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Non-innocent cyanido ligands: tetracyanidoferrate(−II) as carbonyl copycat†

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While a negative oxidation state occurs rarely for metals in general, this is commonly known for metal carbonyl anions, *i.e.* carbonyl metalates. Although CO and CN[−] are isoelectronic, cyanidometalates usually do not exhibit metal centers with negative oxidation states. However, we report on the electron-rich tetrahedral tetracyanidoferrate(−II) anion [Fe(CN)₄]^{6−}, which was stabilized in (Sr₃N)₂[Fe(CN)₄] (space group *R*3̄*c*, *a* = 702.12(2) pm, *c* = 4155.5(2) pm). Microcrystalline powders were synthesized by a solid-state route, single crystals were obtained from Na metal flux. In comparison to classical cyanidometalates, C–N distances are longer and stretching frequencies are lower as indicated by X-ray diffraction, IR and Raman spectroscopy. Weak C–N, strong Fe–C bonds as well as the anion geometry resemble the isoelectronic tetrahedral carbonyl ferrate [Fe(CO)₄]^{2−}. ⁵⁷Fe Mössbauer spectroscopic measurements reveal a negative isomer shift in agreement with substantially delocalized d electrons due to strong π back-bonding. These results point to a very similar bonding situation of both 18e tetracyanido and tetracarbonyl ferrates including non-innocent redox-active ligands and a d¹⁰ closed shell configuration on iron. Hereby, new tetracyanidoferrate(−II) provides a missing link for a more in-depth understanding of the chemical bonding trends of highly-reduced cyanidometalates in the quest for even higher reduced transition metals in this exceptional class of compounds.

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Introduction

The possibility of metal anions has fascinated chemists for over 100 years.¹ Systematic studies of transition metals with negative oxidation states started in the 1930s with metal carbonyl anions such as [Fe^{II}(en)₃][Fe^{−II}(CO)₄] (en = ethylenediamine), although its ionic nature was not revealed until later.^{2–4} During the following decades, carbonyl metalates were applied as starting materials and catalysts in (metal)organic syntheses.^{5,6} Additionally, a quest for even further reduced metalates resulted in extreme examples such as [Co(CO)₃]^{3−} and [Cr(CO)₄]^{4−}.^{1,7–10}

Although the cyanide anion is isoelectronic to carbon monoxide, respective cyanidometalates typically differ significantly from carbonyl metalates with regard to chemical bonding, properties and applications. The σ-donor function of the typically redox-inactive CN ligand allows for stabilization of relatively high oxidation states of the transition metal. In contrast, negative oxidation states for carbonyl metalates are achieved by strong π back-bonding shifting electron density towards the non-innocent, redox-active CO ligands.¹¹ These differences are best investigated by IR and Raman spectroscopy: stretching frequencies of the CN ligand ν(CN) are similar for complexes and simple salts (typically 2000–2200 cm^{−1}).^{12,13} For carbonyl metalates, ν(CO) frequencies are much lower in comparison to gaseous CO (2143 cm^{−1}),¹⁴ *e.g.* 1614 cm^{−1} for [Co(CO)₃]^{3−}.^{8,9}

However, exotic examples of highly reduced cyanido complexes have been reported, *e.g.* [Co(CN)₃]^{6−} and [Fe(CN)₃]^{7−}.^{15,16} These metalates mimic the bonding situation of carbonyl metalates including unusual non-innocent CN ligands exhibiting very low ν(CN), such as 1641–1696 cm^{−1} for Ba₃[Co(CN)₃].¹⁵ Quantum chemical calculations revealed a closed shell d¹⁰ configuration for the Co and Fe centers and strong π back-bonding yielding intermediate-valent CN^{1.67−} ligands due to occupied CN pπ* antibonding orbitals.^{15,16}

Taking into account the striking similarities between isoelectronic [Co(CO)₃]^{3−} and [Co(CN)₃]^{6−}, it can be anticipated,

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two Raman and one IR mode are observed for $\nu(\text{CN})$ at similar frequencies for both anions (see Table 1). In contrast, $\nu(\text{FeC})$ and $\delta(\text{FeCN})$ modes are split as a result of the symmetry reduction for $[\text{Fe}(\text{CN})_4]^{6-}$ in the solid state structure (site symmetry C_3). An unambiguous assignment of $\nu(\text{FeC})$ and $\delta(\text{FeCN})$ modes within that region is not possible without further investigations. For molecular site group analysis, see ESI.†

Comparison of $[\text{Fe}(\text{CN})_4]^{6-}$ and related metalates

To the best of our knowledge, $[\text{Fe}(\text{CN})_4]^{6-}$ is the first homoleptic $18e$ cyanidoferrate with four ligands. The only other four-coordinated cyanidoferrate is $14e$ square-planar $[\text{Fe}(\text{CN})_4]^{2-}$.²³ On the other hand, $18e$ tetraisocyanidometalates were reported, such as $[\text{Fe}(\text{CNXyl})_4]^{2-}$ (Xyl = 2,6-dimethylphenyl).²⁴

In contrast to simple cyanide salts and classical cyanidometalates such as $[\text{Fe}(\text{CN})_4]^{2-}$ or $[\text{Fe}(\text{CN})_6]^{3-}$,^{23,25} C–N bond lengths in $[\text{Fe}(\text{CN})_4]^{6-}$ are unusually long and $\nu(\text{CN})$ valence frequencies are unusually low pointing towards severely weakened C–N bonds (Table 1). This is accompanied by much stronger Fe–C bonds than in $[\text{Fe}(\text{CN})_6]^{3-}$ evidenced by shorter distances and higher $\nu(\text{FeC})/\delta(\text{FeCN})$ frequencies. These observations are in good accordance with the textbook description of π back-bonding: electrons are shifted from metal d orbitals to antibonding π^* orbitals of the CN ligand, which strengthens the Fe–C bond and weakens the C–N bond. High values of $\delta(\text{FeCN})$ vibrations likewise point to a stiffer Fe–C–N unit due to increased π bonding.²⁶ Similar trends have been discussed for the complexes $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, with the higher charged metalate exhibiting more pronounced π back-bonding.^{11,12} However, changes for hexacyanidoferrates are small in comparison to the tetracyanidoferrates $[\text{Fe}(\text{CN})_4]^{2-}$ and $[\text{Fe}(\text{CN})_4]^{6-}$ (Table 1). Instead of classical cyanidoferrates, chemical bonding in $[\text{Fe}(\text{CN})_4]^{6-}$ resembles the situation in isoelectronic and likewise tetrahedral $[\text{Fe}(\text{CO})_4]^{2-}$ evidenced by similar values for bond lengths and stretching frequencies.

With regard to the previously reported highly reduced cyanidometalates, a qualitatively similar bonding situation can be assumed for all $18e$ complexes $[\text{Co}(\text{CN})_3]^{6-}$, $[\text{Fe}(\text{CN})_3]^{7-}$, and $[\text{Fe}(\text{CN})_4]^{6-}$ based on interatomic distances and vibrational frequencies. Quantitatively, C–N bonds are stronger (shorter $d(\text{C–N})$, higher $\nu(\text{CN})$) and Fe–C bonds are weaker for $[\text{Fe}(\text{CN})_4]^{6-}$ in comparison to $[\text{Fe}(\text{CN})_3]^{7-}$ pointing to somewhat less π back-bonding for the tetracyanidoferrate. This is reasonable since the lesser charge of $[\text{Fe}(\text{CN})_4]^{6-}$ is distributed over more ligands which is equivalent to less π back-bonding in contrast to $[\text{Fe}(\text{CN})_3]^{7-}$. A similar trend is observed for the pair $[\text{Co}(\text{CO})_3]^{3-}$ and $[\text{Co}(\text{CO})_4]^{-}$ (Table 1).

The isoelectronic $[\text{Fe}(\text{CNXyl})_4]^{2-}$ exhibits somewhat longer C–N distances and lower $\nu(\text{CN})$ frequencies than $[\text{Fe}(\text{CN})_4]^{6-}$ due to the bridging CN groups instead of terminal cyanido ligands.

Physical properties

$(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ exhibits electrically insulating behavior consistent with mainly ionic interactions between Sr^{2+} , N^{3-} , and complex anions $[\text{Fe}(\text{CN})_4]^{6-}$. This accords well with reported

Table 1 Synopsis of cyanide and carbonyl compounds (M = transition metal) with respect to their bond lengths d (pm), as well as stretching and deformation frequencies^a ν , δ (cm^{-1})

Ligand	Anion	Compound	Geometry	$d(\text{C–N})$	$\nu(\text{CN})/\nu(\text{CO})$	$d(\text{M–C})$	$\nu(\text{MC})$ & $\delta(\text{MCN})/\delta(\text{MCO})$	Ref.	
CN	$[\text{Fe}(\text{CN})_4]^{6-}$	$(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$	Tetrahedral	120(1), 122(2)	1688; 1690, 1706	183(1), 187(1)	482–582; 415–619	This work	
	$[\text{Fe}(\text{CN})_3]^{7-}$	$\text{Li}_2\text{Sr}_3[\text{Fe}(\text{CN})_3]$	Trigonal-planar	126.7(3)	1490; 1581	178.6(4)	557–664; 464–611	16	
	$[\text{Co}(\text{CN})_3]^{6-}$	$\text{Ba}_3\text{Co}(\text{CN})_3$	Trigonal-planar	123.5(5)	1641; 1696	176.9(3)	542, 569; 420–582	15 and 27	
	$[\text{Fe}(\text{CN})_4]^{2-}$	$[\text{Ni}(\text{dien})_2][\text{Fe}(\text{CN})_4]^b$	Square-planar	114–116	2077, 2117	185–186		23	
	$[\text{Fe}(\text{CN})_6]^{3-}$	$\text{Rb}_2\text{Na}[\text{Fe}(\text{CN})_6]$	Octahedral	114, 115	2122	194	394, 523	25	
	$[\text{Fe}(\text{CN})_6]^{4-}$	$\text{Ba}(\text{NH}_4)_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	Octahedral	115	2041; 2060, 2095	191	<585	28	
	$[\text{Fe}(\text{CNXyl})_4]^{2-}$	$[\text{K}([2.2.2]\text{cryptand})]_2[\text{Fe}(\text{CNXyl})_4]^c$ NaCN	Tetrahedral	123–124 116	1675 2088	176–177		24 29	
	CO	$[\text{Fe}(\text{CO})_4]^{2-}$	$\text{A}_2[\text{Fe}(\text{CO})_4]$ (A = K, Na)	Tetrahedral	118	1729–1786; 1788	175	555, 646; 464–785	22, 30–32
		$[\text{Co}(\text{CO})_4]^{-}$	$\text{Al}[\text{Co}(\text{CO})_4]$ (A = QuinH, Na) ^d	Tetrahedral	115	1886; 1883, 1918	176–178	530, 555; 439–715	22, 30 and 33
		$[\text{Co}(\text{CO})_3]^{3-}$	$\text{Na}_3[\text{Co}(\text{CO})_3]$	Trigonal-planar	126 ^e	1614	177 ^e		8 and 9
CO		CO (gas)		113	2143			14 and 29	

^a *Italic*: IR data; regular: Raman data. ^b dien = diethylenetriamine. ^c Xyl = 2,6-dimethylphenyl. ^d QuinH = quinclidinium. ^e Calculated values.

properties of similar reduced cyanidometalates such as $\text{Sr}_3[\text{Co}(\text{CN})_3]$ and $\text{Ba}_{3.5}[\text{Fe}(\text{CN})_3]$.^{15,16} Unfortunately, the conclusive examination of magnetic susceptibility data of $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ was hindered by too large contaminations of elemental Fe from synthesis.

⁵⁷Fe Mössbauer spectroscopy

To get a closer look into the valence state of the iron atoms in $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$, ⁵⁷Fe Mössbauer spectroscopic measurements were conducted at 293 and 78 K (Fig. 3). Both spectra could be well reproduced with a superposition of two sub-signals in a ratio of 63(1):37(1) at 293 K (top) and 59(1):41(1) at 78 K (bottom), respectively. Both spectra show similar fitting parameters (Table 2) for the particular simulated sub-spectra,

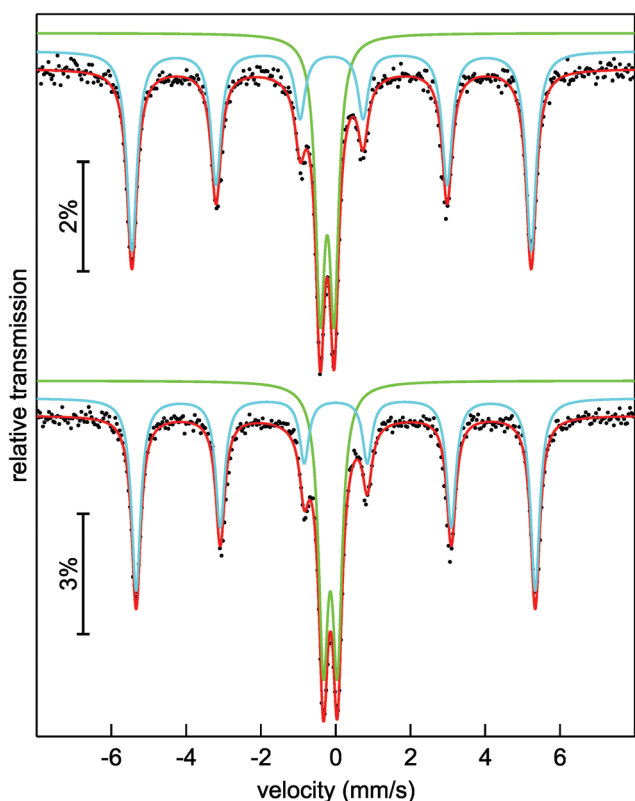


Fig. 3 Experimental (black dots) and simulated (lines) ⁵⁷Fe Mössbauer spectra of $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ at 293 K (top) and 78 K (bottom).

Table 2 Fitting parameters of ⁵⁷Fe Mössbauer spectroscopic measurements of $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ at 293 and 78 K; δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ = experimental line width, B_{Hf} = hyperfine field splitting

T/K	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ (mm s ⁻¹)	B_{Hf} (T)	Area (%)
293	-0.110(1)	0*	0.328(5)	33.12(1)	63(1)
	-0.227(2)	0.373(2)	0.297(4)	—	37(1)
78	0.001(1)	0*	0.298(4)	33.10(1)	59(1)
	-0.143(1)	0.374(2)	0.307(3)	—	41(1)

* Parameter was kept fixed during fitting procedure.

hence we will focus on the 293 K data. The blue sub-signal can be ascribed to residual elemental iron from the synthesis, since the isomer shift and the hyperfine field splitting accord well with the reported data ($\delta = -0.1 \text{ mm s}^{-1}$, $B_{\text{Hf}} = 33.1 \text{ T}$ for elemental Fe);^{34,35} these iron atoms in cubic environment show no quadrupole splitting. The green sub-spectrum with an isomer shift of $\delta = -0.227(2) \text{ mm s}^{-1}$ and a quadrupole splitting parameter of $\Delta E_Q = 0.373(2) \text{ mm s}^{-1}$ can be assigned to the iron atoms in the tetrahedral cyanidoferrate(-II) units of $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$. In ⁵⁷Fe Mössbauer spectroscopy, a more negative isomer shift indicates a higher s-electron density at the iron nucleus. The d-electrons shield the s-electrons, which leads to a lower delocalization and a higher s-electron density at the nucleus with a decreasing number of d-electrons. As a result we observe more negative shifts for compounds with iron atoms in highly positive oxidation states like $\text{K}_2\text{Fe}^{\text{VI}}\text{O}_4$ with an isomer shift of $\delta = -1.013 \text{ mm s}^{-1}$ (the original value in the literature is $\delta = -1.262 \text{ mm s}^{-1}$ referred to a ⁵⁷Co/Pt source).^{36,37} For iron in the formal oxidation state -II we would hence assume (just by extrapolation) a positive isomer shift at first sight. Unlike this assumption we observe a negative isomer shift for the iron atoms in the $[\text{Fe}(\text{CN})_4]^{6-}$ unit. A similar shift is reported for the isoelectric anion $[\text{Fe}(\text{CO})_4]^{2-}$ in $\text{Na}_2[\text{Fe}(\text{CO})_4]$ by Erickson and Fairhall.³⁸ $\text{Na}_2[\text{Fe}(\text{CO})_4]$ shows an isomer shift of $\delta = -0.251 \text{ mm s}^{-1}$ relative to elemental iron which corresponds to an isomer shift of $\delta = -0.351 \text{ mm s}^{-1}$ relative to a ⁵⁷Co/Rh source.^{35,36}

Erickson and Fairhall assigned the observation of the negative isomer shift to the strong π back-bonding between the carbonyl ligands and the iron d-orbitals, leading to substantial delocalization of the d-electrons which results in a reduced shielding of the s-electrons and therefore a higher s-electron density at the nucleus. This is underlined by the observed long C-N distances within the $[\text{Fe}(\text{CN})_4]^{6-}$ anion and the low valence vibration frequencies $\nu(\text{CN})$. The bonding situation in $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ is thus very similar to $\text{Fe}(\text{CO})_4^{2-}$ anion in $\text{Na}_2[\text{Fe}(\text{CO})_4]$.³⁸ The less negative isomer shift for $[\text{Fe}(\text{CN})_4]^{6-}$ in comparison to the $[\text{Fe}(\text{CO})_4]^{2-}$ anion can be ascribed to the ligands. The carbonyl ligand is a stronger π -acceptor than cyanide which leads to a weaker π back-bonding and a weaker delocalization of the d-electrons in $[\text{Fe}(\text{CN})_4]^{6-}$.

The slightly distorted coordination tetrahedron of $[\text{Fe}(\text{CN})_4]^{6-}$ leads to weak quadrupole splitting (Table 2). The small increase of the isomer shifts at 78 K of around 0.1 mm s^{-1} is caused by the second order Doppler shift which describes a temperature dependent contribution to the total isomer shift and which depends on the mean square of velocity of the nucleus.^{35,36} The experimental line widths Γ (Table 2) are in the usual range for ⁵⁷Fe Mössbauer signals.

Conclusions

Tetracyanidoferrate(-II) extends the growing class of highly reduced cyanidometalates to tetrahedral complexes. Judging from bond lengths, vibrational frequencies, as well as



Mössbauer spectroscopic measurements, chemical bonding in the isolated $[\text{Fe}(\text{CN})_4]^{6-}$ anion corroborates well to the isoelectronic tetrahedral $[\text{Fe}(\text{CO})_4]^{2-}$. Thus, a chemical bonding scheme consisting of strong π back-bonding between non-innocent ligands and a d^{10} metal center can be assumed for $[\text{Fe}(\text{CN})_4]^{6-}$ too, as previously confirmed for the famous carbonyl metalate prototype.^{9,39,40} The tetrahedral anion geometry of $[\text{Fe}(\text{CN})_4]^{6-}$ corroborates well with that picture: considering cyanide as a pseudohalide, the title complex resembles other tetrahedral d^{10} halide complexes such as $[\text{ZnCl}_4]^{2-}$ and $[\text{AlCl}_4]^-$ anions.^{41,42} Although the qualitative bonding scheme seems similar to previously known reduced cyanidometalates, it differs on a quantitative level of π back-bonding strength as observed by differences of interatomic distances and vibrational frequencies, e.g. in comparison to the $[\text{Fe}(\text{CN})_3]^{7-}$ anion.¹⁶

Crystal structures of highly reduced cyanidometalates resemble those known from ternary nitridometalates: the structure of $(\text{Sr}_3\text{N})_2[\text{Fe}(\text{CN})_4]$ shows similarities to $(\text{Ca}_3\text{N})_2[\text{FeN}_3]$,¹⁹ while $\text{LiSr}_3[\text{Fe}(\text{CN})_3]$ and $\text{Ba}_3[\text{Co}(\text{CN})_3]$ are closely related to $\text{Ba}_3[\text{FeN}_3]$.⁴³

Thus, the new tetracyanidoferrate(-II) provides a missing link for a more in-depth understanding of the trends regarding crystal chemistry and chemical bonding of electron-rich cyanidometalates. Bearing these concepts in mind will enable the future extension of highly charged cyanidometalates beyond group 8 and 9 – following the quest for even higher charged metalates. In view of the numerous applications of carbonyl metalates, similar usages can be anticipated for reduced cyanidometalates.

Author contributions

F.J., P.H., and M.R. planned and carried out the material synthesis. F.J., P.H., Yu.P., and M.R. planned and carried out the single-crystal X-ray diffraction measurements and analyzed the data. Yu.P. collected synchrotron powder diffraction data, while F.J. analyzed these. F.J. recorded and analyzed IR and Raman spectra. Th.B. and R.P. recorded and analyzed Mössbauer spectra. M.S. performed thermal analyses. M.B. performed physical property measurements. All authors contributed in writing the manuscript. M.R., P.H., and R.P. supervised the project.

Conflicts of interest

There are no conflicts to declare.

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