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Electronic Structures and Spectra of Nitrido Complexes of Osmium(VI)

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The complexes $[(n\text{-Bu})_4N][OsNX_4]$, $[(n\text{-Pr})_4N][OsNX_4]$, and $[(n\text{-Pr})_4N][OsNX_4(OH_2)]$ ($X^- = Cl^-, Br^-$) have been prepared and characterized. Infrared spectral data suggest that the $OsNX_4^-$ units in all six complexes possess C_{4v} symmetry. The $[(n\text{-Bu})_4N][OsNCl_4]$ complex exhibits relatively weak electronic absorption spectral bands at 20 300 (ϵ 93), 22 700 (ϵ 77), and 25 600 cm^{-1} (ϵ 50) in dichloromethane solution at 298 K. Low-temperature (77 and 5 K) spectral measurements on solid samples show that the lowest band system consists of two components. Both components are perpendicularly polarized and exhibit similar vibrational structure (a_1(Os≡N), ~800-cm^{-1} spacing). Assignment of the components to transitions to a Jahn-Teller split $E(^3E)$ excited state is proposed. It is estimated that the Os≡N bond is lengthened by about 0.09 Å in the $E(^3E)$ state. Measurements on a single crystal at 5 K show that the band centered at 22 810 cm^{-1} is parallel polarized and exhibits a 390-cm^{-1} progression attributable to a_1(Os—Cl). Assignment of this band to $^1A_1 \rightarrow A_1(^3A_2)$ is suggested. The band that peaks at 25 490 cm^{-1} in the 5-K crystal spectrum appears to be only vibronically allowed and is attributed to $^1A_1 \rightarrow A_2(^1A_2)$. A progression in quanta of about 410 cm^{-1} is observed on $^1A_1 \rightarrow A_2(^1A_2)$ at low temperature. Additional bands are observed at 5 K and are assigned as follows: 30 340 cm^{-1} (a_1(Os≡N) progression, ~840 cm^{-1}), $^1A_1 \rightarrow E(^3B_2)$; 34 710 cm^{-1} (a_1(Os≡N) progression, ~1000 cm^{-1}), $^1A_1 \rightarrow E(^1E)$. The estimated Os≡N bond lengthening in $E(^3B_2)$ is 0.17 Å, which is consistent with a large degree of axial σ-antibonding character in that excited state. A spin–orbit crystal field calculation of the d-orbital energy levels of C_{4v} $OsNCl_4^-$ has been performed. Satisfactory agreement with the band positions in the spectrum was obtained for the following parameter values: $\Delta_1(b_1\text{–}b_2) = 26\,000$ cm^{-1}; $\Delta_2(e\text{–}b_2) = 36\,000$ cm^{-1}; $\Delta_3(a_1\text{–}b_2) = 49\,000$ cm^{-1}; $F_2 = 1400$ cm^{-1}; $F_4 = 55$ cm^{-1}. The unusually high energies of the a_1 and e levels are taken to indicate that both the σ and π bonds in the Os≡N unit of $OsNCl_4^-$ are very strong. The electronic spectra of crystals containing related tetrahalonitrido complexes of osmium(VI) have also been measured at 5 K. The spectral features in each case are similar to those of $OsNCl_4^-$, and analogous assignments have been made.

Introduction

Nitrido (N^{3-}) complexes of transition metal ions have attracted considerable attention in recent years.[1] Although the M≡N unit is formally analogous to M≡O of the well-studied oxo cation complexes,[2-6] it is not known to what extent electronic structural parallels between the two can be drawn. For this reason, we have undertaken a detailed electronic spectroscopic investigation of a series of tetrahalonitrido complexes of osmium(VI).

In this paper we report the preparation, characterization, and electronic spectra of $[(n\text{-Bu})_4N][OsNX_4]$, $[(n\text{-Pr})_4N][OsNX_4]$, and $[(n\text{-Pr})_4N][OsNX_4(OH_2)]$ ($X^- = Cl^-, Br^-$). Griffith and Pawson have independently prepared the five-coordinate complexes $OsNX_4^-$,[7,8] and the structure of $[Ph_4As][OsNCl_4]$ has been determined.[9] In the present work, single-crystal polarized electronic spectra of several key compounds have been measured at 5 K.[10] Interpretation of the spectra has been aided by a spin–orbit crystal field calculation of $OsNCl_4^-$.

Experimental Section

Preparation of Compounds. $K[OsO_3N]$ was prepared by a standard method.[11] $[(n\text{-Bu})_4N][OsNX_4]$ and $[(n\text{-Pr})_4N][OsNX_4(OH_2)]$ ($X^- = Cl^-, Br^-$) were prepared by adding the appropriate tetraalkylammonium halide to an HX solution of $K[OsO_3N]$. Details are given for $[(n\text{-Bu})_4N][OsNCl_4]$. $K[OsO_3N]$ (1.0 g, 0.0034 mol) was dissolved in hydrochloric acid (8 ml, 4 M). The solution, which immediately turned red, was placed on a steam bath for 5 min. The solution was then diluted by addition of an equal volume of water. Dropwise addition with stirring of a concentrated aqueous solution of $[(n\text{-Bu})_4N]Cl$ to the cooled solution immediately precipitated the pink $[(n\text{-Bu})_4N][OsNCl_4]$ product. The compound was filtered off, was washed with boiling dilute hydrochloric acid and then with water, and was dried in a vacuum oven at 80 °C for 6 h; yield 1.4 g, 70%. The $[(n\text{-Pr})_4N][OsNX_4]$ complexes were obtained by dehydrating the corresponding $[(n\text{-Pr})_4N][OsNX_4(OH_2)]$ compounds in a vacuum oven at 78 °C for 5 h. $[(n\text{-Bu})_4N][OsNCl_4]$ was recrystallized from dichloromethane–hexane and dichloromethane–chloroform solutions. Large square crystalline plates of the compound were grown. The other compounds were recrystallized from acetonitrile solution. Analytical data for these compounds are given in Table I.

Physical Measurements. Electronic spectral data were obtained using a Cary 17 spectrophotometer equipped with an Andonian liquid helium Dewar and double Glan Taylor air-spaced calcite polarizers. For the low-temperature spectroscopic studies, crystals were grown on aluminum oxide and quartz substrates. Crystals of $[(n\text{-Bu})_4N][OsNCl_4]$ are tetragonal, space group $P4/n$, with lattice parameters $a = b = 11.757$ (1), $c = 8.789$ (1) Å.[12] The osmium–nitrogen bond line coincides with the crystallographic fourfold axis. As crystals formed on the (001) face, only perpendicular (or σ) polarized spectra were obtained.

Results and Discussion

Infrared spectral similarities suggest[12] that the $OsNX_4^-$ and $OsNX_4(OH_2)^-$ units all possess C_{4v} symmetry, by analogy to the geometrical structure of $OsNCl_4^-$ found in crystalline compounds.[9,12,13] In the ground state, the Os≡N bond distance is extremely short, being 1.60 Å in $[Ph_4As][OsNCl_4]$.[9] Under the assumption of a strong axial ligand field, the d orbitals are expected to increase in energy according to b_2 (d_{xy})

Table I. Analytical Data for Tetrahalonitrido Complexes of Osmium(VI)

	% calcd				% found			
Complexes	C	H	N	X	C	H	N	X
$[(n\text{-Bu})_4N][OsNCl_4]$	32.6	6.16	4.75	24.1	32.5	6.20	4.69	24.2
$[(n\text{-Pr})_4N][OsNCl_4]$	27.1	5.30	5.26	26.6	27.2	5.33	5.12	26.8
$[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$	26.2	5.49	5.09	25.8	26.4	5.35	4.97	26.0
$[(n\text{-Bu})_4N][OsNBr_4]$	25.1	4.74	3.66	41.7	25.1	4.73	3.64	41.3
$[(n\text{-Pr})_4N][OsNBr_4]$	20.3	3.97	3.95	45.0	20.4	4.02	3.97	44.8
$[(n\text{-Pr})_4N][OsNBr_4(OH_2)]$	19.8	4.15	3.85	43.9	20.0	3.99	3.87	43.7

Table II. Ligand Field Transitions in C_{4v} $OsNCl_4^-$ [a]

One-electron transition	Excited state	One-electron transition	Excited state
$b_2 \rightarrow e$	$A_1(^3E)$	$b_2 \rightarrow b_1$	$A_1(^3A_2)$
$(d_{xy} \rightarrow d_{xz}, d_{yz})$	$A_2(^3E)$	$(d_{xy} \rightarrow d_{x^2-y^2})$	$E(^3A_2)$
	$B_1(^3E)$		$A_2(^1A_2)$
	$B_2(^3E)$	$b_2 \rightarrow a_1$	$B_1(^3B_2)$
	$E(^3E)$	$(d_{xy} \rightarrow d_{z^2})$	$E(^3B_2)$
	$E(^1E)$		$B_2(^1B_2)$

[a] Ground state is $^1A_1(b_2^2)$.

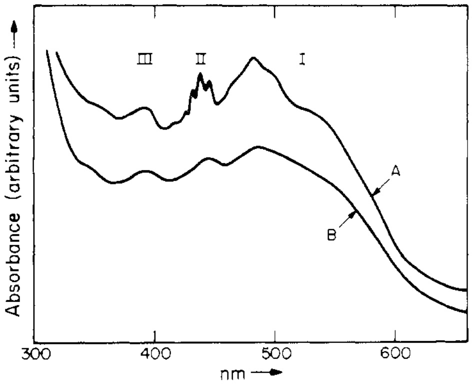

Figure 1. Electronic absorption spectra of a Nujol mull of $[(n\text{-Bu})_4N][OsNCl_4]$: A, 77 K; B, 298 K.

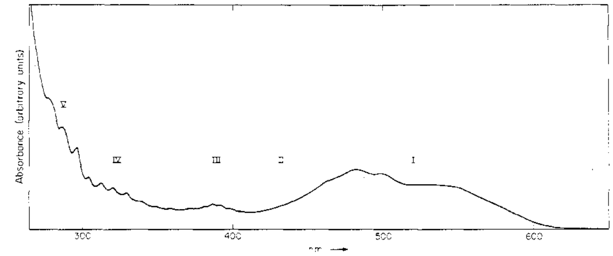

Figure 2. Electronic absorption spectrum measured on the (001) face of a single crystal of $[(n\text{-Bu})_4N][OsNCl_4]$ at 5 K.

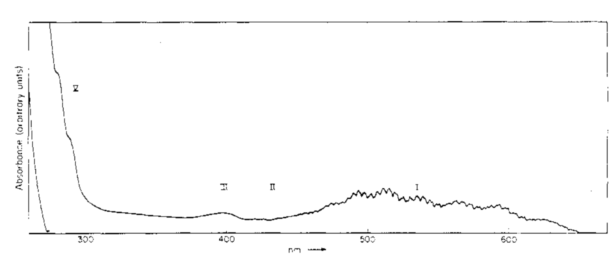

Figure 3. Electronic absorption spectrum of a single crystal of $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$ at 5 K.

$< e\ (d_{xz}, d_{yz}) \sim b_1\ (d_{x^2-y^2}) < a_1\ (d_{z^2})$. The ground state for d^2 $OsNX_4^-$ is therefore $^1A_1(b_2^2)$. The e and a_1 orbitals possess nitrogen–osmium π- and σ-antibonding character, respectively. Table II gives the symmetries of the ligand field excited states for transitions from b_2 to the e, b_1, and a_1 orbitals. Spin–orbit coupling is included, as it is expected to be of considerable importance in an Os(VI) complex. In C_{4v} symmetry, transitions from a $^1A_1$ ground state to A_1 and E excited states are allowed.

The electronic absorption spectrum of $[(n\text{-Bu})_4N][OsNCl_4]$ in dichloromethane solution at 298 K shows distinct bands centered at 20 300 (ε 93), 22 700 (ε 77), and 25 600 cm^{-1} (ε 50). Additionally, shoulders are observed at 18 300 and 28 000 cm^{-1}. Intense absorption occurs at energies greater than 33 000 cm^{-1}. The relatively low intensities of the bands below 33 000 cm^{-1} suggest that many of them may arise from transitions to excited states derived from spin triplets.

In a solid sample of $[(n\text{-Bu})_4N][OsNCl_4]$ at low temperature, the lowest energy shoulder is resolved at 18 120 cm^{-1} (Figure 1). The band at 20 410 cm^{-1} sharpens and vibrational fine structure with a spacing of 750–860 cm^{-1} is observed. We shall refer to the 20 410-cm^{-1} maximum and its low-energy shoulder as band system I. An analogous system is observed in $[(n\text{-Bu})_4N][OsNBr_4]$. Peak positions in system I taken from 5-K measurements on single crystals of $[(n\text{-Bu})_4N][OsNCl_4]$ and $[(n\text{-Bu})_4N][OsNBr_4]$ are given in Table III.

The fact that band system I is observed in the axial (001) spectrum of $[(n\text{-Bu})_4N][OsNCl_4]$ at 5 K clearly demonstrates that it is perpendicularly polarized (Figure 2). The lower energy component is slightly red-shifted and therefore more pronounced in the 5-K spectrum of $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$ (Figure 3). Moreover, sharper vibrational structure is detected in the axially aquated compound. The main vibrational progression of 800–900 cm^{-1} is attributed to the excited-state a_1(Os≡N) stretching mode (ground state ~1120 cm^{-1}).[12] The fact that a reduction of the Os≡N stretching frequency is observed indicates an increase in that bond distance in the excited state. As the Poisson formula[14] may be fit with a Franck–Condon factor of 1.68 for band I in $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$, we estimate that the Os≡N bond lengthening is approximately 0.09 Å (taking 9.67 mdyn/Å for the stretching force constant).[15] The progression in a_1(Os≡N) is split by 162 cm^{-1} in $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$ (Figure 3) and by 119 cm^{-1} in $[(n\text{-Pr})_4N][OsNBr_4(OH_2)]$ (Table IV). From the dependence on halide, assignment of this low-frequency mode to an $a_1(OsX_4)$ umbrella deformation is proposed. For comparison, the analogous ground-state deformations in $[Ph_4As][OsNCl_4]$ and $[Ph_4As][OsNBr_4]$ occur[15] at 184 and 122 cm^{-1}, respectively.

It is unlikely that the lowest σ-polarized band is $^1A_1 \rightarrow E(^3A_2)$ (i.e., $b_2 \rightarrow b_1$), as the $E(^3A_2)$ excited state has σ* character with respect to the halide ligands. Such σ* character is inconsistent with the relative insensitivity of the position of band system I to halide substitution and also with the fact that a progression in a_1(Os–X) is *not* present. We conclude, therefore, that band system I results from the one-electron excitation $b_2 \rightarrow e$. Population of an antibonding e orbital effectively reduces the Os≡N bond order and is consistent with a lower stretching frequency (and bond lengthening) in the excited state.

Assuming band system I is derived from $b_2 \rightarrow e$, it remains to assign the excited states associated with the two components. The two components could be attributable either to $^1A_1 \rightarrow E(^3E)$ split by Jahn–Teller vibronic interactions or to the two

Table III. Electronic Absorption Spectra of Tetrahalonitrido Complexes of Osmium(VI) at 5 K

	$[(n\text{-Bu})_4N][OsNCl_4]$			$[(n\text{-Bu})_4N][OsNBr_4]$			
Band	nm[a]	cm^{-1}	Spacing	nm[a]	cm^{-1}	Spacing	$^1A_1 \to$
I	527.0	18 200	800	575.3	17 380	920	$E(^3E)$
	549.5	19 000	950	546.5	18 300		
	501.3	19 950	780	508.0	19 690	850	
	482.4	20 730	860	486.9	20 540	910	
	463.2	21 590		466.2	21 450	1040	
				444.7	22 490		
II	446.0	22 420	390 120				$A_1(^3A_2)$
	443.7	22 540					
	438.4	22 810	380 140		b		
	435.9	22 940					
	431.2	23 190	390 130				
	428.8	23 320					
	424.1	23 580	120				
	421.9	23 700	400				
	414.9	24 100					
III	406.5	24 600	420				$A_2(^1A_2)$
	399.7	25 020	470				
	392.3	25 490	390	416.2	24 030		
	386.4	25 880	370				
	381.0	26 250					
IV	358.9	27 860	790	390.2	25 630[c]		$E(^3B_2)$
	349.0	28 650	810	388.1	25 770		
	339.4	29 460	880	382.1	26 170		
	329.6	30 340	880	378.5	26 420		
	320.3	31 220	760	373.8	26 750		
	312.7	31 980	860	364.1	27 460		
	304.5	32 840		358.7	27 880		
				355.8	28 100		
				347.0	28 810		
				337.3	29 650		
				328.1	30 480		
				322.1	31 050		
				316.4	31 600		
V	296.9	33 680	1030				$E(^1E)$
	288.1	34 710	1000				
	280.0	35 710					

[a] Uncertainties in peak positions are generally ±1.0 nm. [b] A band attributable to $^1A_1 \to A_1(^3A_2)$ was observed at 21 325 cm^{-1} in dichloromethane solution. [c] A complex series of peaks begins here. It is likely that transitions to $E(^3B_2)$ and $E(^1E)$ overlap in this region.

transitions $^1A_1 \to E(^1E)$ and $^1A_1 \to E(^3E)$.[16] Complete spin–orbit crystal field calculations show that the latter interpretation is untenable (vide infra). Therefore, we conclude that band system I is attributable to split components of the transition $^1A_1 \to E(^3E)$.

Spectral data for the higher energy band systems in $[(n\text{-Bu})_4N][OsNX_4]$ and $[(n\text{-Pr})_4N][OsNX_4(OH_2)]$ complexes are set out in Tables III and IV, respectively. Band II, which is centered at 22 810 cm^{-1} in $[(n\text{-Bu})_4N][OsNCl_4]$ at 5 K, is not observed in perpendicular polarization. The parallel polarization of this band suggests that it be assigned to $^1A_1 \to A_1(^3E)$ or to $^1A_1 \to A_1(^3A_2)$. The fact that band II shifts over 1400 cm^{-1} to the red in the spectrum of $OsNBr_4^-$ supports the latter choice, as the $A_1(^3A_2)$ excited state is antibonding with respect to the equatorial ligands. The doubled vibrational progression of 390 cm^{-1} split by 130 cm^{-1} for $[(n\text{-Bu})_4N][OsNCl_4]$ indicates an excited-state distortion in a_1(Os–Cl), which is additional evidence in favor of the one-electron $b_2 \to b_1$ origin of $A_1(^3A_2)$. The corresponding a_1 metal–halide stretching frequency in the ground state has been reported[15] to be 358 cm^{-1}. The 130-cm^{-1} splitting observed at 5 K could result from coupling of the a_1 deformation (ground state 184 cm^{-1})[15] to the a_1 stretch. Thus band II may be assigned confidently to the transition $^1A_1 \to A_1(^3A_2)$.

The weak band that peaks at 25 490 cm^{-1} (III) in $[(n\text{-Bu})_4N][OsNCl_4]$ at 5 K is perpendicularly polarized. This band is assigned to the orbitally forbidden transition $^1A_1 \to A_2(^1A_2)$, which, in the Herzberg–Teller coupling scheme,[17] is vibronically allowed *only* in perpendicular polarization. Band III is red-shifted in the bromide complexes, as was found for band II. Band III also slightly blue-shifts upon cooling, consistent with a vibronic intensity-giving mechanism. Vibrational structure with a spacing of about 410 cm^{-1} is assigned to an excited-state deformation in a_1(Os–Cl), as expected for a one-electron excitation to the b_1 orbital. Note that $^1A_1 \to E(^3A_2)$ is not observed, presumably because it is weak and obscured by band system I.

The next feature in the 5-K spectrum of $[(n\text{-Bu})_4N][OsNCl_4]$ is a broad, perpendicularly polarized band (IV) with a maximum at 30 340 cm^{-1}. A long progression with a spacing of about 840 cm^{-1} is observed, and standard analysis[14] gives a Franck–Condon factor of 6 or greater. Taking an Os≡N stretching force constant of 9.67 mdyn/Å,[15] as before, we estimate an Os≡N bond lengthening of about 0.17 Å in the excited state in question. Assignment of band IV to $^1A_1 \to E(^3B_2)$ is consistent with such large Os≡N bond lengthening, as substantial axial σ^* character is predicted for the $E(^3B_2)$ excited state. Band IV is not found in the same region in the spectrum of $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$ (Figure 3), and we assume it falls at higher energy. In $[(n\text{-Bu})_4N][OsNBr_4]$, a complex system of overlapping bands begins at 25 630 cm^{-1}. It is likely that transitions to $E(^3B_2)$ and $E(^1E)$ occur in this region, but we are not able to make any specific peak assignments at this time. Band IV in the 5-K spectrum of $[(n\text{-Pr})_4N][OsNBr_4]$ appears less complex, being comprised of a ~750-cm^{-1} progression beginning at 26 830 cm^{-1}.

A relatively intense, perpendicularly polarized progression (V) in quanta of about 1000 cm^{-1} originates at 33 680 cm^{-1} in the spectrum of $[(n\text{-Bu})_4N][OsNCl_4]$ at 5 K. Band V, which does not appreciably shift upon axial H_2O coordination, is assigned to $^1A_1 \to E(^1E)$. As noted above, transitions to $E(^1E)$ in the bromide complexes are not well separated from

Table IV. Electronic Absorption Spectra of Tetrahalonitridoaquo Complexes of Osmium(VI) at 5 K

	$[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$			$[(n\text{-Pr})_4N][OsNBr_4(OH_2)]$			
Band	nm[a]	cm^{-1}	Spacing	nm[a]	cm^{-1}	Spacing	$^1A_1 \rightarrow$
I	617.8	16 190		626.6	15 960		$E(^3E)$
	611.7	16 350	160	621.9	16 080	120	
	605.7	16 510	160	616.9	16 210	130	
	599.7	16 680	170	612.4	16 330	120	
	593.8	16 810	160	607.9	16 450	120	
	588.2	17 000	160	603.5	16 570	120	
	585.2	17 090	900	599.2	16 690	120	
	579.6	17 250	160	592.8	16 870	910	
	574.1	17 420	160	588.6	16 990	120	
	568.8	17 580	160	584.5	17 110	120	
	563.5	17 750	170	580.4	17 230	120	
	558.4	17 910	160	576.4	17 350	120	
	555.9	17 990	900	572.4	17 470	120	
	550.8	18 160	170	568.5	17 590	120	
	545.9	18 320	160	562.7	17 770	900	
	541.2	18 480	160	559.0	17 890	120	
	536.5	18 640	160	555.6	18 000	110	
	530.0	18 870	880	551.9	18 120	120	
	525.6	19 030	160	548.2	18 240	120	
	521.2	19 190	160	544.7	18 380	120	
	516.8	19 350	160	541.4	18 470	110	
	507.1	19 720	850	538.5	18 570	100	
	502.9	19 880	160	535.3	18 680	110	
	498.9	20 040	160	532.8	18 770	1000	
	495.1	20 200	160	526.6	18 990	120	
	491.4	20 350	150	523.3	19 110	120	
	486.2	20 570	850	520.0	19 230	120	
				516.5	19 360	130	
				513.3	19 480	120	
				510.2	19 000	120	
				507.1	19 720	120	
				507.6	19 700	930	
				504.5	19 820	120	
				501.8	19 930	110	
				498.5	20 060	130	
				495.5	20 180	120	
				492.6	20 300	120	
				485.0	20 620	920	
				481.9	20 750	130	
				479.2	20 870	120	
				476.2	21 000	130	
				471.5	21 120	120	
				471.0	21 230	110	
II	463.5	21 570					$A_1(^3A_2)$
	460.4	21 720	150				
	455.4	21 960	390				
	452.4	22 100	380				
	449.6	22 240	380 +2 (145)				
	447.7	22 340	380				
	444.8	22 480	380				
	441.9	22 630	390				
	440.5	22 700	360				
	437.5	22 860	380				
	434.8	23 000	370				
	430.2	23 250	390				
III	398.0	25 100		427.4	23 400		$A_2(^1A_2)$
IV				372.7	26 830		$E(^3B_2)$
				361.5	27 660	830	
				350.8	28 510	850	
				342.2	29 220	710	
				333.9	29 950	730	
				326.5	30 630	680	
V	344.4	34 440					$E(^1E)$
	355.3	35 530	1090				
	363.6	36 360	830				

[a] Uncertainties in peak positions are generally ±1.0 nm.

those attributable to $^1A_1 \rightarrow E(^3B_2)$.

Our assignments for the five-band systems were based in part on a spin–orbit crystal field calculation of the energy levels of $OsNCl_4^-$. Matrix elements for all single excitations in $OsNCl_4^-$ were expressed in terms of a spin–orbit parameter $\alpha = \zeta/2$, the three crystal field splittings $\Delta_1 = E(b_1) - E(b_2)$, $\Delta_2 = E(e) - E(b_2)$, and $\Delta_3 = E(a_1) - E(b_2)$, and the Slater–Condon parameters, F_2 and F_4.[18] In the calculation, α was fixed at 1000 cm^{-1}, which accords with the value of 950 cm^{-1} found[19] for the $(t_{2g})(e_g)$ configuration of OsF_6. Various combinations of Δ_1, Δ_2, Δ_3, F_2, and F_4 were employed in the crystal field calculations. Satisfactory agreement with the spectral data for $OsNCl_4^-$ was achieved for $\Delta_1 = 26000$, $\Delta_2 = 36000$, $\Delta_3 = 49000$, $F_2 = 1400$, and $F_4 = 55$ cm^{-1} (Table

Table V. Calculated and Observed Electronic Transitions in $OsNCl_4^-$

$^1A_1 \rightarrow$	$\bar{\nu}_{max}$(obsd), cm^{-1}	$\bar{\nu}_{max}$(calcd), cm^{-1}
$E(^3E)$	19 300[a]	19 596
$A_1(^3E)$	*b*	20 395
$E(^3A_2)$	*b*	21 360
$A_1(^3A_2)$	22 810	22 749
$A_2(^1A_2)$	25 490	25 246
$E(^3B_2)$	30 340	29 544
$E(^1E)$	34 710	32 675

[a] Average position of the two components. [b] Not observed.

V). More precise fitting would be meaningless in view of the crudeness of the theory. It is somewhat reassuring that the assigned values of parameters F_2, F_4, and Δ_1 for $OsNCl_4^-$ are in good agreement with those obtained[20] from a detailed analysis of the electronic spectrum of $PtCl_4^{2-}$ ($F_2 = 1406$, $F_4 = 54$, $\Delta_1 = 25\,961$ cm^{-1}). Such close correspondence is to be expected, as the Os–Cl (2.31 Å)[10] and Pt–Cl (2.32 Å)[21] bond distances are nearly equal.

It should be pointed out that in *all* of our computations,[18] even when the values of F_2 and F_4 were greatly reduced, the ^1E–^3E splitting was found to be greater than 6000 cm^{-1}. This is the main basis of our assignment of both components of band system I to transitions to a split $E(^3E)$ state. It is not likely that the higher component is $^1A_1 \rightarrow E(^1E)$, as in that case the implied singlet–triplet splitting would be well below the lower limit set by theory.

The unusually high energies of the osmium d orbitals (e, a_1) that interact with the nitrido group are particularly noteworthy. Indeed, the antibonding character of the e level in Os≡N appears to be much greater than that inferred for M≡O from spectral studies of oxo cation complexes containing second- and third-row metals.[22,23] We take this result to mean that nitride is a much better π donor than is oxide, a conclusion not incompatible with recent Mössbauer spectral experiments on Ru(VI)[24] and Os(VI)[25] nitrido complexes that clearly indicate the presence of a high degree of ligand → metal electron donation. It should also be emphasized that our analysis suggests that both σ and π nitrido–osmium bonds are very strong. As electron donation from N^{3-} to a metal center increases, the nucleophilic character of the coordinated nitrido group decreases. Our electronic structural model for Os≡N, then, would suggest a rather low nucleophilicity for the nitrido ligand, which accords well with experimental observations made previously.[26]

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Registry No. $[(n\text{-Bu})_4N][OsNCl_4]$, 42993-50-0; $[(n\text{-Pr})_4N][OsNCl_4]$, 59219-46-4; $[(n\text{-Pr})_4N][OsNCl_4(OH_2)]$, 59187-87-0; $[(n\text{-Bu})_4N][OsNBr_4]$, 42720-45-6; $[(n\text{-Pr})_4N][OsNBr_4]$, 59187-88-1; $[(n\text{-Pr})_4N][OsNBr_4(OH_2)]$, 59187-90-5; $K[OsO_3N]$, 21774-03-8.

Supplementary Material Available: Crystal field matrices with inclusion of spin–orbit coupling and sample calculations (2 pages). Ordering information is given on any current masthead page.

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Raman Studies of Sulfur-Containing Anions in Inorganic Polysulfides. Barium Trisulfide

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The present work reports an investigation of the S_3^{2-} anion from −125 to 580 °C using laser-Raman and rotating scattering arrangements as principal techniques, with BaS_3 (mp 554 °C) as the model system. The room-temperature and low-temperature spectra are understood in terms of a C_{2v} symmetry for S_3^{2-}. A unique spectral transformation occurs at higher temperature and in addition the compound exhibits a temperature-independent but magnetic-field-dependent paramagnetism. These changes are discussed from the viewpoint of bond angle changes, resonance Raman effect, and rotation of the S_3^{2-} species in the solid state.

Introduction

The alkali and alkaline earth metals form a series of polysulfides containing S_n^{2-} anions. Since complex equilibria undoubtedly occur between species such as S^{2-} and S_n^{2-}, we have undertaken the characterization of some of the S_n^{2-} anions using, as model systems, a series of inorganic polysulfides for which the structures have been well characterized by careful x-ray crystallographic studies. The present work reports the results of an investigation of the S_3^{2-} anion using laser-Raman spectroscopy as the principal technique and, as