Small Molecules

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"Guilty" Verdict—Evidence for the Noninnocence of Cyanide

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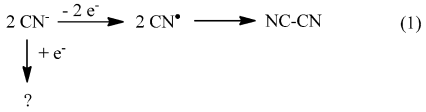
cyanometalates · diatomic ligands · electronic structure · noninnocent behavior · oxidation states

Cyanide was accidentally prepared in 1706 as a component of the then quickly commerzialized dye Prussian Blue,[1a–e] $\{Fe_4[Fe(CN)_6)]_3\}$,[1f] which is believed to have been the first synthetic coordination compound.[1g,h] The chemistry of cyanide was later developed by Marggraf (1745), Macquer (1752), Scheele (1783) and, in a way, by Goethe (1793);[1i] Scheele also obtained the conjugated acid, HCN.[2] Cyanide has long proved to be a potent poison,[2] inhibiting the cellular respiration (O_2 reduction) performed by the FeCu center of mitochondrial cytochrome *c* oxidase. However, for more than a decade now cyanide has also been established as a true bioligand of iron centers in hydrogenases.[3] (The cyanocobalt(III) complex known as vitamin B_{12} represents a stable storage form of cobalamin coenzymes, discovered during the isolation procedure[4])

Cyanide is the classical "strong" ligand,[5] effecting low-spin ground-state configurations of binding transition metals because of the double function as a σ-donating basic anion and as an acceptor for π back donation from the metal to low-lying π*(C≡N) orbitals.[6] The electron-transfer reactivity related to the donor function is well known in the form of cyanide oxidation to yield cyanogen via the CN· radical [Eq. (1)].



(1)

In contrast, the *acceptance* of electrons by negatively charged CN^- (a "pseudohalide") has been less well established for ground-state species. (Metal-to-ligand charge transfer excitation can lead to short-lived population of π*(CN)). Reduction of CN^- would imply major charge acquisition by the π*(CN) orbitals, which should result in C–N bond lengthening and weakening (i.e. lowered stretching frequencies ν_{CN}). However, the C–N distances and ν_{CN} values of the known cyanometalates have proven remarkably invariant.[5,7]

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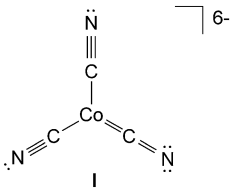
Höhn et al. have now reported[8] a completely documented case of reduced cyanide, that is, three $CN^{1.67-}$ ions stabilized by cobalt(−I) in $M_3[Co(CN)_3]$ (M = Sr, Ba). Remarkably, the material was obtained by a high-temperature (≈1200 K) "solid-state" route and not by a less harsh coordination chemistry procedure.

The reactions between cobalt powder, NaCN, and the corresponding subnitride M_2N[9] in strictly defined ratio at about 1200 K in pressed pellets under argon produced diamagnetic $M_3[Co(CN)_3]$ (M = Sr, Ba), which apparently contain the 18-valence-electron species $[Co(CN)_3]^{6-}$. The compounds could be analyzed by a variety of physical methods:[8] Structure determination by X-ray diffraction of single crystals (M = Ba) or powders revealed trigonal-planar tricyanocobaltate with significantly lengthened C–N bonds of about 1.24 Å relative to the typical[5,7] 1.15 Å of coordinated CN^-. Consequently, the CN stretching vibrations were found at remarkably lowered frequencies of 1670–1700 cm^{-1} (IR and Raman), shifted by about 400 cm^{-1} from the typical 2100 cm^{-1} [5,7] as found for related cyanometalates such as $Na_2[Cu(CN)_3]\cdot 3H_2O$,[7b] or $K_3[Co(CN)_6]$ with low-spin cobalt(+III).[7c] To understand this C–N bond weakening, unprecedented in cyanometalate chemistry, XANES (Sr-K edge) and XPS spectroscopy (Co $2p_{1/2}$ and Co $2p_{3/2}$) were used to establish the metal configurations. While Sr^{2+} was clearly ascertained, a closed-shell configuration was also inferred for the cobalt center, suggesting a d^{10} configuration, equivalent to cobalt(−I). The absence of ligand-field effects in a d^{10} situation is compatible with the trigonal-planar arrangement of $[Co(CN)_3]^{6-}$, the high negative charge of which is offset by three dipositive cations. A low, but not excessively negative oxidation state for cobalt was also suggested by density of states (DOS) calculations and the quantum theory of atoms in molecules (QTAIM) approach,[8] which yielded approximate charges of +1.4 (Ba), 0.0 (Co), and −1.4 (CN).[8] The internal charge distribution in the 18-valence-electron ion $[Co(CN)_3]^{6-}$ would thus favor $[Co^{-I}(CN^{(5/3)-})_3]^{6-}$ rather than $[Co^{-III}(CN^-)_3]^{6-}$ or $[Co^{o}(CN^{2-})_3]^{6-}$ (a d^9 species). To avoid fractional charges and bond orders (here: $2^2/_3$), mesomeric structures $[Co^{-I}(CN^-)_2(CN^{3-})]^{6-}$ (**I**) with a "percyano" group CN^{3-} can be formulated,[8]



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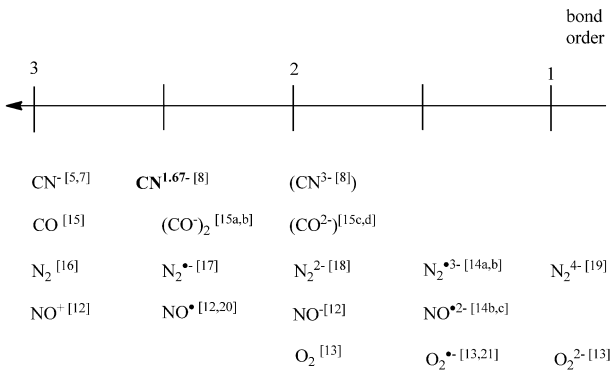

Figure 1. Noninnocent diatomic ligands.

where CN^{3-} is isoelectronic with N_2^{2-}, NO^-, and O_2 (see Figure 1).

These unambiguous results for coordinated CN^{n-} ligands with $n>1$ thus provide the first hard evidence for the plausible but hitherto undocumented noninnocent behavior[10] of the cyanide ligand. "Noninnocence" as introduced by Jørgensen[10a] and as elaborated by Ward and McCleverty,[10b] as well as Wieghardt and co-workers[10c] pertains to redox-active ligands that can create an *ambi-valence* in the electron distribution and thus in the oxidation state formulation of the corresponding coordination compounds. Among the typical noninnocently behaving ligands are often π conjugated organic systems, with[11a] or without bioinorganic relevance,[11] as well as diatomic ligands such as the classical $NO^{+/\bullet/-}$ [10a,b,12] or $O_2^{0/\bullet-/2-}$ [11a,13] series. Following the detection of super-reduced paramagnetic $N_2^{\bullet 3-}$ [14a,b] and, in analogy, of $NO^{\bullet 2-}$,[14b,c] the now fully characterized $CN^{1.67-}$ [8] can be fitted into a corresponding scheme of noninnocent diatomic ligands (Figure 1).

The left column of Figure 1 displays the 10-valence-electron species NO^+, N_2, CO, and CN^- with strong triple bonds between the atoms. It is obvious that σ donation increases and π back donation decreases along that series, leaving detectable but moderate backbonding for normal coordination compounds of cyanide.[6] Electron uptake produces ligands such as the nitrosyl radical, $NO^{\bullet}$,[12,20] which are much less π accepting, but increasingly σ and π donating, or which dimerize [Eq. (2)] to form a strong covalent bond as in bridging $(\mu\text{-}\eta^1{:}\eta^1\text{-}C_2O_2)^{2-}$.[15a,b]

$$2\,CO \xrightarrow{+2e^-} 2\,CO^{\bullet -} \rightarrow {}^-O{-}C{\equiv}C{-}O^- \qquad (2)$$

In connection with Figure 1 the results from Höhn et al. invite speculation about further "super-reduced" monomeric diatomic ligands such as CO^{n-}, as earlier discussed for $[Co(CO)_3]^{2-}$.[15c,d] Although it occupies a prominent position in the spectrochemical series, cyanide has been mostly regarded as a rather conventional ligand, as its exclusion from organometallic chemistry (despite the metal–carbon bond) confirms. The oxidation to cyanogen and apparent reluctance towards reduction have contributed to this notion, illustrated by the use of the "pseudohalide" attribute. Reduced CO thus appears more plausible than reduced CN^-, because the existence of a stable neutral carbon monoxide ligand remains suspicious from an electrostatic point of view. In contrast to the cyanide case, a reduced CO has thus been discussed[15c,d] for several "super-reduced" carbonylmetalates.[15a,b]

On the other hand, the C_2^{2-} ion, $^-C{\equiv}C^-$, (bridging acetylide),[22] another diatomic 10-electron species, may also behave in a noninnocent way as illustrated by the binding modes in Figure 2. However, the oxidation state formalism is rarely employed in this area of organometallic chemistry.

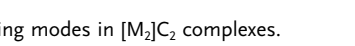

Figure 2. Bonding modes in $[M_2]C_2$ complexes.

The report and exhaustive experimental and theoretical study[8] of $M_3[Co(CN)_3]$ illustrates that small ligands can still hold surprises. Most notably, a high-temperature (1200 K) synthetic approach as typical for solid-state chemistry yielded a hitherto undocumented situation, which can be understood in its peculiarity from principles like the 18-valence-electron stability rule (for $[Co(CN)_3]^{6-}$), from closed-shell stabilization (for Co^{-I} (d^{10})), from the concept of noninnocent behavior of ligands with accessible π* orbitals, and from quantum-chemical approaches. Nevertheless, the Coulombic stabilization through higher-valent metal species such as Sr^{II}, Ba^{II},[8] Y^{III},[14] Dy^{III},[14a] or U^{IV} [15b,23] remains extremely important for the isolation of small anions with unusually negative charges, as demonstrated for $CO_2^{\bullet -}$,[23] $N_2^{\bullet 3-}$,[14a] $NO^{\bullet 2-}$,[14c] and now for $CN^{(5/3)-}$ in $[Co(CN)_3]^{6-}$.[8] Considering the propensity of cyanide to act as a bridge (like in Prussian Blue[1]) and to adopt several other coordination modes,[5] the now proven potential for noninnocent behavior adds an additional, an electron-transfer dimension, promising exciting developments for the 4th century of cyanometalate chemistry.

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