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Communications

Valence Delocalization despite Weak Metal−Metal Coupling in a Bis(organoosmium(III,II)) Complex with a Pyrazine Bridge

Markus Glöckle[†] and Wolfgang Kaim*[,†]

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70550 Stuttgart, Germany

Jan Fiedler[‡]

J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,
Dolejškova 3, CZ-18223 Prague, Czech Republic

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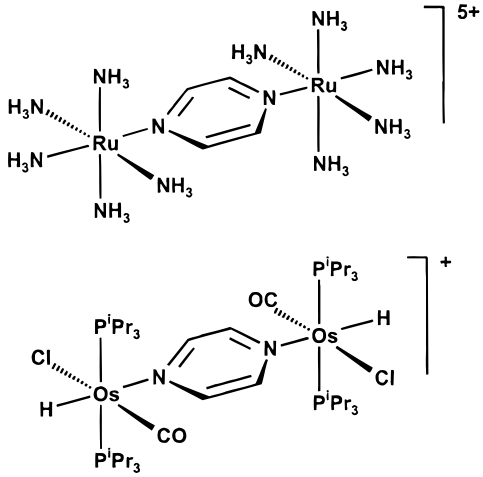
Summary: Carbonyl vibrational spectroelectrochemistry of $\{(\mu\text{-pz})[Os(P^iPr_3)_2(CO)(H)Cl]_2\}^{0/+}$ *in dichloromethane reveals valence delocalization of the mixed-valent state despite relatively weak metal−metal coupling, as evident from the comproportionation constant* $K_c = 10^{4.3}$ *and the intervalence charge-transfer band at 1705 nm* ($\epsilon = 1250$ M^{-1} cm^{-1}, $\Delta\nu_{1/2} = 3700$ cm^{-1}). *The rather low charge and nonpolar medium, i.e., the absence of valence trapping by counterions or solvent molecules, favor this particular situation.*

Chart 1



Due to its structural simplicity, the pyrazine-bridged Creutz−Taube ion $\{(\mu\text{-pz})[Ru(NH_3)_5]_2\}^{5+}$ has become the epitome of a mixed-valent coordination compound[1,2] (Chart 1). Such materials are of interest for their role in the study of reaction mechanisms,[3] for their unusual spectroscopic features such as very long wavelength intervalence charge-transfer bands,[4] for their biochemical relevance,[5] and for their potential in the area of “molecular electronics”.[6] While the Creutz−Taube ion was discussed controversially for some time with regard to localization (Ru^{II}/Ru^{III}) or delocalization (2 × $Ru^{2.5}$)

[†] Universität Stuttgart. E-mail address: kaim@iac.uni-stuttgart.de.
[‡] Academy of Sciences of the Czech Republic.
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of the valence,[1,7] the corresponding osmium analogue $\{(\mu\text{-pz})[\mathrm{Os(NH_3)_5}]_2\}^{5+}$ was clearly identified as a valence-averaged system with two $\mathrm{Os}^{2.5}$ centers.[8] Among the evidence for this notion was the large comproportionation constant $K_c = 10^{13.0}$ for this intermediate ion in aqueous solution;[8] the Creutz-Taube ion exhibits $K_c = 10^{6.6}$ in aqueous medium[1] and $10^{7.3}$ in acetonitrile.[2]

$$K_c = 10^{\Delta E/59\ \mathrm{mV}} = [\mathrm{M}^{(n+1)}]^2/[\mathrm{M}^n][\mathrm{M}^{(n+2)}] \qquad (1)$$

$$\mathrm{M}^n + \mathrm{M}^{n+2} \rightleftharpoons 2\mathrm{M}^{n+1}$$

Recently we reported the observation that the $\{(\mu\text{-pz})[\mathrm{Os(CN)_5}]_2\}^{5-}$ ion exhibits $K_c = 10^{5.8}$ in acetonitrile; however, the appearance of an aromatic ring vibration at 1582 cm^{-1} *exclusively* for this mixed-valent intermediate suggested asymmetry and thus valence localization on the time scale of about 10^{-12} s for this experiment.[9]

We have now studied another pyrazine-bridged diosmium(III,II) species, $\{(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2\}^+$, which contains two organometallic complex fragments and a relatively small charge. The $[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]$ fragment is capable of binding $\mathrm{H_2}$, $\mathrm{O_2}$, and several interesting organic functions for possible catalytic conversion.[10,11] When it is bound to TCNE or TCNQ, this fragment exhibits the ability to donate electrons into the π system of acceptor ligands.[12] Due to the very limited solubility of the mixed-valent material and its diosmium(II,II) precursor we could investigate the dinuclear pyrazine complex only in dichloromethane solution. However, the results obtained shed some light on the variability of mixed-valent systems, on the possibly large role of the medium, and on the correlation between valence delocalization and the extent of metal−metal coupling.

Reaction of 2 equiv of $[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]$ with coordinatively unsaturated osmium(II) ($5d^6$ configuration) with pyrazine in degassed toluene produced neutral dinuclear $(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2$, which proved to be poorly soluble in dichloromethane (saturation concentration approximately 1.6×10^{-4} M) and insoluble in all other common solvents. Nevertheless, characterization by analysis, cyclic voltammetry, ^{1}H NMR (solution), and IR and UV/vis spectroscopy (solid state and solution) established the identity of this precursor material for the mixed-valent monocation.[13] Two one-electron waves are observable on oxidation of $(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2$ (Figure 1); their separation by 250 mV leads to a K_c value of $10^{4.3}$.

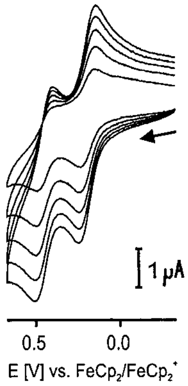

Figure 1. Cyclic voltammogram of $(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2$ in dichloromethane/0.2 M $\mathrm{Bu_4NPF_6}$ at 0.5, 1.0, 1.5, 2.0, and 2.5 V/s scan rates. Potentials vs $[\mathrm{Fe(C_5H_5)_2}]^{+/0}$: +0.20 and +0.45 V.

Spectroelectrochemical monitoring of the more reversible (Figure 1) first couple $\{(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2\}^{0/+}$ in an optically transparent thin-layer electrolytic (OTTLE) cell[14] exhibits the expected[8,9,15] decrease of the intense ($\epsilon = 19\,660\ \mathrm{M^{-1}\,cm^{-1}}$) metal-to-ligand charge-transfer band at 534 nm and the appearance of a broad, symmetrical intervalence charge transfer (IVCT) band at 1705 nm ($\epsilon = 1250\ \mathrm{M^{-1}\,cm^{-1}}$, band half-width $\Delta\nu_{1/2} = 3700\ \mathrm{cm^{-1}}$). Not unexpectedly, the mixed-valent species remained EPR-silent down to 3.3 K due to very rapid relaxation;[16] however, the carbonyl stretching band in the infrared spectrum of the homovalent $\mathrm{Os^{II,II}}$ precursor was observed to simply shift to higher energy on oxidation to the mixed-valent intermediate (Figure 2). The shift of the osmium hydride vibrational band could not be observed due to the low band intensity and the thin-layer situation of the OTTLE experiment; a pyrazine ring vibration in the 1580 $\mathrm{cm^{-1}}$ region was not detected.

Whereas the IR spectroelectrochemical experiment clearly indicates[17−19] two equivalent organometal frag-

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[13] (a) $\{(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2\}$: satisfactory C, H, N analysis; ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ −14.45 (t, 2H, Os−H, J = 20 Hz), 1.14 (m, 72H, $\mathrm{CH_3}$), 2.66 (m, 12H, CH), 9.7 (br, pz H); IR (KBr) ν_{CO} 1879 (s) $\mathrm{cm^{-1}}$, $\nu_{\mathrm{Os-H}} = 2171$ (w) $\mathrm{cm^{-1}}$; IR ($\mathrm{CH_2Cl_2}$) ν_{CO} 1878 $\mathrm{cm^{-1}}$; UV/vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max}$ 534 nm ($\epsilon = 19\,660\ \mathrm{M^{-1}\,cm^{-1}}$, $\Delta\nu_{1/2} = 2430\ \mathrm{cm^{-1}}$); UV/vis (solid) $\lambda_{\max}$ 530 nm; cyclic voltammetry ($\mathrm{CH_2Cl_2}$/0.2 M $\mathrm{Bu_4NPF_6}$, platinum electrode, 2 V/s scan rate) $E_{1/2}$ = +0.20 and +0.45 V vs $[\mathrm{Fe(C_5H_5)_2}]^{+/0}$, peak potential differences 99 and 108 mV, respectively; no reduction until −1.9 V. (b) $\{(\mu\text{-pz})[\mathrm{Os(P^iPr_3)_2(CO)(H)Cl}]_2\}^+$: no EPR signal down to 3.3 K; IR ($\mathrm{CH_2Cl_2}$) ν_{CO} 1933 $\mathrm{cm^{-1}}$; UV/vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max}$ 356, 645, 1705 nm.

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Table 1. Characteristics of Pyrazine-Bridged Diosmium(III,II) Complexes and Related Compounds $\{(\mu\text{-pz})[ML_x]_2\}^n$

ML_x	n	K_c	λ_{IVCT} (nm)	ϵ (M^{-1} cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	solvent	ref
$Os(NH_3)_5$	5+	$10^{13.0}$	3330[a]	4000	n.r.[b]	H_2O/HCl	8
			2940[a]	3000	n.r.		
			890[a]	2700			
$Os(CN)_5$	5−	$10^{5.8}$	5071[a]	7000	220	CH_3CN	9
			4032[a]	8100	960		
			1395[a]	6600	1450		
$Os(P^iPr_3)_2(CO)(H)Cl$	1+	$10^{4.3}$	1705	1250	3700	CH_2Cl_2	this work
$W(P^iPr_3)_2(CO)_3$	1+	10^{11}	2004	4600	730	CH_2Cl_2	22
$Ru(NH_3)_5$	5+	$10^{7.3}$	1600	n.r.	n.r.	CH_3CN	2

[a] Main bands in the near-infrared region (including singlet−triplet transitions). [b] n.r. = not reported.

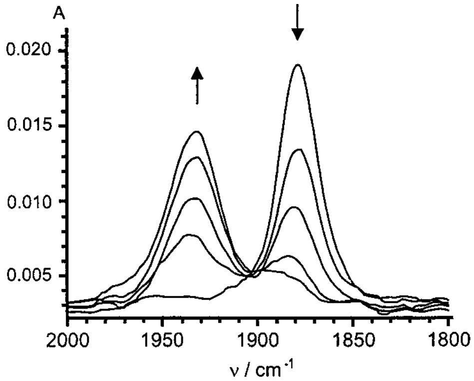

Figure 2. IR spectroelectrochemistry of $\{(\mu\text{-pz})[Os(P^iPr_3)_2(CO)(H)Cl]_2\}^{0/+}$ in the carbonyl vibration region (CH_2Cl_2/0.2 M Bu_4NPF_6, band shift from 1878 to 1933 cm^{-1} on oxidation).

ments and thus the symmetrical, delocalized situation $\{(\mu\text{-pz})[Os^{2.5}(P^iPr_3)_2(CO)(H)Cl]_2\}^+$, the value of $10^{4.3}$ for K_c signifies relatively weak metal−metal coupling across the pyrazine bridge (Table 1).

Similarly, the reproducibility of the IVCT band energy by eq 2 supports the description of this ion as a weakly coupled system.[20]

$$\Delta\nu_{1/2} = [2310\nu_{IVCT}]^{1/2} \qquad (2)$$

$$\Delta\nu_{1/2}(\text{calc}) = [2310 \times 5860]^{1/2} = 3679\ \text{cm}^{-1}$$

$$\Delta\nu_{1/2}(\text{exptl}) = 3700\ \text{cm}^{-1}$$

We attribute this infrequently described situation of a valence-delocalized yet only weakly coupled mixed-valent dimer to the low overall charge and largely nonpolar environment (CH_2Cl_2 solution)—a familiar situation for organometallic compounds. The absence of charge and valence trapping as a consequence of rather weak solute−solvent interactions[21] has been similarly invoked for the $5d^5/5d^6$ mixed-valent organometallic compound $\{(\mu\text{-pz})[W^{0.5}(P^iPr_3)_2(CO)_3]_2\}^+$, which, however, displays higher K_c values $>10^8$ despite smaller oxidation numbers (Table 1).[22] Within the series of diosmium(III,II) species (Table 1), the $\{(\mu\text{-pz})[Os(CN)_5]_2\}^{5-}$ ion appears to be localized despite the higher K_c value of $10^{5.8}$, probably due to charge trapping.[9] In contrast, the metal−metal interaction in the $\{(\mu\text{-pz})[Os(NH_3)_5)_2\}^{5+}$ ion is apparently large enough ($K_c = 10^{13.0}$) to compensate charge trapping even in aqueous medium.[8] Unfortunately, the poor solubility precludes an extensive investigation of solvent dependence in the present, weaker coupled but not charge-trapped case; better soluble analogues of organometallic mixed-valent systems will have to be developed for further such studies.

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Supporting Information Available: Text giving a summary of experimental procedures and figures giving IR and UV/vis/near-IR spectra (4 pages). Ordering information is given on any current masthead page.

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