A Novel Framework Type for Inorganic Clusters with Cyanide Ligands: Crystal Structures of $Cs_2Mn_3[Re_6Se_8(CN)_6]_2 \cdot 15\,H_2O$ and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5\,H_2O$[**]

Nikolaj G. Naumov, Alexander V. Virovets,
Maxim N. Sokolov, Sofia B. Artemkina, and
Vladimir E. Fedorov[*]

Transition metal cyanides have been known for nearly three centuries. These compounds demonstrate unique properties, structures, and chemical reactivity.[1, 2] The ambidentate nature of CN^- ligands with terminal and bridging bonding modes along with the wide variety of coordination numbers and arrangements for metal centers favor the formation of unusual structures both for binary and complex cyanides of transition metals. The best known examples of these compounds are Prussian Blue and analogues,[3–5] and Hofmann clathrates.[6–9]

Recently complex clusters with cyanide ligands and alkali metal or organic cations were described.[10–15] They contain isolated cluster anions: $[Re_6X_8(CN)_6]^{4-}$ (X = S,[10] Se,[11] Te[12]), $[Re_4X_4(CN)_{12}]^{4-}$ (X = S, Se,[13] Te[14]), $[Mo_4S_4(CN)_{12}]^{8-}$.[15] Undoubtedly, the systematic study of the interactions between complex cluster cyanide anions of varying nuclearity and charge ($[Re_6X_8(CN)_6]^{4-}$, $[Re_4X_4(CN)_{12}]^{4-}$, $[Mo_4S_4(CN)_{12}]^{8-}$) and transition metals is of major importance. Here we report the first polymeric inorganic clusters with cyanide ligands, $Cs_2Mn_3[Re_6Se_8(CN)_6]_2 \cdot 15\,H_2O$ (**1**) and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5\,H_2O$ (**2**), which contain the anionic cluster $[Re_6Se_8(CN)_6]^{4-}$ (Figure 1) and transition metal cations (Mn^{2+}, Co^{2+}). These compounds were prepared by reaction of $Cs_4[Re_6Se_8(CN)_6]$ and $K_4[Re_6Se_8(CN)_6]$ with $Mn(NO_3)_2$ and $CoCl_2$ in aqueous media.

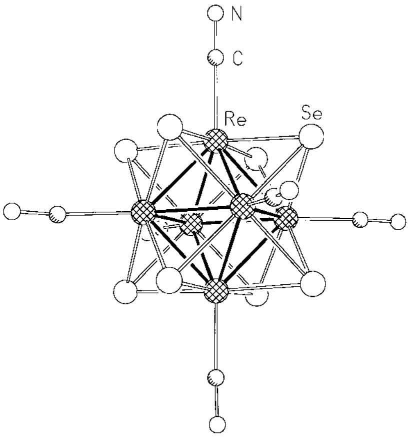

Figure 1. The structure of the cluster anion $[Re_6Se_8(CN)_6]^{4-}$.

The crystal structure of **1** consists of $[Re_6Se_8(CN)_6]^{4-}$ units connected by $Re-C\equiv N-Mn$ bonds to an infinite lattice structure. The structure arises from the bridging behavior of the CN ligands coordinated to the Mn atoms and further similar $Re-C\equiv N-Mn$ interactions involving other CN groups of the anion, which expand the structure into a polymeric framework. No linkage isomerism of the type $Re-C\equiv N-Mn/Re-N\equiv C-Mn$ was found.[16] Two oxygen atoms, O1 and O2, from water molecules complete the coordination shell of the Mn atom. A fragment of the crystal structure of **1** is presented in Figure 2 to show the transition metal–anion bonding. The extended crystal structure is rather complicated, as can be seen in Figure 3. Compound **2** crystallizes in a similar structure type. The Mn–N and Co–N distances in **1** and **2** are close to those encountered in polymer cyanide complexes.[17–19]

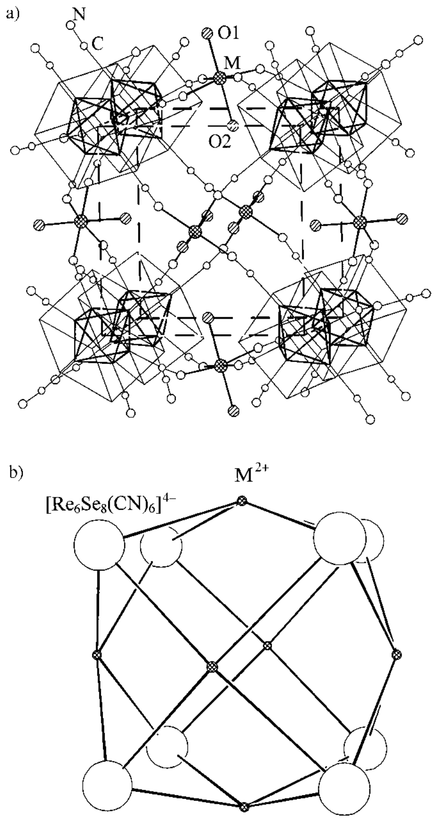

Figure 2. a) The coordination of transition metal cations by cluster anions in compounds **1** and **2**. The circles for the Re and Se atoms have been omitted for clarity. The μ_3-Se ligands are arranged in a cubic geometry around the Re_6 octahedra. The cube of cluster anions is shown by a dashed line. b) Simplified view in which the cluster anions are presented as large circles and all atoms except M (M = Mn, Co) have been omitted.

Magnetic data show that the manganese and cobalt ions are in high-spin Mn^{2+} ($S = 5/2$) and Co^{2+} states ($S = 3/2$). Thus, the framework $\{M_3[Re_6Se_8(CN)_6]_2\}^{2-}$ (M = Mn, Co) is negatively charged and requires additional counterions to maintain the charge balance. In **1**, caesium ions are accommodated in the

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[*] Prof. V. E. Fedorov, N. G. Naumov, A. V. Virovets, M. N. Sokolov
Institute of Inorganic Chemistry SB RAS
Ak. Lavrentiev prosp. 3, Novosibirsk 630090 (Russia)
Fax: (+7) 3832-344-489
E-mail: naumov@che.nsk.su

S. B. Artemkina
Novosibirsk State University, Novosibirsk (Russia)

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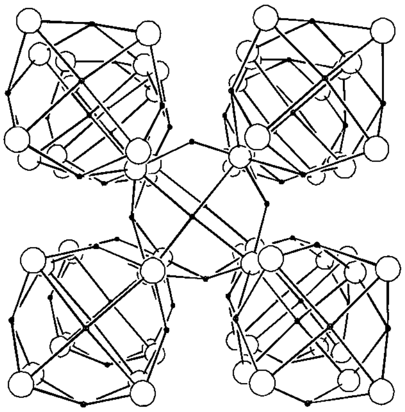

Figure 3. The extended crystal structure of **1** and **2** shown in the same style as Figure 2b. All atoms except M (M = Mn, Co) have been omitted for clarity.

cavities of the framework. In **2**, no potassium cations were found by chemical or structural analysis; the presence of one H_3O^+ cation per cluster anion $[Re_6Se_8(CN)_6]^{4-}$ is deduced from the charge balance.

An increase in the wavelength of the $\nu(\mathrm{C{\equiv}N})$ absorption band is observed for the transition from terminal cyanide ligands of the $[Re_6Se_8(CN)_6]^{4-}$ anion to the linear bridging mode (from 2107 cm^{-1} in $K_4[Re_6Se_8(CN)_6]\cdot 3.5\,H_2O$[11] to 2125 cm^{-1} for **1** and 2139 cm^{-1} for **2**).

Two water molecules (O1 and O2) are coordinated to the metal atom. The water molecules (atoms O1 – O4) are located in the cavities of structure, and are bonded to each other and nitrogen atoms of CN ligands by hydrogen bonding. The O $\cdots$ O and O $\cdots$ N distances of 2.77 – 3.00 Å indicate the presence of relatively weak hydrogen bonds. Some oxygen atoms have large thermal motion parameters ($U_{eq} = 0.13 - 0.25$ Å^2). When **1** and **2** are heated in vacuo, irreversible decomposition (at 80 – 160 °C) and loss of water occurs, which confirms that the water molecules play a major role in the stabilization of these structures. Powder diffractograms show that the dehydrated phases have different structures from the parent compounds.

From structures **1** and **2**, it is clear that the transition metal cations and cluster cyanide anions form three-dimensional frameworks with cavities that are occupied by cations and water molecules, as is also the case for mononuclear cyanides.[1–9, 18] The cavities in the $\{M_3[Re_6Se_8(CN)_6]_2\}^{2-}$ framework are large enough for the inclusion of other guest molecules.

Experimental Section

1: A solution of $Mn(NO_3)_2\cdot 6\,H_2O$ (0.095 g, 0.4 mmol) in H_2O (10 mL) was added to a solution of $Cs_4[Re_6Se_8(CN)_6]$ (0.487 g, 0.2 mmol) in H_2O (10 mL). Product **1** was separated by filtration, washed with water, and dried in air. Yield: 0.437 g (97 %). Elemental analysis (%): calcd for $Cs_2Mn_3[Re_6Se_8(CN)_6]_2\cdot 15\,H_2O$ (found): Cs 5.89 (5.92), Mn 3.65 (3.60), Re 49.54 (49.58), Se 28.01 (27.95), H_2O 5.99 (6.07); IR (KBr): $\tilde{\nu} =$ 2129 cm^{-1}($\mathrm{C{\equiv}N}$); $\mu_{eff}(298\,K) = 5.97\,\mu_B$; powder diffraction: $a =$ 19.223(2) Å, $\alpha =$ 89.50(1)°.[20] Single crystals suitable for structural analysis were obtained by slow cooling of a hot aqueous solution of **1**.

2: A solution of $CoCl_2\cdot 6\,H_2O$ (0.119 g, 0.5 mmol) in H_2O (10 mL) was added to a solution of $K_4[Re_6Se_8(CN)_6]$ (0.531 g, 0.24 mmol) in acetic buffer (10 mL, pH 4). Product **2** was separated by filtration, washed with water, and dried in air. Yield: 0.509 g (95 %). Elemental analysis (%): calcd for $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2\cdot 14.5\,H_2O$ (found): Re 52.13 (52.15), Se 29.28 (29.32), H_2O 6.98 (7.05); IR (KBr): $\tilde{\nu} = 2139$ cm^{-1} ($\mathrm{C{\equiv}N}$); $\mu_{eff}(298\,K) =$ 4.88 μ_B; powder diffraction: $a = 18.968(2)$ Å, $\alpha = 89.33(2)$°.[20] A solution of commercial waterglass (10 mL) in water (100 mL) was titrated to pH 4 with acetic acid (0.5 M). Then the mixture was placed into a U-tube, and the gel was allowed to set for two days. Diffusion of aqueous solutions of $K_4[Re_6Se_8(CN)_6]$[11] (0.1 mol L^{-1}) and $CoCl_2$ (0.5 mol L^{-1}) through the silica gel for four weeks resulted in single crystals of **2** suitable for X-ray single-crystal analysis. The cubelike crystals could be easy separated from the silica gel. X-ray powder diffractometry (Philips APD 1700), IR spectroscopy (Brucker IFS-85), and TGA measurements (Sinku-Riku TA-7000) confirmed that the crystals were identical with the powder sample.

X-ray structural analyses: Data for both **1** and **2** were collected by standard techniques at room temperature on an Enraf Nonius CAD-4 diffractometer ($\theta_{max} = 25°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $\theta/2\theta$ scan mode). Data were corrected for absorption with azimutal scans. The structures were solved by direct methods and were refined by full-matrix least squares, with the SHELX-97 program package.[21] The occupancy factors of the Cs atoms in **1** were refined under the assumption that the total number of Cs atoms in the cell is eight, in accordance with the chemical analysis and charge balance. The residual electron density peaks do not correspond to any chemically appropriate positions.

1: red prism, crystal dimensions $0.24 \times 0.54 \times 0.60$ mm^3, trigonal, space group $R\bar{3}c$, $Z = 4$, $a = 19.226(2)$ Å, $\alpha = 89.52(1)°$, $V = 7106(1)$ Å^3, $\rho_{calcd} =$ 4.216 g cm^{-3}, $\mu = 30.108$ mm^{-1}, 6076 measured reflections, 3550 independent, min/max transmission 0.579/1.421, 237 parameters, $R(F) = 0.0399$ and $R_w(F^2) = 0.0608$ for 1840 reflections with $F_o^2 > 2\sigma(F_o^2)$, residual electron density 1.73 e Å^{-3}.

2: red prism, crystal dimensions $0.15 \times 0.22 \times 0.24$ mm^3, trigonal, space group $R\bar{3}c$, $Z = 4$, $a = 18.969(4)$ Å, $\alpha = 89.35(2)°$, $V = 6824(2)$ Å^3, $\rho_{calcd} =$ 4.172 g cm^{-3}, $\mu = 30.475$ mm^{-1}, 4727 measured reflections, 3250 independent, min/max transmission 0.776/1.225, 217 parameters, $R(F) = 0.0336$ and $R_w(F^2) = 0.0546$ for 1600 reflections with $F_o^2 > 2\sigma(F_o^2)$, residual electron density 1.62 e Å^{-3}.

Further details of the structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-407787 and -407788.

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[16] The anion [Re$_6$Se$_8$(CN)$_6$]$^{4-}$ is kinetically very stable and does not undergo inversion or elimination of CN ligands. All known [Re$_6$X$_8$(CN)$_6$]$^{4-}$ (X = S, Se, Te) salts contain CN ligands bound to the Re atom by the carbon atom. The Re–C bond distances in **1** and **2** are very close to those in K$_4$[Re$_6$Se$_8$(CN)$_6$]·3.5H$_2$O. The M–N bond distances are also in agreement with those encountered in transition metal cyanides with M^{2+} ions bonded to N atoms (2.19–2.21 Å for M = Mn and 2.03–2.15 Å for M = Co). The metal–carbon distances are shorter (1.85–1.90 Å). The IR spectra demonstrated single, sharp peaks due to the CN stretching vibration, in the case of linkage isomerism at least two peaks would be observed.

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[20] The composition and structure of the solids depend on the experimental conditions such as pH, M^{2+}/[Re$_6$Se$_8$(CN)$_6$]$^{4-}$ ratio, and the nature and concentration of the alkali metal and transition metal cations. Several phases with related and differing structures were isolated and characterized by single-crystal and powder diffraction and chemical analysis, for example: Co$_2$Re$_6$Se$_8$(CN)$_6$·12H$_2$O (space group $P2_1/n$, $Z = 2$, $a = 9.926$, $b = 16.465$, $c = 12.196$ Å, $\beta = 96.00°$) and (H$_3$O)$_2$Mn$_3$[Re$_6$Se$_8$(CN)$_6$]$_2$·22H$_2$O, (space group $Im\bar{3}m$, $Z = 8$, $a = 19.857$ Å).

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Consequences of Triplet Aromaticity in 4*n*π-Electron Annulenes: Calculation of Magnetic Shieldings for Open-Shell Species**

Valentin Gogonea, Paul von Ragué Schleyer*, and Peter R. Schreiner

Dedicated to Professor Andrew Streitwieser
on the occasion of his 70th birthday

This paper presents evidence that triplet states of 4*n*π-electron annulenes are aromatic[1] rather than antiaromatic. Not only the geometric and energetic, but also the magnetic properties of open-shell species, which are generally not accessible experimentally[2] but can be computed,[3] may be used to assess the aromaticity and antiaromaticity of a basic set of 4*n*π-electron annulene singlets and triplets: C$_4$H$_4$ (**1**), C$_5$H$_5^+$ (**2**), C$_6$H$_6^{2+}$ (**3**), C$_7$H$_7^-$ (**4**), C$_8$H$_8$ (**5**), and C$_9$H$_9^+$ (**6**).

According to simple Hückel MO theory, planar 4*n*π-electron annulenes in D_{nh} symmetry have degenerate ground states[4] and should be nonaromatic.[5] Breslow provided experimental evidence that the cyclopropenyl anion, **1**, **2**, and **4**[6] (or their derivatives) are destabilized and coined the "antiaromatic" designation.[6a] As early as 1959 Berthier and co-workers found that Pariser–Parr calculations favor the D_{7h} triplet as the ground state of **4**.[7] Borden[8] explained why **2**[9] and **4**[7] should have triplet ground states, whereas **1**[10] and **5**[11] favor singlet ground states and undergo Jahn–Teller distortion.

The idea that triplet 4*n*π-electron annulenes may be regarded as being aromatic rather than antiaromatic was suggested in 1972 by Baird, who concluded that the rules for aromaticity and antiaromaticity are exactly reversed in the lowest triplet state of annulenes.[1a] He pointed out that the proper way to evaluate the aromaticity or antiaromaticity of the lowest triplet state of a cyclic hydrocarbon is to define the aromatic stabilization energy (ASE) relative to the bonding energy for the lowest triplet state of the open-chain polyene which contains the same number of carbon atoms.[1a] The Dewar resonance energies of triplet D_{4h} cyclobutadiene (**1**T, 14.1 kcal mol^{-1}) and of triplet D_{8h} cyclooctatetraene (**5**T, 17.7 kcal mol^{-1}), calculated on this basis (NNDO semiempirical level), supported the aromaticity of these species.[1a] Other investigations support the aromaticity of triplet 4*n*π-electron annulenes.[1b–1h] We report here the first comprehensive high level ab initio calculations[12] of the adiabatic singlet/triplet separations (S → T), the ASEs, and the magnetic properties of the six neutral or charged 4*n*π-electron annulenes **1**–**6**.

The singlet/triplet separation energies (S → T, Table 1) for acyclic reference compounds butadiene and the pentadienyl cation C$_5$H$_7^+$ are much larger (57.0 and 47.1 kcal mol^{-1}, respectively) than for the cyclic species **1** (11.5 kcal mol^{-1}) and **2** (–7.6 kcal mol^{-1}). Consistent with triplet aromaticity, all triplet 4*n*π-electron annulenes are highly stabilized relative to the corresponding acyclic triplet reference species. The

Table 1. Singlet–triplet (S → T) adiabatic transitions for 4*n*π-electron annulenes calculated at B3LYP and CCSD(T) ab initio levels.[a]

Compound	Transition	B3LYP/ 6–311 + G(d,p)	CCSD(T)/cc-pVDZ// B3LYP/6–311 + G(d,p)
C$_4$H$_4$	**1**S → **1**T	5.9	11.5[b]
C$_4$H$_6$	S → T	54.2	57.0
C$_5$H$_5^+$	**2**S → **2**T	– 10.5	– 7.6
C$_5$H$_7^+$	S → T	44.1	47.1
C$_6$H$_6^{2+}$	**3**S → **3**T	– 2.3	0.5
C$_7$H$_7^-$	**4**S → **4**T	– 2.6	– 1.0
C$_8$H$_8$	**5**S → **5**T[c]	15.5	24.3
C$_9$H$_9^+$	**6**S → **6**T[d]	– 1.2	–

[a] In kcal mol^{-1}. [b] 11.2 (CCSDT) and 12.4 (MRCCSD(T))[10c]; 12.0 kcal mol^{-1} by flash photolysis of peralkylated cyclobutadiene (J. Wirz, A. Krebs, H. Schalstieg, H. Angliker, *Angew. Chem.* **1981**, *93*, 192; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 192). [c] Borden, Lineberger, and co-workers found experimentally a S → T separation of 12.1 kcal mol^{-1} for cyclooctatetraene ($D_{4h} \rightarrow D_{8h}$).[11a] The calculated [11b] and experimentally determined (J. F. M. Oth, *Pure Appl. Chem.* **1971**, *25*, 573) barrier for the ring inversion ($D_{2d} \rightarrow D_{4h} \rightarrow D_{2d}$) is around 13 kcal mol^{-1}. This gives a total S → T adiabatic transition ($D_{2d} \rightarrow D_{8h}$) of about 25 kcal mol^{-1}, which compares well with our result of 24.3 kcal mol^{-1} calculated at the coupled cluster level. [d] B3LYP/6–31G(d) geometries.

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[*] Prof. Dr. P. von R. Schleyer, Dr. V. Gogonea
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestrasse 42, D-91054 Erlangen (Germany)
Fax: (+49) 9131-859132
E-mail: pvrs@organik.uni-erlangen.de

Dr. P. R. Schreiner
Institut für Organische Chemie der Universität Göttingen (Germany)

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