3760 *Inorg. Chem.* **1999,** *38,* 3760−3761

Effect of Stepwise Oxidation on Molecular Structure in Osmium Hydrazido Complexes

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Received June 11, 1999

Changes in electron content between different oxidation states of transition metal complexes can cause significant changes in molecular structure. Reduction of d^3 $[Cr^{III}(H_2O)_6]^{3+}$ to d^4 $[Cr^{II}(H_2O)_6]^{2+}$ results in a change from octahedral symmetry with Cr−O = 1.966 Å[1] to tetragonally distorted symmetry with Cr−O = 1.985 Å (equatorial) and Cr−O = 2.30 Å (axial). Excluding clusters, extending this analysis to more than two adjacent oxidation states is difficult because changes in electron content lead to changes in coordination number, or the adjacent oxidation states are unstable.[2] Exceptions are found in the series $[M^n(Cl)_x(PR_3)_y]$ (n = I → III, IV, or V and $x + y = 6$ with M = Mo,[3] Tc,[4] W,[5] Mn,[6] and Re[7]) and a series of multidentate, nitrogen-based Co compounds.[8] In the literature examples, there is no obvious correlation between electron content at the metal and molecular structure. We report here, however, that systematic structural changes occur as electron content is changed in a series of Os−hydrazido complexes from Os(IV) to Os(VI).

The Os(V) forms were prepared by reaction between precursor Os(VI)−nitrido complexes and secondary amines.[9]

For *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ (tpy = 2,2′:6′,2″-terpyridine; $N(CH_2)_4O$ = morpholide), chemically reversible oxidation to Os(VI) and reduction to Os(IV) occur in cyclic voltammograms at $E_{1/2} = +0.98$ and 0.00 V in CH_3CN, 0.1 M in tetra-*n*-butylammonium hexafluorophosphate (TABH) vs SSCE.[9a] In addition, a chemically reversible Os(IV/III) wave appears at $E_{1/2} = -0.79$ V vs SSCE in 0.1 M TBAH/CH_3CN. The Os(V) form can be chemically reduced to Os(IV) or oxidized to Os(VI) although there are nuances in the chemistry. For example, chemical or electrochemical reduction of *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ to Os(IV) is accompanied by Cl^- ligand loss and isomerization to give *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)$.

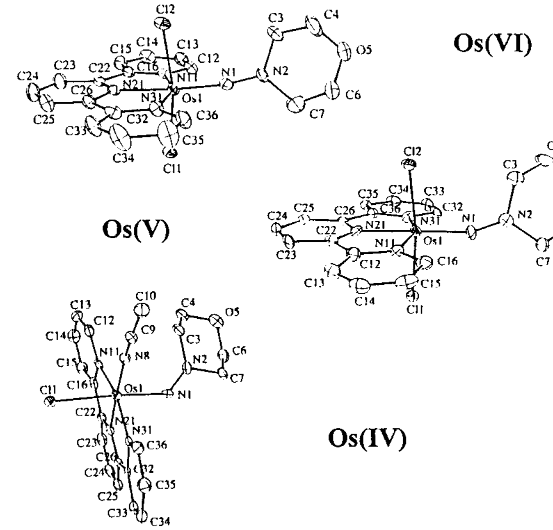

Figure 1. ORTEP diagrams and labeling schemes for Os(VI), Os(V), and Os(IV) cations in *trans*-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)_2$, *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4CH_2)](PF_6)$, and *cis*-$[Os^{IV}(tpy)(Cl)(CH_3CN)(NN(CH_2)_4O)](PF_6)$.

Crystals of the Os(V) salts, *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4CH_2)](PF_6)$ ($N(CH_2)_4CH_2$ = piperidide) and $[Os^V(tpm)(Cl)_2(NN(C_2H_5)_2)](BF_4)$ (tpm = tris(1-pyrazolyl)methane and $N(CH_2CH_3)_2$ = diethylamide),[10] were grown by slow diffusion of Et_2O into CH_3CN solutions containing the salts. *trans*-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)_2$ was electrochemically generated by electrolysis at E_{app} = 1.23 V in CH_3CN (0.1 M TBAH), and crystals were grown by introducing Et_2O to the solution containing the salt with a stream of argon. A crystal of *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)$ was obtained in a manner similar to that for the Os(VI)−hydrazido complex. A crystal of *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)$ was grown by diffusion of Et_2O over a period of 4 days into a solution containing *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)$ prepared by electrochemical reduction of *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ at E_{app} = 0.29 V. The molecular structures of *trans*-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$, *trans*-$[Os^V(tpy)(Cl)_2(NN(CH_2)_4CH_2)]^+$, and *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)]^+$ are shown in Figure 1. Important structural details from five crystal structures are summarized in Table 1.

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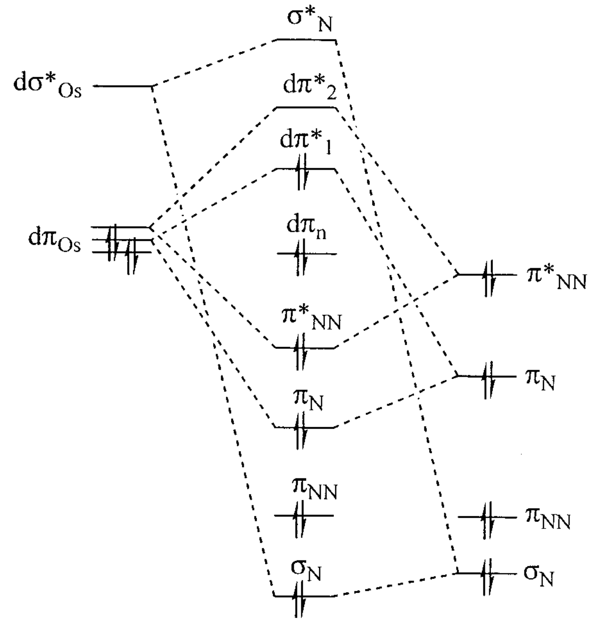
10.1021/ic990680a CCC: $18.00

Table 1. Important Structural Features in the Os−Hydrazido Complexes

salt (d-electron config)	Os−N (Å) (hydrazido)	∠Os−N−N (deg)	Os−Cl (Å)	Os−N (Å)[a]	N_α−N_β (Å)
trans-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2CH_2)_4O)](PF_6)_2$ (d^2)	1.778(8)	170.3(7)	2.3193(22) 2.3472(22)	2.086(7) 2.004(7)[b] 2.099(7)	1.243(12)
trans-$[Os^{V}(tpy)(Cl)_2(NN(CH_2CH_2)_2CH_2)](PF_6)$ (d^3)	1.855(9)	157.2(9)	2.373(3) 2.377(3)	2.089(9) 2.014(10)[b] 2.078(9)	1.243(15)
$[Os^{V}(tpm)(Cl)_2(NN(CH_2CH_3)_2)](BF_4)$ (d^3)	1.855(4)	148.5(4)	2.3661(13) 2.3718(12)	2.062(4) 2.116(4)[b] 2.059(4)	1.231(6)
cis-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2CH_2)_2O)](PF_6)$ (d^4)[d]	1.984(10)	129.3(7)	2.455(3)	2.079(10) 1.983(9)[b] 2.041(10) 2.039(9)[c]	1.241(15)
cis-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2CH_2)_2O)](PF_6)_2$ (d^4)[d]	1.971(7)	130.9(5)		2.093(7) 1.982(6) 2.072(7) 2.062(7)[b,c] 2.062(7)[c]	1.243(15)

[a] Os−N bond distance from Os to the N atom of the tpy, tpm, or $NCCH_3$ ligand. [b] Os−N bond distance for the N atom trans to the hydrazido ligand. [c] Os−N bond distance for the $NCCH_3$ ligand. [d] These complexes are diamagnetic as shown by ^1H NMR.

Scheme 1



The existence of three adjacent oxidation states, structurally characterized, in a common six-coordinate ligand environment is unique for hydrazido complexes and also for Os coordination chemistry. The structural differences in the table can be rationalized by considering a recently presented bonding model for transition metal hydrazido complexes.[11] In this model, the dianionic hydrazido ligand, $N_\alpha N_\beta R_2^{2-}$, forms molecular orbitals by mixing σ_N, π_N, and π^*_{NN} orbitals with the d orbitals of the metal (Scheme 1).[12] The π_{NN} orbital is not significantly involved in bonding with the metal and retains its multiple-bond character with sp^2 hybridization at N_β. After mixing with the metal-based $d\pi$ orbitals, this results in the ground state electronic configuration $\sigma^2_N\ \pi^2_{NN}\ \pi^2_N\ \pi^{*2}_{NN}\ d\pi^2_n\ d\pi_1^{*2}$ for Os(IV). Of the three $d\pi$ orbitals at Os, $d\pi_n$ is nonbonding with regard to π-mixing with the hydrazido ligand orbitals. The $d\pi^*$ orbitals are largely $d\pi$ in character but extensively mixed with π_N and π^*_{NN}. ^1H NMR measurements on $[Os^{IV}(tpm)(Cl)_2(N(H)N(CH_2)_4O)]^+$, *cis*-$[Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)]^+$, and $[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^+$ show the complexes to be diamagnetic, having the ground state configuration $d\pi^{*2}$ rather than $d\pi_1^{*1}\ d\pi_2^{*1}$, which would be paramagnetic.

From the data in Table 1, the Os−N (hydrazido) bond distance decreases from d^4 Os(IV) to d^3 Os(V) by 0.11 Å and from d^3 Os(V) to d^2 Os(VI) by another 0.08 Å. This trend is mirrored in Os−Cl bond lengths, but to a lesser degree, with Os−Cl decreasing from 2.45 Å for Os(IV) to 2.37 Å for Os(V) to 2.32 Å for Os(VI). The π_{NN} orbital is not directly involved in bonding with the metal, and the N_α-N_β bond length remains unchanged with oxidation state (1.23−1.24 Å). The Os−N−N angle opens up as the Os≡N distance shortens with Os−N−N increasing from 130° for Os(IV) to 148−157° for Os(V) to 170° for Os(VI).

These structural changes are consistent with the electronic configuration predicted by the molecular orbital scheme. Stepwise electron loss from antibonding $d\pi_1^{*2}$ increases Os−N multiple-bond character and decreases the Os−N bond length. The bending of ∠Os−N−N in Os(IV) reduces electron−electron repulsion caused by electron occupation of $d\pi_1^*$. Removal of electrons from $d\pi_1^*$ decreases M−N antibonding character and increases the Os−N−N angle.[11] In the transformation from Os(IV) to Os(VI), loss of two electrons results in the configuration $\sigma^2_N\ \pi^2_{NN}\ \pi^2_N\ \pi^{*2}_{NN}\ d\pi^2_n$. With the accompanying change in electron content from d^4 Os(IV) to d^2 Os(VI), the ligand is converted from a four-electron donor into a six-electron donor with d^3 Os(V) intermediate between the two.

Our results show that electronic structure theory provides a remarkably effective rationale for explaining the novelty of the structural changes that occur among three different oxidation states in this novel series of Os−hydrazido compounds.

Acknowledgment is made to the National Science Foundation under Grant No. CHE-9503738 and the Department of Energy under Grant No. LM 19X-SX 092C for supporting this research. E.-S.E.-S. wishes to thank the Egyptian Government for the Data Collection Grant.

Supporting Information Available: Tables containing crystal data, atomic coordinates, isotropic thermal parameters, bond distances and angles and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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