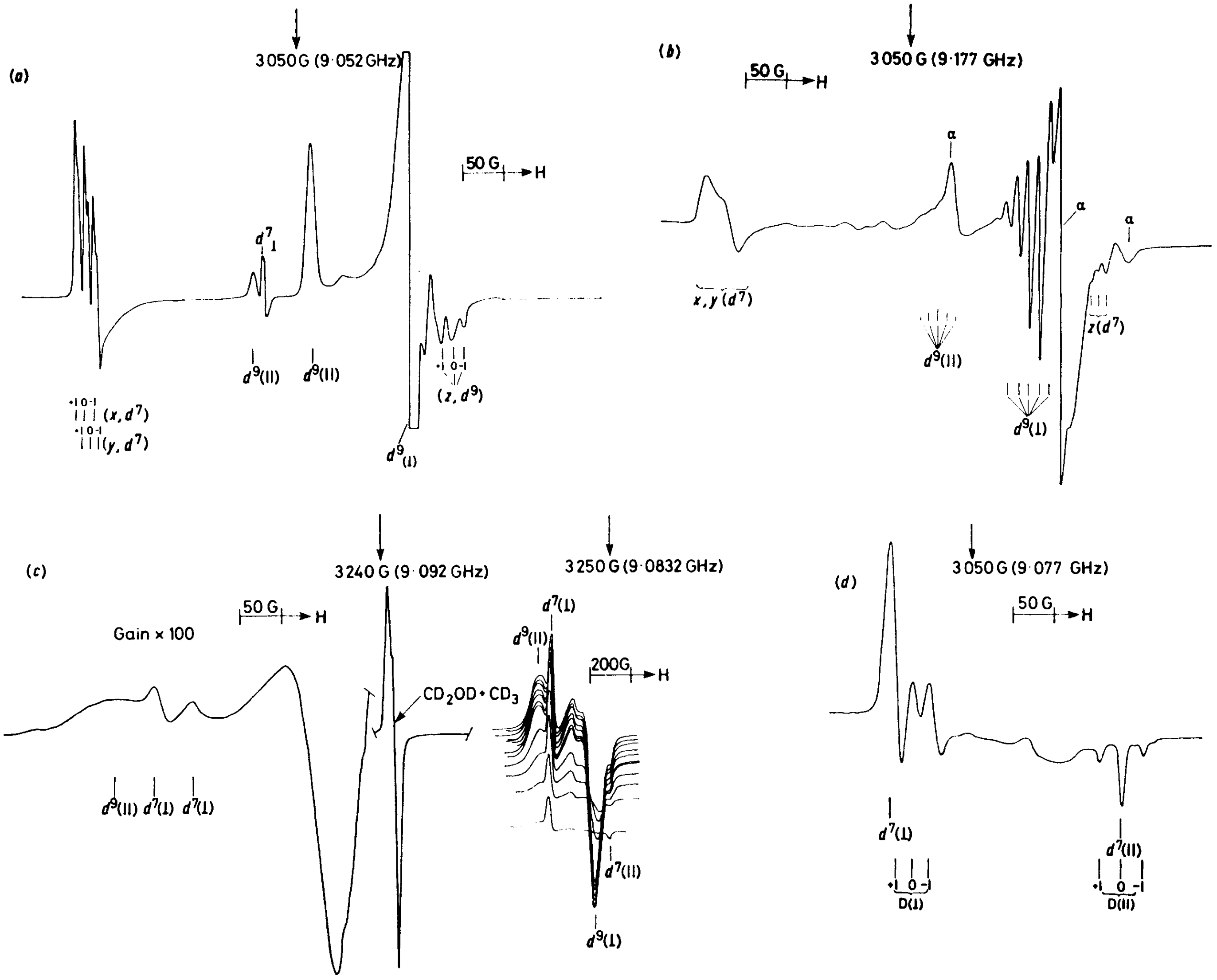


FIGURE 1 First-derivative X-band e.s.r. spectra for systems containing $[Ni(CN)_4]^{2-}$ ions after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to d^7 and d^9 ions: (*a*) $K_2[Ni(CN)_4]\cdot H_2O$; (*b*) as (*a*), enriched in ^{13}C {α features are probably due to $[HNi(CN)_4]^{2-}$ ions}; (*c*) as (*a*), in CD_3OD (80%)–D_2O (20%), reversible loss of the d^9 signal on warming being indicated in the insert; (*d*) as (*c*), after annealing to near the glass temperature and recooling to 77 K

that the width arises primarily from small variations in the environment of individual complexes. These may be increased by the tendency of the complexes to distort in order to minimize the antibonding character of the extra electron.

When considering possible causes of the large variations in Δg it may be helpful to refer to Figure 2, which summarizes our results and those of others. It is noteworthy that our results for $K_2[Ni(CN)_4]\cdot 1H_2O$ are almost identical with those for $[Ni(CN)_4]^{2-}$ ions in KCl. This strongly suggests that the shifts are not caused by ligand substitution in axial sites (along z). This is reasonable since there is no direct coupling between the d_{z^2} and $d_{x^2-y^2}$ orbitals contributing to Δg. We postulate that the shifts are controlled primarily by interaction between the medium and the nitrogen atoms of the cyanide ions. These are directly co-ordinated to the alkali-metal or alkaline-earth metal cations in those structures that have been reported.[17] The stronger this interaction the weaker the σ bonding to nickel. This will lower the σ^* ($d_{x^2-y^2}$) orbital containing the unpaired electron thus moving it closer to the π orbitals with which it couples, thereby increasing Δg. There is only a small trend for the alkaline-earth metal salts, but a large shift to smaller Δg on going to the potassium salt. The data for $[Ni(CN)_4]^{2-}$ in water and methanol are close to those for the alkaline-earth metal systems. This is reasonable in the light of our n.m.r.[18] and i.r.[19] results for cations in methanol. These strongly suggest that $K^+ \cdots$ MeOH interactions are weaker than MeOH $\cdots$ MeOH interactions, whilst $Ca^{2+} \cdots$ MeOH or $Ba^{2+} \cdots$ MeOH interactions are comparable with, or slightly greater than, MeOH $\cdots$ MeOH interactions.

The results obtained after exposing the potassium salt

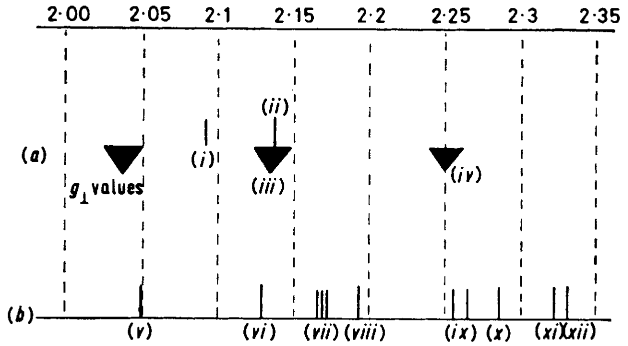
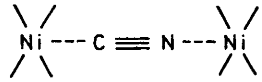


FIGURE 2 Display of g values for (a) $g_{\parallel}$ for d^9 complexes and (b) $g_{\perp}$ for d^7 complexes, derived from $[Ni(CN)_4]^{2-}$ ions. (a) (i) strong and (ii) weak centres in $K_2[Ni(CN)_4]$, (iii) centre in KCl (ref. 12), (iv) salts of Ca, Sr, and Ba and in MeOH–H_2O solution. (The range for $g_{\perp}$ values is also indicated.) (b) (v) Ni–H derivative, (vi) K salt, weak centre, (vii) centre in KCl (ref. 12), ($viii$) in MeOH–H_2O solution, (ix) K salt, strong centre [$A_{\perp}(^{14}N) = 7.3$ G, $A_{\parallel} = 9$ G], (x)—(xii) salts of Sr, Ba, and Ca

to γ-rays at *ca.* 35 °C are noteworthy (Figure 3). Although the parallel features were never well defined, the perpendicular features showed definite signs of hyperfine coupling to a group of ^{14}N nuclei, comprising probably seven lines. This suggests only three coupled nuclei, but we stress that there could well be two more lines in the wings of the spectrum, especially if these are relatively broad. We tentatively suggest that at room temperature one of the $[CN]^-$ ligands has been lost or displaced, thus relieving the antibonding character of the extra electron. This loss of symmetry might well allow the remaining $[CN]^-$ ligands to ' bend ' off axis and hence permit some hyperfine interaction to ^{14}N. The coupling of *ca.* 2.0 G is close to values previously assigned to such ' bent ' ligands.[3,8-10] (Other workers [5] have taken the detection of such ^{14}N hyperfine coupling to mean that the $[CN]^-$ ligands have turned through 180° to give *N*-bonded groups. However, we would then have expected to obtain ^{14}N coupling constants in the region of 15 G.[20]) One mode of distortion that could account for the linewidth effects and the appearance of ^{14}N coupling in the high-temperature product is a small distortion away from a planar towards a tetrahedral configuration.[12] It is noteworthy that the isoelectric carbonyl $[Co(CO)_4]$ was found to have a distorted (C_{3v}) tetrahedral structure, with the unpaired electron primarily in d_{z^2}.[21]

Electron-loss Complexes.—These complexes were again identified from the form of their g tensors, all complexes having $g_{\perp} > g_{\parallel} \approx 2.00$, this being characteristic of d^7 complexes with a $\cdots d^1_{z^2}$ configuration.[16] The features were much sharper than those for the d^9 complexes. The $g_{\perp}$ trends now reflect changes in axial bonding, as expected for a $d^1_{z^2}$ configuration. The structure of those salts that have been characterized by *X*-ray crystallography is invariably one in which the planar anions are stacked above each other with relatively short Ni-Ni distances, but tilted and usually twisted relative to their neighbours.[17] The fact that the electron is lost from d_{z^2} rather than from the π levels of $[Ni(CN)_4]^{2-}$ shows that the interaction that occurs between the complex anions must be such as to destabilize the d_{z^2} orbital. This statement is supported by recent theoretical calculations on $[Ni(CN)_4]^{2-}$, which indicate that the highest filled orbitals are largely or entirely π, localized on the ligands.[22] In water–methanol glasses we expect weak axial (z) bonding from the oxygen atoms of the solvent in addition to strong hydrogen bonding to the cyanide ligands. This creates a well defined σ^* orbital for the unpaired electron, raising it further above the π levels with which it couples in a perpendicular magnetic field and so the $\Delta g_{\perp}$ is reduced (Figure 2). This antibonding effect is slightly greater for the dichloro-complex in KCl crystals, the presence of the axial ligands being clearly established by the appearance of hyperfine coupling to two equivalent chlorine nuclei.[12,13] As discussed below, a single hydrogen ligand decreases $\Delta g_{\perp}$ still further.

Results for the major d^7 complex formed in the potassium salt are curious in displaying well defined hyperfine coupling to a single ^{14}N nucleus [Figure 1(a)]. The large, nearly isotropic coupling shows that this interaction involves the $\sigma[CN]^-$ orbital rather than a π orbital. It is possible that, very rarely, $[CN]^-$ bridges occur at crystal imperfections, as in (I), but we have no independent evidence for this. Certainly this would serve to destabilize the $\sigma^*(d_{z^2})$ orbital and hence could act as a



(I)

$Ni---C\equiv N---Ni$

FIGURE 3 First-derivative *X*-band e.s.r. spectrum for $K_2[Ni(CN)_4]\cdot H_2O$ after exposure to ^{60}Co γ-rays at *ca.* 35 °C, showing perpendicular features assigned to a d^9 complex exhibiting hyperfine coupling to several ^{14}N nuclei

hole trap. Also holes might be expected to be able to migrate along the stacks until they reach such defects. It is noteworthy that $\Delta g_{\perp}$ is greater than that for the aqua- or chloro-ligand complexes. This suggests that the bonding to cyanide is relatively weak. In that case we might have expected to detect a second d^7 complex in the irradiated potassium salt with a smaller $\Delta g_{\perp}$, having an Ni–CN linkage. Such a centre was indeed detected, but, as can be judged from Figure 1 and the fact that the signal is spread over a far smaller field range, this is a much less abundant centre. The observation of unexpectedly large coupling to a single ^{14}N nucleus is reminiscent of our results for irradiated $[Hg(SCN)_4]^{2-}$ complexes.[23] In this case electron addition gave $[Hg(SCN)_4]^{3-}$ ions, whose e.s.r. spectra also showed the presence of a single interacting nitrogen. We suggested that electron trapping occurred preferentially at imperfections in which, fortuitously, one thiocyanate ligand was *N*- rather than *S*-bonded.

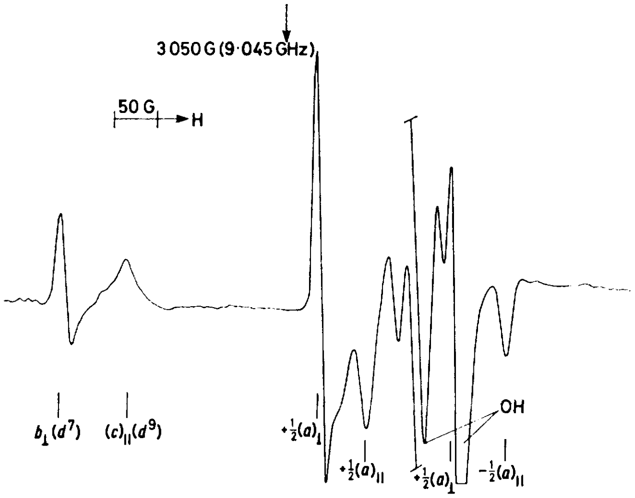


FIGURE 4 First-derivative *X*-band e.s.r. spectra for $Ba[Ni(CN)_4]\cdot H_2O$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[HNi(CN)_4]^{2-}$ (*a*) (see also, Figure in ref. 22), $[Ni(CN)_4]^-$ (*b*), and $[Ni(CN)_4]^{3-}$ (*c*). The perpendicular feature for (*b*) is resolved into *x* and *y* features in the D_2O sample and the *Q*-band spectra

The $[HNi(CN)_4]^{2-}$ *Ion.*—A major centre in irradiated $Ba[Ni(CN)_4]\cdot H_2O$, and a minor centre in some of the other systems studied, exhibited a very large hyperfine coupling (*ca.* 150 G) to a single proton (Figure 4). That the splitting indicated in Figure 4 is due to ^1H hyperfine coupling was inferred from a comparison of the *X*- and *Q*-band spectra. The line positions only corresponded if the 150 G separation is due to hyperfine coupling rather than to two centres having different *g* values and fortuitously equal concentrations. It was confirmed by studying samples containing D_2O for which a well defined triplet was observed (Figure in ref. 24). The form of the *g*-tensor components ($g_{\perp} = 2.05$, $g_{\parallel} = 2.00$) suggests that the nickel contribution is d_{z^2}, and hence we suggest that hydrogen atoms formed from water molecules add axially to $[Ni(CN)_4]^{2-}$ ions [equations (1) and (2)]. The alternative, involving addition to one of the cyanide ligands to give a $^{\bullet}CH(=N)$ ligand, could never give rise to such a large proton coupling and still retain considerable nickel character since the coupling in $H\dot{C}N^-$ radicals is only *ca.* 130 G.[25] If this is correct, we have succeeded in preparing a transition-metal complex in which there is an unpaired electron σ to a hydrogen ligand.[25] In our studies of transition-metal carbonyl systems [10] this was one of our major aims.

$$H_2O + e^- \longrightarrow [OH]^- + H^{\bullet} \qquad (1)$$

$$H^{\bullet} + [Ni(CN)_4]^{2-} \longrightarrow [HNi(CN)_4]^{2-} \qquad (2)$$

The results are significant. The greatly reduced value for $\Delta g_{\perp}$ shows that covalency in the H–Ni bond is high. The ^1H proton coupling corresponds to a spin density in the 1*s* orbital of *ca.* 0.33, again showing that the σ^* orbital is highly covalent. (This delocalization must, of course, reduce $\Delta g_{\perp}$, but not to the extent observed.) There is some anisotropy in the ^1H coupling, of the form expected for the postulated σ^* structure, but our results are not sufficiently reliable to warrant an attempt to estimate the H–Ni separation therefrom.

Effects of Annealing.—In all cases the signals from the d^9 complexes were broadened reversibly on annealing. This effect was much less marked for the d^7 complexes even when the *g*-value variation was greater. This effect may well be linked with a distorted tetrahedral structure, since in the pure tetrahedral arrangement the σ orbitals are degenerate. This reversible loss enabled us to see the d^7 spectra more clearly and this was particularly helpful in the water–methanol systems [Figure 1(*c*)]. In these water–methanol systems a minor d^7 centre ($g_{\perp} = 2.15$) was lost quite rapidly and a new centre ($g_{\perp} = 2.11$) grew in. We tentatively suggest that the major d^7 centre is formed by electron loss, and the labile centre by $^{\bullet}OH$ addition to nickel [equation (3)].

$$[Ni(CN)_4]^{2-} + {}^{\bullet}OH \longrightarrow [HO{-}Ni(CN)_4]^{2-} \qquad (3)$$

On annealing this could protonate to give the normal species (which does gain slightly in intensity prior to loss). The second minor species could be formed by reaction with $^{\bullet}CD_3$ or $^{\bullet}CD_2OD$, being comparable in structure with the H-atom adduct, since its growth coincided with loss of the central lines due to these species.

The d^7 centre showing ^{14}N hyperfine structure became axially symmetric with a small increase in $A_{\perp}(^{14}N)$ (from 7.5 to *ca.* 11 G) on annealing. This change was irreversible and presumably corresponds to some readjustment of the $4[CN]^-$ ligands. It is hard to understand how the structure could become axial and yet retain a coupling to a single ^{14}N nucleus if one of the in-plane $[CN]^-$ ions were responsible.

On annealing the aqueous-methanolic solutions to just below their glass-transition temperatures a new d^7 species exhibiting hyperfine coupling to a single ^{14}N nucleus grew in. In Figure 1(*d*) this is shown together with parallel and perpendicular features for the original

d^7 complex. The $g_\perp$ value of 2.174 is close to that of the original complex, but the ^{14}N coupling ($A_\parallel = 21$ G; $A_\perp = 25$ G) is very high, and certainly corresponds to σ delocalization onto ^{14}N which must lie on the *z* axis. We suggest that slight hydrolysis must have occurred during the dissolution and freezing process to give some uncomplexed cyanide ions. On annealing these are thought to have become bound to the d^7 complex giving $[Ni(CN)_5]^{2-}$ with a square-pyramidal structure.

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