

Table I. Data for the Calorimetric Titrations of Eu(III) and Cm(III)^a

titrant addition, mL	ΔQ , J			
	Eu + Ac	Cm + Ac	Eu + EDTA	Cm + EDTA
0.10	0.013 55	0.01 62	0.068 69	0.057 24
0.20	0.011 99	0.01 16	0.074 29	0.053 94
0.30	0.009 74	0.00 84	0.069 59	0.051 24
0.40	0.008 07	0.00 92	0.067 69	0.051 34
0.50	0.010 37	0.00 93	0.069 09	0.054 34
0.60	0.007 25	0.00 74	0.066 79	0.051 54
0.70	0.003 97	0.00 49	0.064 49	0.045 54
0.80	0.004 08	0.00 48	0.061 39	0.036 94
0.90	0.006 44	0.00 598	0.064 99	0.027 94
1.00	0.002 93	0.00 450	0.054 39	0.015 04
1.10	0.004 08	0.00 410	0.042 39	0.010 84
1.20	-0.000 02	0.00 030	0.027 29	0.007 44
1.30	0.003 50	0.00 570	0.020 69	0.004 64
1.40	0.001 93	0.00 571	0.009 39	0.006 84
1.50	0.001 54	0.00 450	0.005 39	0.003 54
1.60	0.002 31	0.00 270	0.001 19	0.001 94
1.70	0.002 56	0.00 300	0.000 59	-0.000 26
1.80	0.002 25	0.00 300	-0.001 51	-0.000 16
1.90	0.002 38	0.00 372	-0.001 51	-0.000 96
2.00	0.001 16	0.00 150	-0.003 81	-0.000 56

^a $I = 2.0$ M (NaClO₄) for acetate; $I = 0.5$ M (NaClO₄) for EDTA.

HCl and 4.00 mL of 0.453 M NaClO₄ to produce an ionic strength of 0.50 M. The titrant was a solution of 0.025 M Na₂H₂EDTA at pH 5.00 and ionic strength 0.50 M (NaClO₄).

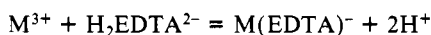
Similar titrations of Eu(III) were conducted, in order to check the validity of the curium data, for comparison with the ΔH values of EuOAc²⁺ and EuEDTA⁻ reported in the literature.⁸

Data Analysis. The data from the calorimetric titrations were analyzed with the ET program⁹ on the Z-80 microcomputer of the FSU laboratory. For the acetate titrations, the curium concentration in the cup was assumed to be 0.00542 M (6.05 mg of Cm) and the ΔH of reaction calculated by the program. The curium concentration was found to be 0.00481 M (5.37 mg of Cm) in the EDTA titration. The Eu(III) concentration was 0.00481 M in the EDTA titration and 0.00594 M for the acetate experiments.

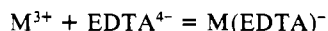
Results

Table I gives the primary titration data for curium and europium with acetate and EDTA. The ΔQ values have been corrected for base line and heats of dilution.

The calorimetric titration with EDTA corresponded to the reaction



To convert to the direct reaction



it was necessary to correct the measured ΔH value for formation of CmEDTA by the deprotonation enthalpy of H₂EDTA²⁻ at 0.50 M (NaClO₄) ionic strength, which has been reported to be -51.8 ± 0.3 kJ·m⁻¹.⁸

Table II lists the calculated enthalpy values of the curium and europium titrations for the reaction of $M + L = ML$ ($L = OAc, EDTA$). The results of a second Eu(III) + OAc titration conducted after the EDTA runs are also included.

Discussion

The values of ΔH and ΔS for CmOAc²⁺ formation in Table II differ substantially from the values ($+18.0 \pm 0.8$ kJ·m⁻¹ and 100 ± 3 J·m⁻¹·K⁻¹, respectively) in ref 3. The values for formation of EuOAc²⁺ in ref 3 are -5.9 ± 0.4 kJ·m⁻¹ (ΔH) and 56 ± 2 J·m⁻¹·K⁻¹ (ΔS), which agree well with the values in Table II. No explanation is apparent for the temperature variation method failing for the Cm system but succeeding for the Eu system in the study in ref 3. However, the direct calorimetric values in Table

Table II. Thermodynamic Parameters of Cm(III) and Eu(III) Complexation ($T = 25.00$ °C)

metal	ΔH , kJ·m ⁻¹	ΔG , kJ·m ⁻¹	ΔS , J·m ⁻¹ ·K ⁻¹
Acetate [$I = 2.0$ M (NaClO ₄)]			
Cm	5.95 ± 0.42	-11.68 ± 0.13^a	57 ± 2
Eu (1)	5.87 ± 0.43	-10.93 ± 0.05^a	56 ± 2
Eu (2)	6.20 ± 0.48		58 ± 2
EDTA [$I = 0.50$ M (NaClO ₄)]			
Cm	-29.3 ± 1.3	-96.2 ± 0.5^b	225 ± 6
Eu	-22.9 ± 1.3	-92.6 ± 0.4^c	234 ± 6

^a Reference 3. ^b Reference 6. ^c Reference 8.

II seem valid and indicate a strong similarity in the behaviors of the trivalent actinides and lanthanides in complexation with acetate anions. The difference in cation dehydration proposed in ref 3 is not evident in our data.

For the EDTA complexation, the only comparable calorimetric datum is for formation of AmEDTA⁻ at $I = 0.1$ M for which the reported enthalpy is $\Delta H = 19.5 \pm 1.0$ kJ·m⁻¹.⁴ In that work, the enthalpy of formation of LaEDTA⁻ was measured also and a value of $\Delta H = -4.8 \pm 8$ kJ·m⁻¹ obtained. This is 8.3 kJ·m⁻¹ more endothermic than the value in ref 5, which reports later and more sensitive work. Moreover, the ΔH value for LaEDTA⁻ obtained in this laboratory⁸ at $I = 0.5$ M is -15.6 kJ·m⁻¹, which, considering the difference in ionic strength, agrees well with that of ref 5. Correcting the AmEDTA⁻ enthalpy by the difference in the enthalpy values for LaEDTA⁻ of ref 4 and 8, -11.8 kJ·m⁻¹, results in a value of $\Delta H = -31.2 \pm 2.2$ kJ·m⁻¹, which agrees with that reported in ref 6 from measurement of $\log \beta_{101}$ at different temperatures. That study also reported a value of $\Delta H = -29 \pm 2$ kJ·m⁻¹ for CmEDTA⁻. The agreement of this latter value as well as that for AmEDTA⁻ with our value in Table II provides strong support for the validity of the latter. The agreement between the EuEDTA⁻ data in Table II ($\Delta H = 24.9 \pm 0.3$ kJ·m⁻¹) and that in ref 8 ($\Delta H = 24.9 \pm 0.3$ kJ·m⁻¹) is further support. Again, the similarity in complexation thermodynamics between trivalent lanthanides and actinides is evident.

Acknowledgment. This research was supported at FSU and ANL by contracts with the USDOE Division of Chemical Sciences. We are indebted for the use of ²⁴⁸Cm to the Office of Basic Energy Sciences, USDOE, through the transplutonium element production facilities at the Oak Ridge National Laboratory. We also wish to thank Barbara Stout and William Cacheris for their assistance in these experiments.

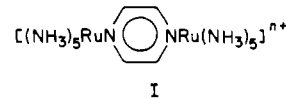
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Back-Bonding Effects of Osmium(III): Crystal Structure of (μ -Pyrazine)decaamminediosmium(III) Chloride Dihydrate

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Received September 24, 1984

Since the initial reports of pyrazine- (pyz-) bridged binuclear ions of ruthenium amines,¹ I, many binuclear ruthenium com-



plexes have been prepared and characterized.²⁻⁴ However, the electronic structure of the mixed-valence ruthenium complex

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Table I. Crystallographic Data for $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$

formula	$\text{C}_4\text{H}_{38}\text{N}_{12}\text{O}_2\text{Cl}_6\text{Os}_2$
fw	879.55
space group	$P2_1/n$
<i>a</i> , Å	7.501 (1)
<i>b</i> , Å	11.384 (1)
<i>c</i> , Å	14.617 (2)
β , deg	100.11 (4)
<i>V</i> , Å ³	1229 (1)
<i>Z</i>	2
cryst size, mm	0.1 × 0.12 × 0.16
μ , cm ⁻¹	105.3
transmission factors	0.287–0.472
range of 2θ , deg	3–52
range of indices	$\pm h, +k, +l$
no. of unique data	2384
no. of data with $F_o^2 > 3\sigma(F_o^2)$	1899
<i>R</i>	0.034
<i>R_w</i>	0.037
<i>w</i>	$(\sigma_{F^2} + 0.000571F^2)^{-1}$

(structure I, $n = 5$) has been the center of considerable controversy. Recently a revision of crystallographic and spectroscopic evidence,⁵ combined with the syntheses of the osmium analogues,^{6,7} has added further support to the contention that the mixed-valence ion is delocalized. We were interested in the molecular structures of the binuclear complexes for several reasons. The first is the relevance of structural information to the electronic structures of the molecules. Secondly, we expected π -back-bonding to be important for Os(III) as well as Os(II), and we wished to compare the M–N(py_z) bond lengths in isostructural ruthenium and osmium complexes to ascertain the relative importance of these effects for the two metals. Thirdly, the Os(III)–Os(III) species proved to be diamagnetic at low temperatures, thus showing a considerable degree of exchange coupling,⁸ and we wished to find if there was any structural evidence that had a bearing on this result. Finally, structural information was needed for single-crystal spectroscopic work, which will be communicated separately.

Experimental Section

$[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ was obtained as dark brown crystals by slow cooling of a hot aqueous HCl (4 M) solution of the chloride salt^{6,7} of the 6+ ion.

X-ray Crystallography. Data were collected at room temperature on a PW 1100 Philips four-circle computer-controlled diffractometer. Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation with a graphite-crystal monochromator in the incident beam was used. General procedures of data collection and reduction have been published elsewhere.⁹ Intensity data were corrected for absorption by the ψ -scan method. The heavy-atom positions were obtained from a three-dimensional Patterson function, and the structure was refined¹⁰ in space group $P2_1/n$ to convergence by using anisotropic thermal parameters for all non-hydrogen atoms. Lists of thermal parameters and observed and calculated structure factors are available as supplementary material.

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Table II. Positional Parameters and Estimated Standard Deviations^a for $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$

atom	<i>x</i>	<i>y</i>	<i>z</i>
Os	0.28406 (4)	0.23858 (3)	0.08578 (2)
Cl(1)	0.3955 (4)	0.2720 (2)	–0.2422 (2)
Cl(2)	0.4839 (4)	0.4135 (2)	0.3320 (2)
Cl(3)	0.2712 (4)	0.1122 (2)	0.4681 (2)
N(1)	0.026 (1)	0.1586 (7)	0.0501 (6)
N(2)	0.154 (1)	0.3796 (7)	0.1416 (5)
N(3)	0.235 (1)	0.3244 (7)	–0.0457 (5)
N(4)	0.322 (1)	0.1636 (7)	0.2210 (5)
N(5)	0.531 (1)	0.3298 (7)	0.1231 (6)
N(6)	0.4115 (9)	0.0955 (6)	0.0332 (5)
C(1)	0.378 (1)	–0.0158 (8)	0.0564 (6)
C(2)	0.538 (1)	0.1103 (7)	–0.0237 (6)
OW	0.636 (1)	0.0105 (7)	0.2557 (6)

^a Estimated standard deviations in the least significant digits are shown in parentheses in this and the following tables.

Table III. Bond Distances (Å) for $[(\text{NH}_3)_5\text{M}(\text{pyz})\text{M}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ (M = Os, Ru)

bond	M = Os	M = Ru ^a
M–N(1)	2.117 (8)	2.095 (2)
M–N(2)(trans)	2.117 (8)	2.089 (1)
M–N(3)	2.130 (7)	2.116 (2)
M–N(4)	2.126 (7)	2.101 (1)
M–N(5)	2.112 (8)	2.091 (2)
M–N(6)(py _z)	2.101 (7)	2.115 (1)
N(6)–C(1)	1.35 (1)	1.341 (2)
N(6)–C(2)	1.38 (1)	1.341 (2)
C(1)–C(2)'	1.37 (1)	1.382 (2)

^a Reference 5b.

Table IV. Bond Angles (deg) for $[(\text{NH}_3)_5\text{M}(\text{pyz})\text{M}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ (M = Os, Ru)

angle	M = Os	M = Ru ^a
N(1)–M–N(2)	87.5 (3)	
N(1)–M–N(3)	88.2 (3)	
N(1)–M–N(4)	91.4 (3)	
N(1)–M–N(5)	175.8 (3)	
N(1)–M–N(6)	91.8 (3)	92.0 (1)
N(2)–M–N(3)	88.9 (3)	
N(2)–M–N(4)	86.7 (3)	
N(2)–M–N(5)	88.4 (3)	
N(2)–M–N(6)	178.4 (3)	178.7 (1)
N(3)–M–N(4)	175.6 (3)	
N(3)–M–N(5)	90.7 (3)	
N(3)–M–N(6)	92.5 (3)	91.5 (1)
N(4)–M–N(5)	89.4 (3)	
N(4)–M–N(6)	91.9 (3)	91.7 (1)
N(5)–M–N(6)	92.3 (3)	92.0 (1)
M–N(6)–C(1)	121.4 (5)	
M–N(6)–C(2)	122.1 (5)	
C(1)–N(6)–C(2)	116.4 (7)	115.6 (1)
N(6)–C(1)–C(2)'	122.1 (8)	122.9 (2)
N(6)–C(2)–C(1)'	121.4 (8)	121.6 (2)

^a Reference 5b.

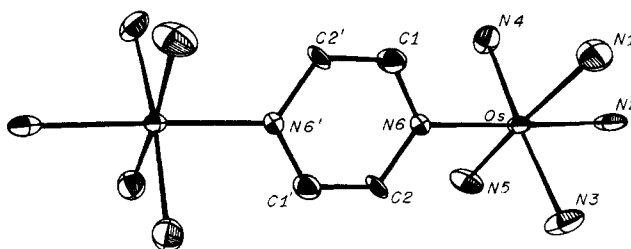


Figure 1. Molecular structure of the $[(\text{NH}_3)_5\text{Os}(\text{py})\text{Os}(\text{NH}_3)_5]^{6+}$ ion in $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$.

Results

$[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ is isostructural with its ruthenium analogue.⁵ Crystallographic data for the complex are presented in Table I. The unit cell, which has the symmetry

elements of the space group $P2_1/n$, contains two formula units of $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ each residing on crystallographic inversion centers. Table II contains positional parameters and estimated standard deviations for the non-hydrogen atoms, while Tables III and IV contain bond lengths and bond angles, respectively. Also shown in Tables III and IV are the equivalent values in the isostructural ruthenium complex.⁵ The molecular structure and numbering system used are given in Figure 1.

The pyrazine ring forms angles of 43.87° with the plane defined by Os, N(2),¹¹ N(3), N(4), and N(6) and 47.32° with the plane defined by Os, N(1), N(2), N(5), and N(6). The cis-NH₃ groups are slightly compressed away from the pyrazine group. The shortest Os-N bond length is observed for the Os-N(py_z) bond. Other variations in the Os-N bonds may be attributed to hydrogen bonding with the water molecules of crystallization and Cl⁻ counterions.

Discussion

The Os-NH₃ bond lengths of 2.112–2.130 Å in $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ are similar to those in $[\text{Os}(\text{en})_3](\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$,¹² where the average Os-N bond length is 2.11 Å. However, the Os-N(py_z) bond length of 2.101 (7) Å is shorter than the Os-N(amine) bonds. The shortening of the Os-N(py_z) bond by π -back-bonding is particularly evident when the isostructural Ru and Os compounds are compared (see Table III). Contrary to the observations for Os, the Ru-N(py_z) bond is the longest bond, and the Ru-N(trans) bond is about the shortest. The ruthenium result is expected when π -bonding is small, since pyrazine and pyrazinium ions are much poorer σ -donors than is ammonia. Further, electrostatic repulsion between the metal centers would tend to weaken the M-N(py_z) bonds. The strength of the π -interaction in the Os(III) complex is demonstrated by both these effects being counteracted. It is expected that the π -back-bonding interaction be stronger for the osmium complex because the Os(III) valence d orbitals are much closer in energy to the π^* ligand orbitals than is the case for Ru(III).

Kinetic, thermodynamic, and spectroscopic data exist to support the structural evidence presented here for significant π -back-bonding for Os(III). For instance, $[\text{Os}(\text{NH}_3)_5\text{NCR}]^{3+}$ complexes undergo nitrile hydrolysis at rates orders of magnitude lower than the ruthenium analogues.¹³ Further, the Os(III) dinitrogen complexes have stabilities toward substitution that are consistent with strong π -bonding.^{14,15} While $[\text{Ru}(\text{NH}_3)_5\text{CO}]^{3+}$ is not known, $[\text{Os}(\text{NH}_3)_5\text{CO}]^{3+}$ does exist²² and shows a carbonyl stretching frequency of 2058 cm^{-1} , significantly lower than that of free carbon monoxide.

In all the known structures^{5,13-21} of Os(II), Os(III), Ru(II) and Ru(III) ammine complexes containing N-heterocyclic ligands, the ligand plane bisects the N-M-N angles formed by the cis ligands.

The major reason for this is that the staggered conformation minimizes steric clashes between the hydrogen atoms of the heterocycle and those of the cis amines. The steric effects of nitrogen heterocycles have frequently been noted in pyridine complexes of Co(III), for example *trans*- $[(\text{NH}_3)_4\text{pyCoNO}_2]\text{Br}_2 \cdot \text{H}_2\text{O}$,²³ *trans*- $\text{Co}(\text{DMG})_2(\text{py})\text{CH}_2\text{C}(\text{CH}_3)_3$,²⁴ and $\text{CoTPP}(\text{OCH}_3)\text{py}$.²⁵ The net result of the staggered conformation is that the $d\pi$ set of orbitals includes d_{xy} , d_{yz} , and $d_{x^2-y^2}$, and the antibonding set consists of the d_{xy} and d_{z^2} orbitals. Due to the low symmetry, the $d\pi$ set is not completely nonbonding with respect to the ligand σ orbitals, and splitting between the orbitals of the $d\pi$ set (before consideration of π effects) is possible. Without a calculation, the direction of the splitting cannot be predicted, but the magnitude is assuredly small, due to the poor overlap of the orbitals involved.

Acknowledgment. P.A.L. is grateful for the receipt of CSIRO and Queen Elizabeth II Fellowships. We are also grateful for support from National Science Foundation Grant No. CHE79-08633 and National Institutes of Health Grant No. GM13638-17 and to Dr. A. Ludi for kindly supplying information on the structures of the ruthenium complexes prior to publication.

Registry No. $[(\text{NH}_3)_5\text{Os}(\text{pyz})\text{Os}(\text{NH}_3)_5]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$, 98194-39-9.

Supplementary Material Available: Listings of structure factor amplitudes (observed and calculated) and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Interaction of $\text{H}_3\text{Os}_4(\text{CO})_{12}\text{I}$ with Bis(triphenylphosphine)nitrogen(1+) Nitrite ($[\text{PPN}][\text{NO}_2]$). Synthesis and Chemical Characterization of $[\text{PPN}][\text{H}_2\text{Os}_4(\text{CO})_{12}\text{I}]$ and $\text{H}_3\text{Os}_4(\text{CO})_{11}(\text{NO})$ and X-ray Crystal Structure Determination of the New Nitrosyl Cluster $\text{H}_3\text{Os}_4(\text{CO})_{11}(\text{NO})$

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Received October 8, 1984

The reactivity of metal carbonyl clusters is often correlated with the metal core arrangements present in these complexes. Compounds with "open" structures tend to be more reactive than those showing "closed" configurations; we have observed this type of metal framework effect, for instance, in the homogeneous hydrogenation of cyclohexene catalyzed by tetranuclear osmium clusters.³

A structural flexibility involving interconversion between "closed" and "open" structures should therefore play an important role in the chemistry and catalytic properties of metal clusters. A number of routes can be envisaged to promote metal core

- (11) The least-squares plane of the pyrazine ring (plane 1) includes N(6), C(1), and C(2) and is defined by the equation $-4.4347x - 0.75989y - 10.049z + 2.2311 = 0$. The osmium atom is 0.072 Å from the plane. Plane 2 contains Os, N(2), N(3), N(4), and N(6) and is defined by the equation $6.387x + 5.356y + 1.147z - 3.190 = 0$. The atoms for plane 3 are Os, N(1), N(2), N(5), and N(6). Plane 3 is defined by $-0.1504x - 5.069y + 12.933z + 0.1415 = 0$. Angles between planes: 1 and 2, 43.87° ; 1 and 3, 47.32° ; 2 and 3, 91.11° .
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