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Missing Link in the Ligand-Field Photolysis of $[Mo(CN)_8]^{4-}$: Synthesis, X-ray Crystal Structure, and Physicochemical Properties of $[Mo(CN)_6]^{2-}$

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Photoinduced dissociation of two Mo–CN bonds in $[Mo(CN)_8]^{4-}$ affords the octahedral complex anion $[Mo(CN)_6]^{2-}$. This hexacyanomolybdate(IV) ion is also obtainable from tetracyanooxomolybdate via a thermal substitutional synthetic route. The anion represents the missing link in the ligand-field photolysis of octacyanomolybdate(IV); it is characterized by means of single-crystal X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility measurements as well as IR, Raman, ^{1}H and ^{13}C NMR, and electronic spectroscopy.

Cyanometalate building blocks are of considerable interest in coordination chemistry primarily because of their useful applications in the field of molecule-based magnetism.[1] Among them, the $[Mo(CN)_8]^{3-/4-}$ ions have been widely used for the self-assembly of novel supramolecular coordination compounds.[2] The octacyanomolybdates(IV) are also known to undergo ligand-field photolysis (within their d−d transition range), and the general mechanism for the photochemical reactions involves the generation of hepta- or hexacyano complexes as intermediates.[3] The final products of this photolysis are tetracyanooxo- and pentacyanooxomolybdates, whose formation depends on the pH and the concentration of the cyanide ions in the reaction mixture. The crystal structures of these mixed-ligand complexes, as well as that of the starting material, $[Mo(CN)_8]^{4-}$, have been determined and reviewed.[4,5] Previously, in the ligand-field photolysis of related $[W(CN)_8]^{4-}$, it was observed that the uptake of molecular oxygen together in the presence of a $[PPh_4]^+$ cation allows for isolation of heptacyano intermediates such as the $[PPh_4]_3[W(CN)_7(\eta^2\text{-}O_2)]\cdot 4H_2O$ salt.[6] It was not possible to obtain the molybdenum analogue under similar conditions, which was explained in terms of different redox potentials of $[M(CN)_8]^{3-}/[M(CN)_8]^{4-}$ couples. Herein, we report the synthesis, structure, and physicochemical properties of the $[Mo(CN)_6]^{2-}$ anion, which could be used as a building block for extended systems. The anion represents the missing link in the series of reported cyanomolybdates(IV) ranging from octacyano to mixed-ligand tetracyano complexes. Early studies have shown the syntheses of related $[Mo(CN)_6]^{3-/4-}$, however with limited characterization.[7] Recently, octahedral $[Mo(CN)_6]^{3-}$ has been synthesized and characterized by means of single-crystal X-ray diffraction.[8] The ab initio calculations were performed to study the ligand-field and charge-transfer transitions of this complex.[9] The cyano complexes with Mo^{III} centers have been demonstrated to be useful in the construction of cyano-bridged compounds with high exchange parameters and zero-field splittings.[8,10] To vary the oxidation state of the Mo atom in the hexacyanomolybdates, we are employing Mo^{IV} and Mo^{V} in the current system.

It has been observed that the use of the $[Me_4N]^+$ countercation in the photolyzed alkaline solutions of $[Mo(CN)_8]^{4-}$ results in the formation of blue $[Me_4N]_2[Mo(CN)_6]\cdot H_2O$ (**1**).[11] The treatment of the same solution with the bulkier $[PPh_4]^+$ cation results in the isolation of the known green $K[PPh_4]_2[Mo(CN)_5O]\cdot 5H_2O$, which was confirmed by IR and UV−vis reflectance spectra.[13] These results indicate that both pentacyanooxo- and hexacyanomolybdate-

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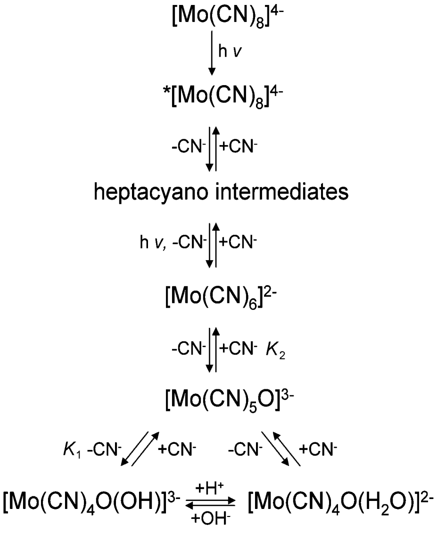
Scheme 1. Ligand-Field Photolysis of the $[Mo(CN)_8]^{4-}$ Anion



(IV) ions in aqueous solution coexist in equilibrium (both complexes are obtainable in yields >50%). It has also been found that the salt **1** can be obtained in higher yields in the reaction of aqueous $[Mo(CN)_4O(OH)]^{3-}$ with KCN (1:2 molar ratio).[11] This is in agreement with the previous findings that $[Mo(CN)_4O(OH)]^{3-}$ ions exist in equilibrium with $[Mo(CN)_5O]^{3-}$ ions. The crystal-packing forces determine which product is isolated in the solid state. This equilibrium is also supported by the results of semiempirical calculations, which indicate that both $[Mo(CN)_5O]^{3-}$ and $[Mo(CN)_6]^{2-}$ have almost identical energy.[14] On the basis of our results, the scheme for the ligand-field photolysis of $[Mo(CN)_8]^{4-}$ given in the literature can be modified (Scheme 1).[3,14]

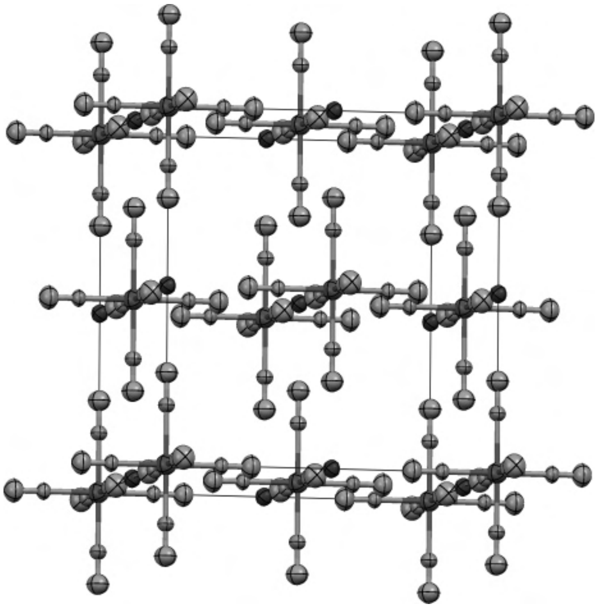


Figure 1. X-ray crystal structure of **1**. H atoms and cations are omitted for clarity. Unit cell axes are shown as thin lines.

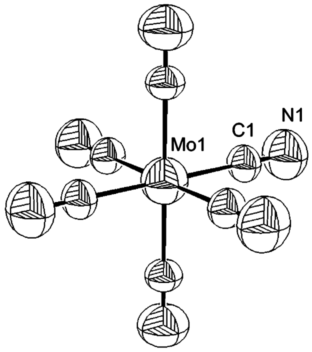


Figure 2. X-ray crystal structure of the complex $[Mo(CN)_6]^{2-}$ in **1** with the selected atom-labeling scheme and 30% displacement ellipsoids. Bond lengths (Å) and angles (deg): Mo1−C1 2.090(8), C1−N1 1.137(12), Mo1−C1−N1 180.0, C1−Mo1−C1 90.0 or 180.0.

Blue prismatic crystals of **1**, suitable for X-ray crystallography, were obtained from the photochemical reaction mixture upon standing for a period of 1 day.[15] The crystal structure consists of four $[Mo(CN)_6]^{2-}$ anions (Figure 1) as well as eight $[Me_4N]^+$ cations and four water molecules in the face-centered unit cell (space group $Fm\bar{3}m$). The water molecules make a network of relatively strong hydrogen bonds to cyanide N atoms of adjacent complexes. The observed donor−acceptor distance (O1···N1) for the O1−H2W···N1 hydrogen bond is 3.068 Å. It is in agreement with thermogravimetric measurements, which show that a water molecule is released at high temperature above 490 K (T_{max} at 561 K). The structure of $[Mo(CN)_6]^{2-}$ is depicted in Figure 2. The complex exhibits ideal octahedral geometry (O_h) with six cyano ligands around the metal center (the Mo−C−N groups are linear). All of the Mo−C (2.090 Å) and C−N (1.137 Å) bond distances are equal and typical for

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(11) Thermal pathway: $K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$ (2.40 g, 5.00 mmol) and KCN (0.65 g, 10 mmol) were dissolved in water (30 mL). The solution was heated until boiling, and $[Me_4N]Cl$ (1.21 g, 11.0 mmol) was added. The crystals of **1** (yield: 1.92 g, 92%), resulting upon cooling, were filtered off, washed with EtOH, and dried in air. Photolytic pathway: $K_4[Mo(CN)_8]\cdot 2H_2O$ (6.00 g, 12.1 mmol) was dissolved in $NH_3(aq)$ (25%, 60 mL), and the resulting mixture was irradiated with a low-pressure mercury lamp in glass conical flask to prevent UV irradiation.[12] The photolysis was monitored with UV−vis spectroscopy, and the irradiation was stopped when the spectral changes finished (ca. 32 h). NH_3 was then removed by heating, and $[Me_4N]Cl$ (2.92 g, 26.6 mmol) was added. The resulting crystals of **1** (yield: 3.64 g, 72%) were filtered off, washed with EtOH, and dried in air. Anal. Calcd for $C_{14}H_{26}MoN_8O$: C, 40.19; H, 6.26; N, 26.78. Found: C, 38.09; H, 6.47; N, 26.57. TG [T_{max}, K (Δm, %)]: 561 (28.8), 605 (37.1). ^1H NMR (300 MHz, D_2O, 293 K): δ 3.17 (s, 24H, CH_3). ^{13}C NMR (300 MHz, D_2O, 293 K): δ 55.36, 55.42, 55.47 (CH_3), 159.79 (CN). IR [ν, cm^{-1} (KBr)]: 3045m, 2088s, 1484s, 1477m, 1418m, 957s, 936s. Raman (ν, cm^{-1}): 3041m, 2981m, 2927m, 2106s, 2094s, 935m, 762m, 181m, 152m. UV−vis (solid state; λ, nm): 243, 295sh, 706. Visible [solution; λ, nm (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)]: 702 (92).

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(15) Crystal data for **1**: $C_{14}H_{26}MoN_8O$, $M = 418.37$, cubic, space group $Fm\bar{3}m$, $a = b = c = 12.5900(13)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 1995.6(4)$ Å^3, $T = 293(1)$ K, $Z = 4$, $D_c = 1.392$ Mg m^{-3}, $\mu = 0.675$ mm^{-1}, 3099 reflections measured, 165 unique ($R_{int} = 0.0268$), and 157 observed [$I > 2\sigma(I)$] used in the refinement. The data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation. The position of the Mo atom was determined by direct methods; the remaining non-H atoms were located in successive difference Fourier syntheses. All H atoms were included in the structure factor calculations at idealized positions and were not refined. All calculations were performed using *SHELXTL* software package. The final refinement gave R1 = 0.0670 and wR2 = 0.1666 [for 157 reflections with $I > 2\sigma(I)$].

cyano complexes of molybdenum.[4,5] They are shorter than the corresponding distances found for the related hexacyanomolybdate(III) (2.181 and 1.160 Å, respectively). The greater the positive charge on the central atom, the less readily the metal can donate electrons into the π^* orbitals of the CN^-, thereby strengthening the C−N bond as evidenced by the shorter C−N bonds in the Mo^{IV} species. In the case of the Mo−C bonds, the structural data of $[Mo(CN)_6]^{2-}$ and $[Mo(CN)_6]^{3-}$ could suggest stronger Mo−C σ bonding, but poorer π back-bonding, as the positive charge on the central metal atom increases.

The IR spectrum of **1** shows bands characteristic for CN^- anions and $[Me_4N]^+$ cations.[11,16] In the region typical for ν(CN) stretching vibrations, only one sharp intense band at 2088 cm^{-1} is observed, which indicates the high symmetry of the anion in the structure. It is in agreement with the theoretical stretching mode analysis for octahedral $[Mo(CN)_6]^{2-}$; one IR-active mode of t_{1u} symmetry is expected among three normal modes of vibration ($\Gamma_{vib} = a_{1g} + e_g + t_{1u}$). All of these three modes should be active in Raman spectroscopy, but the spectrum shows two bands at 2106 and 2094 cm^{-1} in the CN stretching region, which is probably due to the bands overlapping. The effective magnetic moment for **1** at 300 K (0.12 μ_B) gradually decreases upon cooling to a minimum value of 0.02 μ_B at 4.5 K, confirming the diamagnetic character of the sample. Such diamagnetism has also been observed for other related hexacoordinate cyano complexes of Mo^{IV} with a d^2 configuration.[17] Using crystal-field theory, one would expect paramagnetic properties for the d^2 system and the O_h symmetry. However, in the case of molybdenum, there is a strong spin−orbit coupling that could lift the degeneracy of the d orbitals, leading to electron pairing. The diffuse-reflectance spectrum of **1** recorded in the visible region exhibits a band at 706 nm, attributed to a d−d transition. It is considerably red-shifted in comparison to pentacyanooxomolybdate(IV) (680 nm) and tetracyanooxomolybdates(IV).[13,17c] The electronic absorption spectrum of **1** in aqueous solution depends on the concentrations of both the complex and the CN^- ion. The spectrum of **1** in a 1.00 M KCN aqueous solution is presented in Figure 3. The deconvolution of the broad band in the visible range into Gaussian curves gives three absorptions attributable to d−d transitions in $[Mo(CN)_4O(OH)]^{3-}$, $[Mo(CN)_5O]^{3-}$, and $[Mo(CN)_6]^{2-}$ ions, confirming the coexistence of all of these complexes in aqueous solution. The d−d band position for $[Mo(CN)_6]^{2-}$ (702 nm) is almost the same as the one determined from the reflectance spectrum (706 nm) of **1**. The detailed study of electronic spectra of **1** for various concentrations of the CN^- ion (from 0 to 1.00 M) and various temperatures (in the 20−55 °C range) allows the determination of the equilibrium constants (K_1 and K_2) indicated in Scheme 1 for the formation of $[Mo(CN)_4O(OH)]^{3-}$ and $[Mo(CN)_6]^{2-}$ from $[Mo(CN)_5O]^{3-}$ ($K_1 = 0.93$ and $K_2 = 0.20$ at 25 °C).

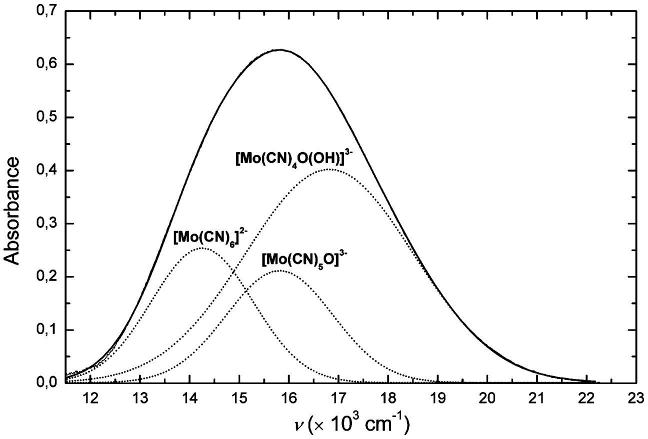

Figure 3. Visible absorption spectrum of **1** (solid line) in a 1.00 M KCN aqueous solution with its deconvolution into Gaussian curves (dashed lines): $c = 2.00 \times 10^{-2}$ M, $d = 1.00$ cm.

In conclusion, this study shows evidence for the existence of hexacyano species in aqueous solution of cyano complexes of Mo^{IV}, surprisingly not isolated and characterized so far. The complex seems to be promising for building extended systems. Further work on the electronic structure of $[Mo(CN)_6]^{2-}$, its equilibrium behavior in aqueous solutions containing cyanide ions, and the construction of supramolecular assemblies based on hexacyanomolybdate(IV) and its oxidized form is currently in progress.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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