Formation and Reactivity of the Osmium(IV)–Cyanoimido Complex $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$**

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Complexes containing the cyanamido ($-N{\equiv}C{-}NH_2$),[1] hydrogen cyanamido ($-N(H){-}C{\equiv}N^-$),[2] and cyanoimido ($-N{-}C{\equiv}N^{2-}$)[3] ligands are all known based on coordination of the ligands. Herein we report a novel synthetic pathway for the formation of Os^{IV}–cyanoimido complexes, based on the formation of the ligands in reactions between Os^{VI}–nitrido precursors and tetraethylammonium cyanide (NEt_4CN), and also the extensive functional-group chemistry of the ligand.

Rapid reactions occur between NEt_4CN and *cis*- or *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]PF_6$ (tpy = 2,2′:6′,2″-terpyridine) and $[Os^{VI}(bpy)(Cl)_3(N)]$ (bpy = 2,2′-bipyridine) in CH_3CN or CH_2Cl_2 to give the Os^{IV}–cyanoimido products, *cis*- or *trans*-$[Os^{IV}(tpy)(Cl)_2(NCN)]$ (**1A** = *trans* isomer; **1B** = *cis* isomer) or $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$ (**2A**$^-$) with retention of stereochemistry [Eq. (1)].

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + CN^- \longrightarrow [Os^{IV}(tpy)(Cl)_2(NCN)] \tag{1a}$$

$$[Os^{VI}(bpy)(Cl)_3(N)] + CN^- \longrightarrow [Os^{IV}(bpy)(Cl)_3(NCN)]^- \tag{1b}$$

Compound **2A**$^-$ was isolated as its tetraethylammonium salt (NEt_4^+), and all three products were characterized by cyclic voltammetry, elemental analysis, and UV/Vis, ^1H NMR, and infrared (IR) spectroscopy (see Supporting Information). The pattern of bands in the UV/Vis spectra is closely related to that observed for related Os^{IV}–hydrazido complexes and arises from a combination of metal-to-ligand and ligand-to-metal charge-transfer bands as well as bands of lower intensity arising from interconfigurational d→d transitions.[4]

As shown by UV/Vis monitoring at 458 nm (λ_{max} for **2A**$^-$), the reaction between $[Os^{VI}(bpy)(Cl)_3(N)]$ and NEt_4CN is first order for both reactants, with $k = (84.4 \pm 0.2)\,M^{-1}s^{-1}$ in CH_3CN at $22.0 \pm 0.1\,°C$. The X-ray crystal structure of **2A**$^-$ (Figure 1) reveals that the meridional geometry of the parent nitrido[5] complex is retained with Os1−N1 = 1.914(9), N1−C2 = 1.282(15), C2−N3 = 1.195(16) Å, ∢Os1-N1-C2 = 131.0(7)°, and ∢N1-C2-N3 = 174.2(11)°. For comparison ($N1 = N_\alpha$, $N3 = N_\beta$), bond distances and angles in $[Mo^{IV}(NCN)_2(dppe)_2]$ (dppe = diphenylphosphinoethane) are $Mo{-}N_\alpha = 1.860(11)$, $N_\alpha{-}C = 1.297(20)$, $C{-}N_\beta = 1.167(19)$ Å, ∢Mo-N_α-C = 173.8(10)° and ∢N_α-C-N_β = 177.8(16)°.[3a] Although the angle Os-N_α-C of 131.0(7)° appears to be the smallest known for cyanoimido and substituted cyanamido complexes,[6] it is consistent with other d^4 Os^{IV} complexes.[7] It is also consistent with a bonding scheme proposed for related Os^{IV}–hydrazido complexes which features Os=N double bonds and a bending at the Os-N-CN or Os-N-NR_2 units to minimize electron–electron repulsion.[8]

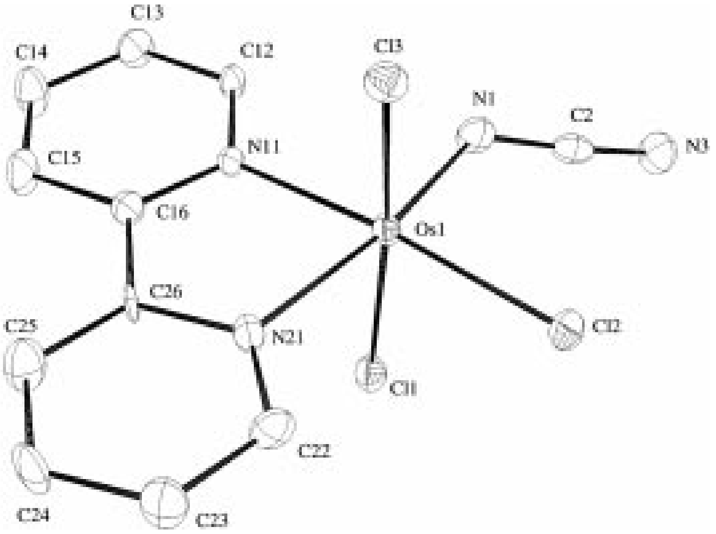
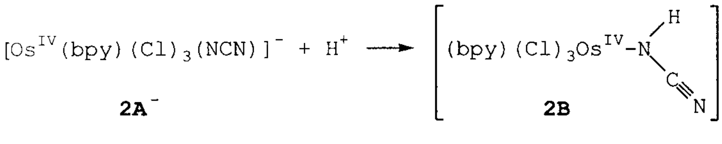


Figure 1. ORTEP diagram (ellipsoids set at the 30% probability level) of the $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$ ion.

There is an extensive chemistry based on the coordinated cyanoimido ligand. Addition of one equivalent of HPF_6, HNO_3, or CH_3COOH to **2A**$^-$ in CH_3CN results in the formation of the monoprotonated Os^{IV}–hydrogen cyanamido complex, $[Os^{IV}(bpy)(Cl)_3(N(H)CN)]$ (**2B**) [Eq. (2)]. The UV/Vis spectral changes that accompany the reaction in Equation (2) are similar to those that occur upon N_α protonation in Os^{IV}–hydrazido complexes.[9]



$$\underset{\mathbf{2A^-}}{[Os^{IV}(bpy)(Cl)_3(NCN)]^-} + H^+ \longrightarrow \underset{\mathbf{2B}}{\left[(bpy)(Cl)_3Os^{IV}{-}N(H){-}C{\equiv}N\right]} \tag{2}$$

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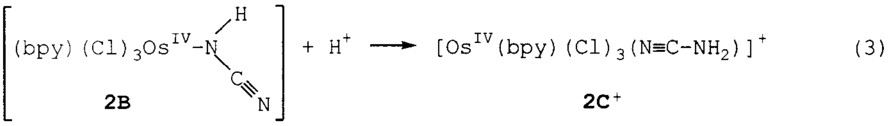
Direct evidence for monoprotonation at N_α comes from the IR spectra. In **2A**$^-$ and its ^{15}N analogue, $[Os^{IV}(bpy)(Cl)_3(^{15}NCN)]^-$ (**2A***$^-$, prepared from the ^{15}N-nitrido complex precursor as in [Eq. (1b)]), the IR band assigned as $\nu(C{\equiv}N_\beta)$ is at 1975 cm^{-1} for **2A**$^-$, and $\nu(C{\equiv}N_\beta)$ at 1977 cm^{-1} for **2A***$^-$. Upon protonation, $\nu(^{14}N_\alpha{-}H) = 3230$, $\nu(C{\equiv}N_\beta) = 2187$ cm^{-1} for **2B** and $\nu(^{15}N_\alpha{-}H) = 3213$, $\nu(C{\equiv}N_\beta) = 2181$ cm^{-1} for **2B***. Based on ^1H NMR spectra, **2A**$^-$ contains a paramagnetic d^4 Os^{IV} center which results in a highly contact-shifted spectrum; **2B** is diamagnetic.

In the presence of a second equivalent of HPF_6 in CH_3CN, a second protonation occurs to give the Os^{IV}–cyanamido complex, $[Os^{IV}(bpy)(Cl)_3(NCNH_2)]^+$ (**2C**$^+$) [Eq. (3)], which was isolated as the PF_6^- salt. Diprotonation at N_β is supported by IR spectra which show $\nu(^{14}N_\alpha{\equiv}C) = 2280$ cm^{-1} for **2C**$^+$ and $\nu(^{15}N_\alpha{\equiv}C) = 2249$ cm^{-1} for **2C***$^+$; the bands for $\nu(^{14}N_\beta{-}H)$ are 3332 ± 4 and 3200 ± 3 cm^{-1} for **2C**$^+$ and **2C***$^+$, respectively.



$$[(bpy)(Cl)_3Os^{IV}{-}N(H)C{\equiv}N] \; (\mathbf{2B}) + H^+ \longrightarrow [Os^{IV}(bpy)(Cl)_3(N{\equiv}C{-}NH_2)]^+ \; (\mathbf{2C^+}) \qquad (3)$$

$$[Os^{IV}(bpy)(Cl)_3(NCN)]^- + 2\,Et_3O^+ \xrightarrow{CH_2Cl_2} \underset{\mathbf{3^+}}{[Os^{IV}(bpy)(Cl)_3(N{\equiv}C{-}NEt_2)]^+} + 2\,Et_2O \qquad (4)$$

$$[Os^{IV}(bpy)(Cl)_3(NCN)]^- + 2\,MeI \xrightarrow{CH_3CN} \underset{\mathbf{4^+}}{[Os^{IV}(bpy)(Cl)_3(N{\equiv}C{-}NMe_2)]^+} + 2\,I^- \qquad (5)$$

$$[Os^{IV}(bpy)(Cl)_3(N(H)CN)] + (CH_3CO)_2O \xrightarrow{DMF} \underset{\mathbf{5^+}}{[Os^{IV}(bpy)(Cl)_3(N{\equiv}C{-}N(H)C(O)CH_3)]^+} + CH_3CO_2^- \qquad (6)$$

Dialkylation of **2A**$^-$ to give the corresponding Os^{IV}–dialkylcyanamido complexes, $[Os^{IV}(bpy)(Cl)_3(NCNR_2)]^+$ (**3**$^+$, R = Et, BF_4^- salt and **4**$^+$, R = Me, PF_6^- salt), occurs under N_2 in reactions with triethyloxonium tetrafluoroborate ($[Et_3O]BF_4$) in CH_2Cl_2 and iodomethane (MeI) in CH_3CN, respectively [Eqs. (4) and (5)].

Acylation[1d] of **2B** by acetic anhydride ($(MeCO)_2O$) in *N,N*-dimethylformamide (DMF) also occurs at N_β to give the Os^{IV}–acetylcyanamido complex, $[Os^{IV}(bpy)(Cl)_3(NCN(H)C(O)Me)]^+$ (**5**$^+$) [Eq. (6)], which was isolated as the PF_6^- salt.

In all three cases, the differences in $\nu(N_\alpha{\equiv}C)$ between the $^{14}N_\alpha$ and $^{15}N_\alpha$ forms are consistent with dialkyl or acyl addition at N_β, that is, **3**$^+$: $\nu(^{14}N_\alpha{\equiv}C) = 2206$ and $\nu(^{15}N_\alpha{\equiv}C) = 2176$ cm^{-1}, **4**$^+$: $\nu(^{14}N_\alpha{\equiv}C) = 2202$ and $\nu(^{15}N_\alpha{\equiv}C) = 2173$ cm^{-1}, and **5**$^+$: $\nu(^{14}N_\alpha{\equiv}C) = 2208$ and $\nu(^{15}N_\alpha{\equiv}C) = 2179$ cm^{-1}.

There is also an extensive electron-transfer chemistry for the cyanoimido complexes reminiscent of the analogous hydrazido complexes. The electron transfer is based on electron occupation and deoccupation of levels largely localized in the Os–hydrazido π-bonding framework.[4, 8] Cyclic voltammetry of the new compounds shows a series of reversible redox waves arising from the multiple oxidation/reduction of the osmium center (Table 1).

Table 1. Redox potentials for the new osmium compounds.[a]

Compound	$E_{1/2}(Os^{VI/V})$	$E_{1/2}(Os^{V/IV})$	$E_{1/2}(Os^{IV/III})$	$E_{1/2}(Os^{III/II})$
1A	1.72	0.90	– 0.40	– 1.30
2A$^-$	1.87	1.19	0.67	– 0.90
3$^+$			0.79	– 0.63
4$^+$			0.74	– 0.58
5$^+$			0.84	– 0.55

[a] Potentials are given in Volts and measured against the sodium saturated calomel electrode (SSCE) in 0.1 M TBAH/CH_3CN, (TBAH = tetrabutylammonium hexafluorophosphate). All processes are reversible.

Our results provide a novel approach to the preparation of the NCN^{2-} ligand and its subsequent derivatization after coordination. The stepwise assembly of the dialkylated ligands provides a potentially general route to substituted cyanamido complexes that cannot be prepared directly because of polymerization of the preformed cyanamido organic precursors. Finally, the existence of multiple oxidation states and the acid–base behavior of the NCN^{2-} ligand in the Os^{IV} complex may point to oxo-like reactivity based on proton-coupled electron transfer or atom transfer involving couples such as $[Os^{VI}(bpy)(Cl)_3(NCN)]^+/[Os^{V}(bpy)(Cl)_3(N(H)CN)]^+$ or $[Os^{VI}(bpy)(Cl)_3(NCN)]^+/[Os^{IV}(bpy)(Cl)_3(NCNH_2)]^+$.

For full details on the preparation and characterization of all the new compounds see the Supporting Information.

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Ferromagnetic Coupling through Spin Polarization in a Dinuclear Copper(II) Metallacyclophane**

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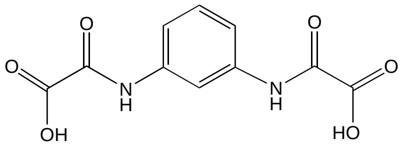
In memory of Olivier Kahn

The design and synthesis of polynuclear coordination compounds with predictable magnetic properties have always interested inorganic chemists working in the field of magnetochemistry.[1, 2] In particular, the preparation of ferromagnetically coupled dinuclear complexes appears intimately linked to the history of this relatively young discipline, namely molecular magnetism. Of the theoretical strategies to achieve a ferromagnetic spin alignment between two metal centers, those based either on orbital symmetry or spin polarization effects are the easiest ones to be managed by the synthetic chemist.[3] The second approach is particularly appealing and, however, has received more limited attention for metal complexes,[4] when compared with the extensive work concerning high-spin organic molecules (polyradicals).[5]

In our research into ligand design as a means to control the electronic and magnetic properties of polynuclear complexes,[6, 7] we prepared the new ligand $H_4[\mathbf{1}]$, the parent acid of *N*,*N*′-1,3-phenylenebis(oxamate). This ligand cannot act in a tetradentate manner towards a Cu^{II} center to give a monomeric four-coordinate copper(II) species, unlike the related ligand *N*,*N*′-1,2-phenylenebis(oxamate). Instead, it can self-assemble with Cu^{II} ions in a 2:2 ratio to give a dimeric copper(II) complex, $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$, where the two ligands adopt the bisbidentate coordination mode, each donating one of its oxamate donor sets to each copper. In this case, two bis(oxamate)copper(II) spin-bearing residues are bridged by two *m*-phenylene moieties, which have already proven to be very effective ferromagnetic spin-coupling units in purely organic π-conjugated polyradicals.[8] Here, we report the synthesis, crystal structure, and magnetic properties of the sodium salt of this novel oxamatocopper(II) complex of formula $Na_4[Cu_2(\mathbf{1})_2]\cdot 10\,H_2O$ (**2**).



$H_4[\mathbf{1}]$

The structure of **2** consists of noncentrosymmetric dinuclear copper(II) complex ions, $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$, sodium cations, and both coordinated and noncoordinated water molecules (Figure 1). Actually, all twelve oxygen atoms from the four oxamato groups of the dicopper anion are bound to the sodium atoms, affording an intricate two-dimensional structure. The intramolecular copper–copper separation, $Cu(1)\cdots Cu(2)$, is 6.822(2) Å, while the shortest intermolecular ones, $Cu(1)\cdots Cu(1'')$ and $Cu(2)\cdots Cu(2')$, are 6.335(3) and 6.999(3) Å, respectively.

The $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$ unit is a metallamacrocycle composed of two bisbidentate oxamate ligands and two copper(II) cations. Moreover, owing to the almost parallel arrangement of the two benzene planes (dihedral angle of only 7.6(8)° and average interplanar separation of 3.4(1) Å), this dinuclear metallamacrocycle is of the cyclophane type (Figure 2a). In fact, a rather unusual near to perfect face-to-face π–π alignment of the two aromatic rings exists, such that a ring carbon atom lies just over the equivalent atom of the other ring (Figure 2b) with strong carbon–carbon contacts (C–C distances in the range 3.20(1)–3.57(2) Å). Hence, the resulting twelve-membered metallaaza-linked [3.3]metacyclophane ring system (internal cavity of ca. 3.4 × 6.8 Å) has an approximate C_{2v} symmetry, with the copper basal planes being almost perpendicular to the benzene planes (dihedral angles in the range 72.1(3)–82.0(3)°). This imposes a non-

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