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VIP Metalates

$Sr_3[Co(CN)_3]$ and $Ba_3[Co(CN)_3]$: Crystal Structure, Chemical Bonding, and Conceptional Considerations of Highly Reduced Metalates[**]

Peter Höhn, Franziska Jach, Barış Karabiyik, Yurii Prots, Stefano Agrestini, Frank R. Wagner, Michael Ruck, Liu Hao Tjeng, and Rüdiger Kniep**

In memory of Hans Georg von Schnering

In going from oxo- via nitrido- to carbometalates the oxidation states of transition-metal elements participating in the formation of respective ternary and higher compounds are significantly lowered.[1] Based on these observations, we started to investigate the effect of elemental carbon as additive to selected nitridometalate systems. By using excess nitrogen during the high-temperature reactions (so-called oxidizing conditions) nitridometalate cyanamides are preferably formed (e.g. $Sr_6[Co^{I}N_2]_2[CN_2]$).[2] In reducing conditions (without excess nitrogen) cyanonitridometalates such as $Sr_2[NNi^{0}(CN)]$[3] are obtained, with the lowest oxidation state observed for nickel in nitrogen-containing compounds to date. The presence of cyano besides nitrido ligands gave the idea to modify the reducing conditions by adding carbon in the form of cyanides to the reaction mixtures.

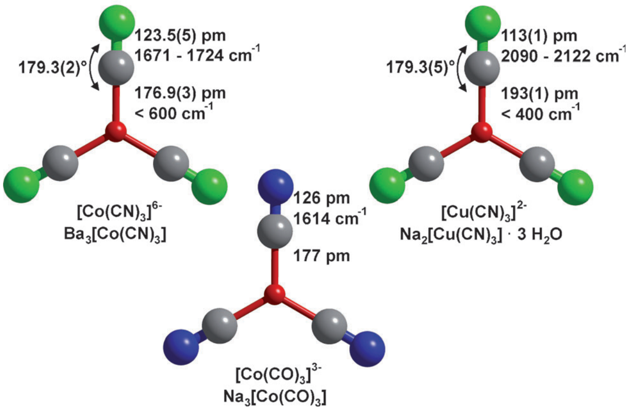

Figure 1. The complex anion $[Co(CN)_3]^{6-}$ (left) together with trigonal-planar complexes in a cyanocuprate[7] and a carbonylcobaltate.[8] Values for bond lengths and vibration frequencies in $[Co(CO)_3]^{3-}$ are based on theoretical calculations.[8]

Single-phase powder samples of the highly air- and moisture-sensitive phases $Sr_3[Co(CN)_3]$ and $Ba_3[Co(CN)_3]$ were obtained by treatment of pressed pellets of mixtures of AE_2N (AE = Sr, Ba), Co, and NaCN under argon at temperatures of about 1200 K. Single crystals of the Ba phase were grown at 1123 K. Crystal structure determinations[4] of the translucent-greenish compounds (hexagonal, space group $P6_3/m$) revealed a close relationship to the nitridometalates $AE_3[M^{3+}N_3]$ (AE = Sr, Ba, M = Cr, Mn, Fe)[5] and the presence of trigonal-planar complex anions (Figure 1). By regarding the CN ligands as formally single-atomic species, the compounds $AE_3[Co(CN)_3]$ and $AE_3[M^{3+}N_3]$ are even strictly isostructural. Besides the successful crystal structure determinations (Figure 2), the chemical analyses of the isotypic phases $Sr_3[Co(CN)_3]$ and $Ba_3[Co(CN)_3]$ did not indicate significant amounts of impurities, and the analytical data were consistent with the given chemical compositions.[6]

In view of these first facts, the isotypic compounds under consideration have to be discussed in terms of cyanocobaltates(3−) with the ionic formula $AE_3^{2+}[Co^{3-}(CN)^{-}_3]$, although the C–N distances are unusually large (Sr: 125(1) pm, Ba: 123.5(5) pm) compared with the tricyanometalate complexes $[Cu(CN)_3]^{2-}$, $[Ag(CN)_3]^{2-}$, $[Zn(CN)_3]^{-}$, $[Cd(CN)_3]^{-}$, and

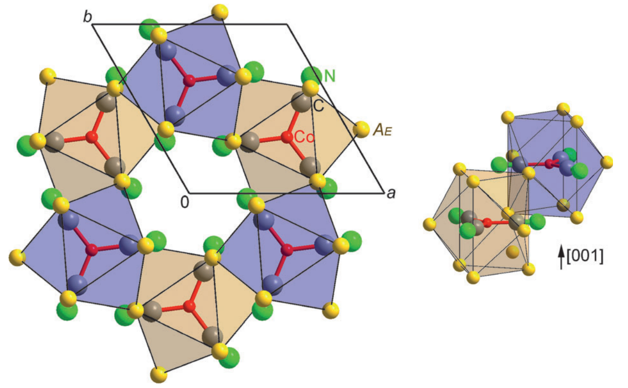

Figure 2. Crystal structure of $AE_3[Co(CN)_3]$. View along [001] (left) and interconnection of neighboring AE_9 polyhedra along [001] (right).

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[*] Dr. P. Höhn, Dipl.-Chem. F. Jach, B. Karabiyik,[+] Dr. Y. Prots, Dr. S. Agrestini, Dr. F. R. Wagner, Prof. Dr. M. Ruck,[++] Prof. Dr. L. H. Tjeng, Prof. Dr. R. Kniep
Max-Planck-Institut für Chemische Physik fester Stoffe
Nöthnitzer Strasse 40, 01187 Dresden (Germany)
E-mail: hoehn@cpfs.mpg.de
kniep@cpfs.mpg.de

[+] Permanent address: Koç University, Sariyer, Istanbul (Turkey)

[++] Max-Planck-Fellow (TU Dresden)

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$[\mathrm{Hg(CN)_3}]^-$, which represent a rather homogeneous group concerning their C–N bond lengths ($d(\mathrm{C{\equiv}N}) = 113$–$116$ pm).[9]

Whereas the high negative oxidation state of cobalt in the new ternary compounds is unusual with respect to the family of cyanometalates of transition-metal elements, this situation is reminiscent of carbonylmetalates, such as $\mathrm{Na_3[Co(CO)_3]}$.[8] The crystal structure of this tricarbonylcobaltate has not been determined to date, and the data (interatomic distances and vibration frequencies) given in Figure 1 are based on theoretical calculations.[8]

C–N distances and relevant IR/Raman frequencies of the compounds under investigation together with respective data from related cyano- and carbonylmetalates are summarized in Table 1.[6] The typical C–N valence vibrations in cyano complexes are observed in a rather narrow range between 2000 and 2200 cm^{-1}, which is in general accordance with the narrow range of the C–N distances in this class of compounds. The symmetry of the complex anion $[\mathrm{Co(CN)_3}]^{6-}$ corresponds to C_{3h} with only small deviations from D_{3h} ($\sphericalangle(\mathrm{Co{-}C{-}N}) = 179.3(2)°$).[6] The C–N stretching modes are most relevant for this work, and the low frequencies (1671–1725 cm^{-1}) of $\mathrm{Sr_3[Co(CN)_3]}$ and $\mathrm{Ba_3[Co(CN)_3]}$ caused by the elongated C–N distances (125/123.5 pm) are unprecedented in cyanometalate chemistry.

Table 1: C–N and C–O distances together with CN and CO stretching frequencies in IR and Raman spectra of $A\mathrm{E_3[Co(CN)_3]}$ in comparison with related cyano- and carbonylmetalates.

Compound	IR [cm^{-1}]	Raman [cm^{-1}]	d(C–N)/ d(C–O) [pm]	Reference
$\mathrm{Sr_3[Co(CN)_3]}$	1671	1682–1725	125(1)	this work
$\mathrm{Ba_3[Co(CN)_3]}$	1680	1696	123.5(5)	this work
$\mathrm{Na_2[Cu(CN)_3]{\cdot}3H_2O}$	2090–2111	2090–2122	113–116	[7]
$\mathrm{Cs[Hg(CN)_3]}$	2156–2162	2157–2164	109–119	[11]
$\mathrm{K_3[Co(CN)_6]}$	2128–2131	2135–2153	116(2)	[12]
$\mathrm{Na_3[Co(CO)_3]}$	1614	–	126	[8]

The isotypic cobaltates are diamagnetic and insulating.[6] XANES spectra (Sr K edge) of $\mathrm{Sr_3[Co(CN)_3]}$ are consistent with a $\mathrm{Sr^{2+}}$ charge for the strontium sites.[6,10] ESR data unambiguously support the exclusive presence of paired electrons and rule out the existence of any type of radicals in $\mathrm{Sr_3[Co(CN)_3]}$.[6]

The local electronic configuration of Co (sample: $\mathrm{Sr_3[Co(CN)_3]}$) was investigated by means of X-ray photoelectron spectroscopy (XPS). The spectrum (Figure 3) consists of two narrow lines representing the spin–orbit-split Co $2p_{3/2}$ and $2p_{1/2}$ states. The simplicity of the spectral line shape is remarkable. The absence of any significant satellite peaks provides evidence for a closed-shell configuration of the Co 3d level.[13,14] Moreover, the symmetric shape of the peaks without the high-energy tail typical for metallic systems also indicates that $\mathrm{Sr_3[Co(CN)_3]}$ has a considerable band gap. X-ray absorption spectroscopy also reveals that the Co $L_{2,3}$ white lines have anomalously high energies, fully consistent with the picture that the Co ions have the $3d^{10}$ configuration and that these transitions therefore must involve higher-lying conduction-band states across the gap.[15]

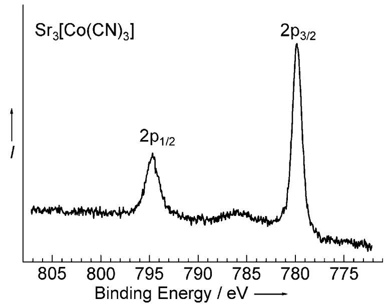


Figure 3. Co $2p_{3/2}$, $2p_{1/2}$ core-level X-ray photoelectron spectrum of $\mathrm{Sr_3[Co(CN)_3]}$.

The calculated density of states (DOS)[6] for $\mathrm{Ba_3[Co(CN)_3]}$ in the energy range between −20 eV and the Fermi level (set to 0 eV) shows six groups of peaks denoted A0, A1, A2, B, C, D (Figure 4, top). A calculated band gap of about 0.7 eV indicates semiconducting behavior, which is consistent with the experimental data. Owing to the purely technical character of the atomic sphere regions and the associated atomic sphere projected DOS, a more founded site projection has been additionally calculated, namely the QTAIM atomic site projection[6] for regions A–D (Table 2). It can be seen that for regions A–C the dominating QTAIM atoms correspond to the ones dominating the atomic-sphere-projected local DOS. Regions A–C are identified as the expected ones for a metalate with the transition metal in d^{10} configuration, namely nominal Ba 5p (A0, 18 e$^-$ per formula

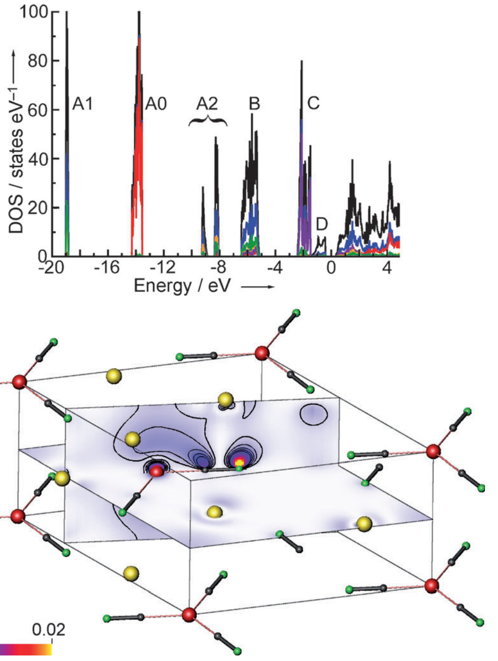


Figure 4. Top: DOS for $\mathrm{Ba_3[Co(CN)_3]}$ (total DOS black, total DOS muffin-tin (MT) part blue, Ba partial DOS (pDOS) red, Co pDOS pink, C pDOS orange, N pDOS green). Bottom: electron density (e$^-$ Bohr^{-3}) for DOS D; spheres denote atoms (Co red, C black, N green, Ba yellow). See text for further details.

Table 2: QTAIM atomic site projection of DOS regions A0–D. The portion of electrons of each unit per formula unit is given in percent. QTAIM effective charges Q^{eff} from the total electron density are given. They are identical to those obtained in sum from DOS A0–D.

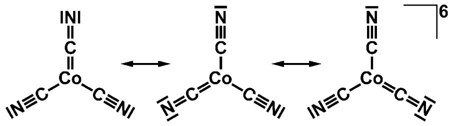
	e^- f.u.$^{-1}$	3 Ba	1 Co	3 CN
DOS A0	18	93	0.4	6
DOS A1	6	3	0.2	97
DOS A2	6	6	12	83
DOS B	18	7	8	85
DOS C	10	7	65	29
DOS D	2	27	21	53
Q^{eff}	–	$\text{Ba}^{1.4+}$	$\text{Co}^{0.0}$	$(\text{CN})^{1.4-}$

unit (f.u.)), CN ssσ (A1, 6 e^- f.u.$^{-1}$), CN ssσ* (A2, 6 e^- f.u.$^{-1}$), CN ppσ/π (B, 18 e^- f.u.$^{-1}$), and Co 3d (C, 10 e^- f.u.$^{-1}$) orbitals. The most interesting and novel part corresponds to DOS D, where it is to be noted that 77 % of the electrons are not contained inside any atomic sphere.

From the corresponding electron-density plot (Figure 4, bottom), an interaction between a CN ppπ* and a diffuse Co state with a node within the molecular plane can be seen. From the electronic occupation (2 e^- f.u.$^{-1}$), region D can be identified as belonging to the A“ representation[6] of the site-symmetry group C_{3h} of the cobalt atom, for which only the p_z orbital contribution is strictly allowed at the Γ point of the Brillouin zone (BZ). At other points of the BZ other states could, in principle, mix, but this mixing does not happen to any significant extent, as is demonstrated by the shape of the partial electron density around Co. The QTAIM atomic site projection of DOS D (Table 2) reveals a portion of 53 % of the electrons belonging to the CN groups, 21 % belonging to the Co atoms, and 27 % to the Ba atoms. Thus, the highest occupied band (HOCO) with its two electrons is to be attributed mainly to the three CN groups, leaving Co with oxidation state −1 and each CN ligand being significantly reduced, with a formal charge of $\text{CN}^{1.67-}$. These results from a formal procedure are consistent with the QTAIM effective charges $\text{Co}^{0.0}$ and $\text{CN}^{1.4-}$ (Table 2), which are expected to lie somewhat closer in value to ±0 than the formal ones.[16]

The occupation of the CN ppπ* antibonding orbital is compatible with the experimentally observed long C–N distance (123.5(5) pm) and the comparatively low C–N stretching frequency (1680 cm^{-1}). The short distance Co–C (176.9(3) pm) could be explained by the partial Co–C ppπ bond established in the HOCO by stabilizing delocalization of the CN π* orbital onto the transition metal.

In summarizing the experimental data and the results of the quantum chemical calculations, the isotypic compounds $\text{Sr}_3[\text{Co(CN)}_3]$ and $\text{Ba}_3[\text{Co(CN)}_3]$ contain the complex anion $[\text{Co(CN)}_3]^{6-}$ with a closed-shell configuration of Co and significantly reduced CN ligands. This situation leads to the oxidation state 1− for Co, and the remaining negative charges belong to the three CN ligands. The quantum chemical calculations resulted in effective charges of $\text{CN}^{1.4-}$ (see Table 2), which sum up to a total charge of 4.2− for the three CN groups (The formal procedure of simple electron counting results in a total charge of 5− for the three CN groups; see comments given above). By taking into account the occupation of CN ppπ* antibonding orbitals, the long C–N distance and the low C–N stretching frequency, as well as the short Co–C distance, the complex anion can be described as $[\text{Co}^{1-}(\text{CN})^{1.67-}{}_3]^{6-}$, involving intermediate-valent CN groups. However, for ease of understanding and for conceptional reasons, an appropriate basic description implies the stabilization of the complex anion by mesomeric forms $[\text{Co}^{1-}(\text{CN})^{3-}(\text{CN})^{-}{}_2]^{6-}$ (Scheme 1), including the $(\text{CN})^{3-}$ ligand, which corresponds to a 12 e^- system, isoelectronic with the O_2 molecule, and called a percyano group. With this consideration, the complex anion can be described as a monopercyanodicyanocobaltate(1−).



Scheme 1. Mesomeric forms of $[\text{Co(CN)}_3]^{6-}$.

The main aspects of the present contribution concern the transition-metal element with closed-shell configuration and the CN ligands, which, in fact, can lose their innocence with respect to the length of the CN bonds. To date, however, the family of cyanometalates was regarded as a rather homogeneous group with only marginal changes in their C–N distances.[9] In the case of carbonylmetalates, the flexibility of bond lengths within the diatomic ligands is a well-known phenomenon (e.g. $\text{Na}_3[\text{Co(CO)}_3]$;[8] see also text and Figure 1). In light of transition-metal elements striving for a closed-shell (d^{10}) configuration, a tendency for percarbonyl $(\text{CO})^{2-}$ formation can be assumed for this class of compounds as well. The closed-shell (d^{10}) concept also holds for the nitridocyanonickelate(0), $\text{Sr}_2[\text{NNi(CN)}]$,[3] containing nickel in the lowest oxidation state observed in complex nickelates to date. Future work will be focused on the preparation of various complex metalates of transition-metal elements, their crystal structures, and their electronic structures in order to evaluate the closed-shell (d^{10}) concept as well as the degree of reduction (bond order) of the CN ligands. Suitable examples from the family of carbonylmetalates will be included.

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Keywords: cobalt · cyanometalates · electronic structure · ligand effects · solid-phase synthesis

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[4] $\text{Ba}_3[\text{Co(CN)}_3]$: space group $P6_3/m$, No. 176, $a = 905.26(11)$, $c = 577.35(9)$ pm, $V = 409.75(10) \times 10^6$ pm^3. $\text{Sr}_3[\text{Co(CN)}_3]$: space

group $P6_3/m$, No. 176, $a = 869.26(1)$, $c = 540.65(1)$ pm.[6] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-423299 and CSD-423302, the names of the authors, and the journal citation. Interatomic distances AE–N (d(Ba–N) = 274.2(3)–334.7(3) pm, $d_{av} = 302.4$ pm; d(Sr–N) = 252(3)–331(1) pm, $d_{av} = 288$ pm) correspond well with data from related compounds ($Ba_3[FeN_3]$: d_{av}(Ba–N) = 288.7 pm;[5a] $Sr_2[NNi(CN)]$: d_{ave}(Sr–N) = 275 pm).[2]

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