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ESR Characterization of the Redox Orbitals in $[\text{Os}(\text{bpy})_3]^{2+}$

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Recent electron spin resonance (ESR) studies^{1,2} of the first three electrochemically generated reduction products of numerous d^6 transition-metal complexes of the general form $[\text{ML}_3]^{2+}$ ($M = \text{Fe}(\text{II}), \text{Ru}(\text{II})$; $L =$ bidentate diimine such as 2,2'-bipyridine) have afforded a simple, yet thorough, description of the redox orbitals in these species. For the one-, two-, and three-electron-reduction products simple, ligand-localized ($g \approx 2.00$), $S = 1/2$ behavior is observed in frozen and fluid solutions (CH_3CN , DMF) from 77 K to room temperature. In particular, no dipolar spin-spin interactions are manifested in the spectra of the products reduced by two or more electrons. Thus, these species must be multi-radicals^{3,4} with weak interaction between the electrons. Furthermore, the spectra for the one- and two-electron products exhibit an unusually large temperature-dependent variation in fluid solution line width attributable to intramolecular electron-transfer processes. The most consistent interpretation of all these results is in terms of a spatially isolated orbital model^{1,2,5,6} in which each of three lowest lying redox orbitals is localized on a single chelate ring system and electronic interactions between the ligands are minimal. This interpretation is supported by other optical⁷⁻¹¹ and resonance Raman^{12,13} spectroscopic data for both the reduction products and the analogous emissive charge-transfer excited state of the parent ions, all of which indicate orbital localization on individual ligands.

In addition to this uniform behavior from the initial three reduction products, there remains the seemingly anomalous observation in earlier studies^{1,14} of ESR signals for the two-electron products indicative of electron population in orbitals having substantial metal character. These results are obtained only when the reduction is done in a nitrile solvent, and subsequent work^{2,6} has verified that the metal-localized signal ($g \approx 2.1$, $\Delta H_{pp} > 200$ G) is due to the solid resulting from precipitation of the uncharged two-electron product. Thus, a change in the nature of the redox orbitals on going from a solvated product to a solid product is indicated. Recently, ESR results have been obtained for the first

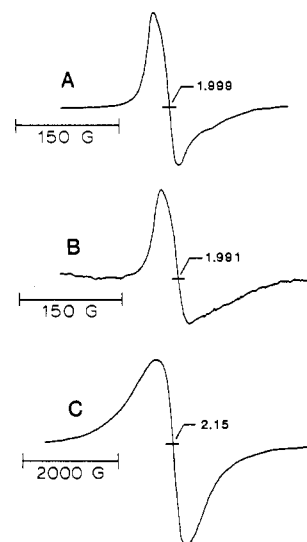


Figure 1. ESR spectra of doubly reduced products: (A) 0.7 mM $[\text{Os}(\text{bpy})_3]^{2+}$ in 0.1 M TBAP/DMF at -110°C ; (B) $[\text{Os}(\text{bpy})_3]^{2+}$ solid at -115°C ; (C) $[\text{Fe}(\text{Me}_2\text{phen})_3]^{2+}$ solid at 22°C .

three reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$. For this complex both solvated and precipitated two-electron products give ligand-localized signals. These new data are presented and discussed in relation to the data for the Fe(II) and Ru(II) complexes to clarify the origin of the unusual metal-localized signal obtained previously.

Results and Discussion

The ESR results for the first three reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$ are summarized in Table I. Similar data for selected Fe and Ru diimine complexes are included for comparison. As for these latter complexes, only simple, ligand-localized, $S = 1/2$ behavior is seen for the first two reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$, indicating that the redox orbitals for this complex are also spatially isolated. Only modest increases are observed in the g shifts ($\Delta g = |2.0023 - g_i|$) for the Os products relative to the Fe and Ru products. This is anticipated since spin-orbit coupling of ligand field and charge-transfer excited states to the ground state will make greater contributions to the g shifts for the Os products due to a larger spin-orbit coupling constant.^{15,16} The fluid solution line widths for $[\text{Os}(\text{bpy})_3]^{+0}$ are much greater at all temperatures than for the corresponding Fe and Ru products. In fact, broad line widths and low intensities make it impossible to distinguish the signal from base-line noise at temperatures above $\sim -40^\circ\text{C}$. Nonetheless, over the range from -60 to -40°C , significant broadening of the lines due to electron hopping between the ligands is observed. For $[\text{Os}(\text{bpy})_3]^{1+}$ it is possible to fit these data to an Arrhenius-type rate law,¹ and the activation barrier (E_a) to electron hopping has been included. The large uncertainty in the data for $[\text{Os}(\text{bpy})_3]^{0}$ (in solution) precludes obtaining a meaningful value for E_a . The triply reduced product, $[\text{Os}(\text{bpy})_3]^{-}$, is unusual in that all three principal g values are resolved in frozen solutions, no fluid solution signal is observed, and the g shifts are quite large. However, the spectral features still are not indicative of any spin-spin interactions, and a $3S = 1/2$ description appears most appropriate.

The most interesting result for the Os complex reduction products is that nearly identical ESR behavior is observed for

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Table I. ESR Data for the Reduction Products of $[M(\text{diimine})_3]^{2+}$ in 0.1 M Supporting Electrolyte Solutions

	<i>n</i>	fluid			frozen			<i>E_a</i> , cm ⁻¹	solv	ref
		<i>g</i>	ΔH^a	<i>T</i> , °C	<i>g</i>	ΔH^b	<i>T</i> , °C			
[Os(bpy) ₃] ⁿ	1+	1.989	118	-40	1.998	59	-140	810	DMF	<i>c</i>
	0	1.990	94	-40	2.001	52	-140	<i>e</i>	DMF	<i>c</i>
	0 (solid)				1.990	84	-120			<i>c</i>
	1-		<i>d</i>		1.968	136	-140	<i>f</i>	DMF	<i>c</i>
[Fe(Me ₂ phen) ₃] ⁿ	1+	1.990	120	0	1.994	17	-120	880	CH ₃ CN	2
	0 (solid)				2.15	600 ^a	-120			2
[Ru(bpy) ₃] ⁿ	1+	1.998	90	25	1.996	26	-100	960	CH ₃ CN	1
	0	1.995	32	25	2.001	17	-120	440	DMF	2
	0 (solid)				2.23	250 ^a	25			1
	1-	1.996	15	25	1.994	25	-100	<i>f</i>	CH ₃ CN	1
[Ru(Me ₂ phen) ₃] ⁿ	1+	1.991	72	0	1.995	52	-120	900	DMF	2
	0	1.990	36	0	1.993	47	-120	250	DMF	2
	0 (solid)				2.3	700 ^a	-120			2
	1-	1.99	30	0	1.99	60	-120	<i>f</i>	DMF	2

^a Peak-to-peak in gauss. ^b $|H_{\parallel} - H_{\perp}|$ in gauss. ^c This work. ^d No fluid solution signal. See text. ^e Not available. See text. ^f No line broadening observed.

[Os(bpy)₃]⁰ when isolated as a precipitate as for this species in DMF solutions as illustrated in Figure 1A,B. Thus, the solid, [Os(bpy)₃]⁰, is also best described as having spatially isolated, ligand-localized redox orbitals. Such behavior is in marked contrast to that for the precipitated, two-electron products of the Fe and Ru complexes for which an extremely broad, substantially *g*-shifted signal (Table I; Figure 1C) is seen indicating electron population in metal-localized orbitals.

The possibility that these unusual metal-localized signals for the doubly reduced solid Fe and Ru complexes result from decomposition products cannot be discarded completely. However, this is unlikely since at low concentrations a third electron can be added to these species without significant interference from precipitation, and the resulting three-electron product is stable, remaining in solution to give a ligand-localized signal. Furthermore, there is a very limited solubility of the two-electron products in CH₃CN. Thus, for sufficiently long electrolysis times it is possible to reduce the small amount of dissolved product by one more electron, enabling additional precipitate to dissolve. In this manner nearly all the precipitate can be redissolved and converted to the triply reduced species. Therefore, the solid obtained in all cases is most likely $[M(\text{bpy})_3]^0$, and precipitation is due to the inability of CH₃CN to effectively solvate the uncharged product. It is also noteworthy that once precipitation has occurred, the isolated solid will not dissolve in DMF to an extent necessary to obtain an ESR signal even though the two-electron products can be generated at ~1 mM concentrations in DMF without interference from precipitation.

Electronic Structure

Since these results demonstrate that the solids, FeL₃⁰ and RuL₃⁰ (L = diimine), have an electronic structure different from [Os(bpy)₃]⁰ (solid), it is necessary to determine the most probable electron configuration(s) that could give rise to the metal-localized ESR signal and to account for the difference between the Os species and the Fe and Ru species. Assuming that no significant orbital mixing takes place, the most likely configurations for these two-electron products are (1) $(L_1\pi^*)^1(L_2\pi^*)^1$, (2) $(L_1\pi^*)^1(d\sigma_1^*)^1$, and (3) $(d\sigma_1^*)^1(d^*\sigma_2^*)^1$ ($L_1\pi^*$ = one of three lowest available ligand-localized orbitals and $d\sigma_1^*$ = one of the two metal anti-bonding orbitals). The first of these configurations cannot give rise to the observed signal, even if spin-spin coupling is invoked since there is no mechanism to account for the observed *g* shift. In fact, this is the configuration proposed for [Os(bpy)₃]⁰ (solid) and all other two-electron products in solution, and the ESR data show that spin-orbit coupling of excited states into this ligand-localized ground state cause only minor *g* shifts.^{2,6} The second configuration might account for the metal-like ESR signal, but it is difficult to determine a priori how coupling (spin-spin and spin-orbit) would manifest itself in the spectrum. The third configuration corresponds to a d⁸ ion in D₃ symmetry. A number of examples of paramagnetic d⁸ ions in distorted octahedral

symmetry exist, most notably the six-coordinate complexes of Ni²⁺. The ESR signal obtained for the solid Fe and Ru diimines is remarkably similar to those for these Ni²⁺ complexes. In particular, the Ni species typically have *g* ~ 2.2, with the *g* shift arising from spin-orbit coupled mixing the "t₂⁵e³" ligand field excited state with the ground state¹⁷⁻¹⁹ while the line widths (ΔH_{pp}) span the range from ~10¹ to ~10³ G.¹⁹ Thus, both *g* values and line widths are in agreement with the present data for $[M(\text{diimine})_3]^0$ (M = Fe, Ru; Table I). Furthermore, strong exchange interactions in the Ni lead to an averaging of the expected fine structure so that only a single, broad line is observed,¹⁸ also in agreement with the present results (Figure 1C). Thus, it appears that the best description of these precipitated products is in terms of a d⁸ ground-state configuration in distorted (likely D₃) symmetry.

The population of these dσ* orbitals is in contradiction to the cyclic voltammetric results (pattern and electron-transfer rate constants²⁰) that indicate that the reduction electrons enter ligand π* orbitals and remain there on a voltammetric time scale. However, spectroscopic data for the parent (d⁶) Fe complexes²¹ indicate that the lowest lying excited state is metal centered (dπ → dσ*). Thus, the dσ* orbitals are lower in energy than the Lπ* orbitals although there is photochemical evidence²² that the energy separation, $E(d\sigma^*) - E(L\pi^*)$, is small. Therefore, for the Fe complexes, occupation of the dσ* orbitals might be considered nominal while the observed behavior in solution (ligand localized) results from an unusual stabilizing influence of the solvent. Similarly, for these Ru complexes, the parent ions have a metal-to-ligand charge-transfer excited state (dπ → Lπ*) lying lowest,⁷ but again photochemical data indicate that the metal-centered excited state is only slightly higher in energy.^{23,24} Apparently the loss of the stabilizing solvation energy is sufficient to effect a reordering of the closely spaced dσ* and Lπ* orbitals so that a d⁸ ground state results. Of course, other factors associated with lattice formation likely contribute to this reordering.

However, the observation of ligand-localized orbital population for [Os(bpy)₃]⁰ is readily rationalized. Whereas the Lπ* and dσ* orbitals are energetically close in Fe and Ru diimines, the spacing is much larger for the Os complex^{25,26} because, while the ligand

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orbitals are little perturbed along the series Fe, Ru, Os, the crystal field splitting ($10Dq$) is much greater for Os than the other two metal ions.²⁶ Thus, the energetic changes associated with precipitation are insufficient to effect the energy level reordering.

In summary, the reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$ can be described by the spatially isolated orbital model discussed previously^{1,2,5,6} whereby the added electrons reside in orbitals localized on single ligand rings with minimal interligand interactions. The three-electron product appears more complicated, but the difference is likely attributable to increased metal character of the redox orbital rather than ligand interaction since no $S > 1/2$ behavior is evident. The unusual signal seen for the solids, $[\text{M}(\text{diimine})_3]^0$ ($\text{M} = \text{Fe}, \text{Ru}$), is concluded to be due to an essentially d^8 metal-localized configuration resulting from energy level reordering on precipitation. This behavior is consistent with the available data on the energy spacing between $L\pi^*$ and $d\sigma^*$ orbitals since $[\text{Os}(\text{bpy})_3]^0$ (solid) for which this spacing is largest gives only simple ligand-localized behavior. A similar metal-localized configuration might also be anticipated for the solid one-electron products of Fe and Ru (d^7 in this case) although it has not been possible to precipitate these species.

Experimental Section

$[\text{Os}(\text{bpy})_3]X_2$ ($X = \text{Cl}^-, \text{ClO}_4^-$) was provided by R. Donohoe of this department. The controlled-potential electrolysis to produce the reduction product for ESR was carried out at a potential at least 50 mV cathodic of the respective voltammetric peaks. The post-electrolysis cyclic voltammetry described previously²⁷ was used to verify the identity and stability of the reduced species. All three reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$ are stable for periods of days. All other reagents, purification procedures, apparatus, and experimental conditions are the same as those described previously.^{2,6} The solid products were isolated by two-electron reductions of millimolar solutions of the parent ions in CH_3CN that resulted in nearly quantitative precipitation. The precipitate was allowed to settle, and the solvent/supporting electrolyte solution was decanted. The resulting moist solid was then pipetted into the ESR tubes and the remaining solvent was removed under vacuum. In all cases a small amount of supporting electrolyte remained mixed with the dry, powdered sample.

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Heteropolyatomic Anions of the Post Transition Metals. Synthesis and Structure of the Dileadantimonide(2-) Anion, $\text{Pb}_2\text{Sb}_2^{2-}$

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As has been recently described,² the general use of crypt to complex the alkali-metal counterions allows one to readily stabilize salts containing the polyatomic Zintl ions of the post transition elements relative to the corresponding intermetallic phases.

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Furthermore, the application of this method to heteroatomic systems allows the sampling of configurations and electronic structures that are evidently unknown or inaccessible in the homoatomic regime, for example, as the butterfly-shaped $\text{Tl}_2\text{Te}_2^{2-3}$ and the bicapped-antiprismatic TlSn_9^{3-4} . Thus, the expected tetrahedral species M_4^{4-} ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) that are isoelectronic with P_4 etc. have not yet been isolated as this kind of salt, the stability of this configuration evidently being limited to the 1:1 intermetallic phases that these elements form with the alkali metals Na-Cs.^{5,6} On the other hand, the lower charge density achieved in the isoelectronic $(\text{M}^{\text{IV}}\text{M}^{\text{V}})_2^{2-}$ ions does appear to favor stability, as the $\text{Sn}_2\text{Bi}_2^{2-}$ example has been isolated and structurally characterized as the 2,2,2-crypt-potassium salt.⁷ In this case the nominal tetrahedra— D_{2d} in fact because of their heteroatomic nature—occur disordered over all possible orientations in the cation matrix so that only the tetrahedral average is found by X-ray diffraction. The present note reports the corresponding data for the antipode $\text{Pb}_2\text{Sb}_2^{2-}$ where the deviation from tetrahedral symmetry is probably greater and the disordering is found to be incomplete.

Experimental Section

Materials and Synthesis. All manipulations were performed either in an inert atmosphere drybox or on a vacuum line. Antimony (99.9999%) was obtained from A. D. MacKay, Inc., lead (Certified Reagent) from Fischer Scientific Co., potassium ("purified") from J. T. Baker Chemical Co., and the 2-2-2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) from Merck. Ethylenediamine (en) (Fisher Scientific Co.) was first dried by refluxing over CaH_2 and then stored over molecular sieve. The dark gray alloy composition KPbSb was prepared by fusion at 970 °C of stoichiometric amounts of the elements in a sealed tantalum tube enclosed in a fused silica jacket after which the sample was air quenched. Vessels used for crypt-alloy reactions have been previously described.^{8,9}

Important parameters in the reaction of this alloy with crypt in ethylenediamine not only include the length of time allowed for the reaction and for any necessary concentration of the solution prior to crystal growth but also include whether the solution is decanted from the alloy some time during the reaction or just before the crystallization step. The KPbSb composition readily formed a reddish brown solution that was decanted from the alloy after 1 week and crystals grown by slow solvent removal over 2 weeks, utilizing the small gradient achieved between the sample container at room temperature and water in an open Dewar flask. Black pseudo-hexagonal plates of $(\text{crypt-K})_2\text{Pb}_2\text{Sb}_2$ (I) separate first, followed by about twice as much of an unknown phase II. The metallic composition of the crystals was confirmed semiquantitatively by X-ray fluorescence. A shorter reaction time and a longer crystal growth period (and possibly inhomogeneities in the alloy) instead first yielded $(\text{crypt-K})_2\text{Sb}_4^{10}$ followed again by major amounts of phase II. If the solution was not decanted from unreacted alloy beforehand, the product crystals were free of lead, consisting of a small amount of the Sb_2^{2-} phase and a good yield of a second phase thought to contain Sb_3^{3-10} . Solution-alloy redistribution reactions that are time and concentration dependent are presumably responsible for some of these differences.

The prominent phase II forms as long thin blades that sometimes curl slightly when a hard vacuum is applied to remove all the solvent. Cutting the crystals for mounting tends to damage them. An adequate crystal for data collection was not found, but the cell volume would indicate a 3- anion without en ($a = 15.12 \text{ \AA}$, $b = 19.82 \text{ \AA}$, $c = 14.41 \text{ \AA}$, $\alpha = 94.3^\circ$, $\beta = 108.8^\circ$, $\gamma = 90.9^\circ$, $V = 4074 \text{ \AA}^3$ from diffractometer alignment after standard selection). A semiquantitative analysis of the products of the second reaction $[(\text{K}^+ - \text{crypt})_2\text{Sb}_4 + \text{II}]$ by X-ray fluorescence indicated the mixture was quite antimony rich; pseudo-square-planar PbSb_3^{3-} is one possibility based on known types of ions.

Crystal Data. Crystals of I were rinsed with dry heptane to remove unreacted crypt, and then suitable members were mounted into 0.3- or

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