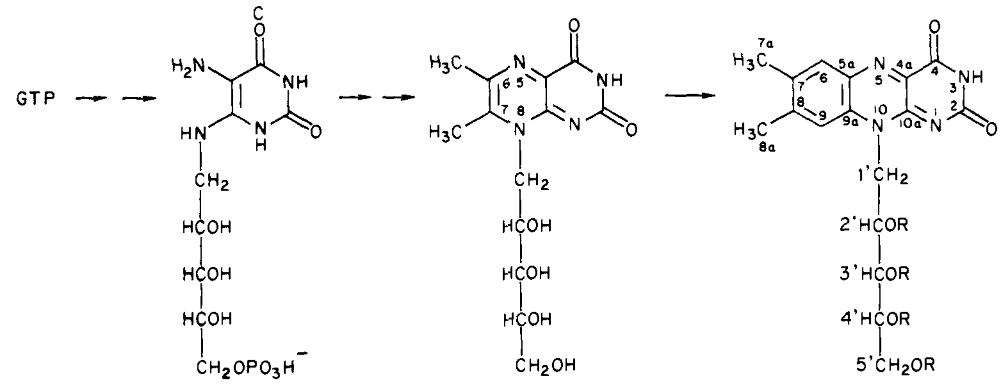
Scheme I. Biosynthesis of Riboflavin

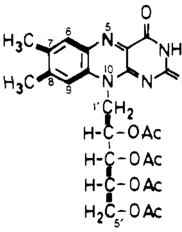


1

2

3a, R = H
b, R = C(=O)CH_3

Scheme II



XL-200) of this material in $CDCl_3$ (Figure 1) exhibits complex multiplets for the ribitol carbons 2', 3', and 4' and for the aromatic carbons 4a, 5a, 6, 7, and 9a. To simplify the spectrum, a ^{13}C-observe variant of the ^1H homonuclear 2-D-*J* spectroscopy method of Aue et al.[4] was implemented with the Varian HOM2DJ program after adjustment of spectral parameters for ^{13}C observation with ^1H decoupling. Projection of the data from this ^{13}C homonuclear 2-D-*J* spectrum onto the chemical shift axis yielded a ^{13}C NMR spectrum that was both ^1H and ^{13}C "broad-band decoupled" (Figures 1 and 2). The $^{13}C-^{13}C$ coupling information was most conveniently displayed in the form of slice plots. Effects of strong coupling are seen in the aromatic region of the projected spectrum (Figure 2). Symmetrization of AB patterns gives projection signals at the midpoints of the doublets. Peaks b and c represent coupled and uncoupled signals for C-5a, respectively, peaks e and f are the analogous signals for C-6, and peak d is a combination line, the slice plot of which depicts the frequency difference between the inner lines of the AB pattern.

Once the multiplicities had been determined, the nontrivial task of assigning the biochemical connectivities[5] required attention. Bax and co-workers[6] have reported on the use of double-quantum coherence NMR (INADEQUATE) to trace the connectivities of a carbon skeleton through a two-dimensional technique. The 2-D INADEQUATE spectrum of the labeled riboflavin tetraacetate was measured (Figure 3) on the Varian instrument using the program denoted as CCC2D, which yields spectra with a mirror plane on the double-quantum axis. The spectrum clearly shows the incorporation of intact two-carbon units from glucose into the xylene moiety (Scheme II). Thus biochemical connectivities are observed for the following coupled pairs: 7–7a, 8–8a, 9–9a, and 6–5a. The connectivities of the ribitol carbons 1'–2' and 4'–5' were also detected, but the 2'–3' and 3'–4' connectivities were not determined.

A powerful attribute of the 2-D INADEQUATE technique is that the revelation of carbon connectivities often directly leads to signal assignments. In the present case, if the well-documented[8,9] assignments of carbons 8a and 9 are accepted, then the assignments of 5a, 6, 7, 7a, 8, and 9a are readily apparent. Distinction between carbons 5a and 6 is made on the basis of a directly bonded proton at C-6. 2-D ^{13}C homonuclear correlation spectroscopy, which was also performed in a manner analogous to the proton experiment,[10] permitted the unambiguous assignments of carbons 2', 3', and 4' based on the couplings of 2' with 1' and 4' with 5'.

On the basis of further ^{13}C NMR studies at 118 MHz (not reported here), it was found that connectivity between carbons 2' and 3' was only partially retained from glucose, while 3'–4' showed a high degree of connectivity. It is concluded that the majority of the fed glucose did not directly enter the pentose pool by decarboxylation, but rather that there was considerable cycling of glucose through the glycolytic pathway before conversion into a pentose. From the present data it can be concluded that the four carbon atoms of **2** in question arise from the sugar pool as either two two-carbon units or one four-carbon unit but probably not via a 1 + 3 or 1 + 2 + 1 carbon combinations, unless such combinations involve intramolecular rearrangements.

Acknowledgment. We thank Dr. Ralph Hurd of Nicolet Instruments, Freemont, CA, for performing the 2-D ^{13}C homonuclear correlation experiment. This work was supported by the Deutsche Forschungsgemeinschaft (Grant Ba/574/5-6 to A.B.) and by the U.S. Public Health Service (NIH Grant AI 11728 to H.G.F.). H.G.F. and P.J.K. are grateful to the Alexander von Humboldt-Stiftung for a U.S. senior scientist award and a fellowship, respectively.

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(5) We call "biochemical connectivities" those atomic connectivities that are retained or generated during the biochemical conversion of a precursor to a product.

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(7) E. Breitmaier and W. Voelter, *Eur. J. Biochem.*, **31**, 234 (1972).

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Mixed-Valence Pyrazine-Bridged Binuclear Complexes of Osmium Ammines

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Received October 12, 1982

We here report the synthesis and properties of the mixed-valence ion $[(NH_3)_5Os(pyz)Os(NH_3)_5]^{5+}$ (I) which exhibits several striking features, including intense electronic transitions in the

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normal IR region (3000–3500 cm^{-1}) and a high stability against disproportionation ($K_{com} = 7 \times 10^{12}$). Species I has particular interest to us as a very close analogue to the still controversial diruthenium complex ion.[1-5] The electrostatic charge types are identical, and the Franck–Condon barriers to optical electron transfer in a valence-trapped approximation (class II) for both Ru and Os are expected to be dominated by solvent effects and thus to be comparable. This accepted, differences are ascribable to the electronic coupling, neglecting for the time being differences in spin–orbit coupling. If communication between metals takes place primarily via π^* levels of the bridging ligand or direct orbital overlap, I is expected to exhibit the greater interaction because of greater d orbital extension of the metal.[6] Conversely, interactions by π-bonding orbitals will be diminished for Os relative to Ru.

The (μ-pyrazine)decaamminediosmium(III) ion, $([(NH_3)_5Os]_2pyz)^{6+}$, was prepared by exploiting the readily substituted triflato group and the high solubility of $[(NH_3)_5Os(OSO_2CF_3)](O_3SCF_3)_2$ in acetone.[7,8] It was separated by cation-exchange chromatography and was isolated as a chloride salt.[9] Cyclic voltammetry (CV) showed two well-separated reversible couples (Table I) with comparable currents for all peaks. A spectrophotometric titration of the 6+ ion under Ar with $[Ru(NH_3)_6]^{2+}$, which can produce only the intermediate oxidation state, required 1.1 ± 0.1 mol of Ru(II)/mol of osmium dimer. The mixed-valence 5+ species separated as a red, air-sensitive tosylate salt when 4-toluenesulfonic acid was added to the reduced solutions.[10] The (II,II) oxidation state was attained by reduction with Zn(Hg) to produce a blue-violet solution. Exposure to air caused very rapid oxidation to the 5+ state, the succeeding stage being much slower.

From the redox potentials K_{com} is calculated as 7×10^{12}—10^7-fold greater than the diruthenium analogue—the large value being indicative of greater interactions in the diosmium complexes. Prominent features in the spectrum of the 4+ ion (Figure 1) are the ligand π to π^* transition (UV) and two visible MLCT bands, with no absorptions in the near-IR region having $\epsilon > 100$ M^{-1} cm^{-1}. The spectrum of the (III,III) species exhibits the ligand π to π^* transition and an intense bimodal band at 420 nm with a higher energy shoulder that we attribute to MLCT. Such features also appear in the spectra of both the monomeric pentaammine(methylpyrazinium)osmium(III) ion[7] and the $[(NH_3)_5Os(pyz)Rh(NH_3)_5]^{6+}$ ion.[11] As expected, for all these Os(III)-containing ions,[7] a rich near-IR spectrum associated with spin–orbital transitions is observed, with that for the diosmium(III) μ-pyrazine complex having the most features and the most intense absorption. The spectrum of $([(NH_3)_5Os]_2pyz)^{5+}$ is radically different and cannot be construed as a summation of the spectra of Os(II) and Os(III). We conclude that the mixed-valence ion is delocalized (class III), as is the case for the μ-dinitrogen analogues.[13-16] In particular, there are no strong bands in the characteristic Os(III) pentaammine spin–orbital region (~2100 nm). However, in the IR region, strong bands ($\epsilon \sim 10^3$–10^4 M^{-1} cm^{-1}) appear at approximately 3000 and 3400 cm^{-1}. Deuteration of the ammines does not substantially alter these bands but gives a new weaker band at 2300–2450 cm^{-1}, corresponding to the N–D stretch. We assign the strong IR bands to electronic transitions, an assignment that is supported by the properties observed for the unsymmetrical species *cis*-$[(NH_3)_4(N_2)Os(pyz)Os(NH_3)_5]^{5+}$. It was prepared from *cis*-$[Os(NH_3)_4(N_2)(pyz)](BPh_4)_2$[6] and $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ in acetone and was converted to *cis*-$[(NH_3)_4ClOs(pyz)Os(NH_3)_5]Cl_5$ by O_2 oxidation in 5 M HCl at 90 °C.[17]

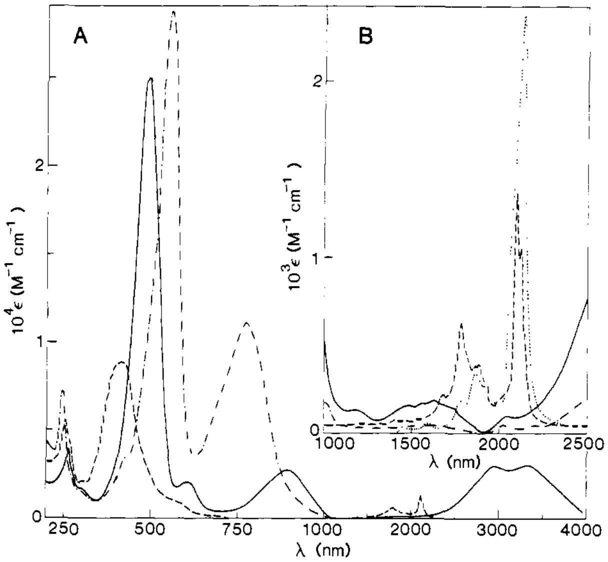

Figure 1. (A) UV–visible (0.01 M HCl), near IR (0.01 M DCl/D_2O), and IR spectra (KBr, N-deuterated) of $[(NH_3)_5OspyzOs(NH_3)_5]^{6+}$ (---), $[(NH_3)_5OspyzOs(NH_3)_5]^{5+}$ (—), and $[(NH_3)_5OspyzOs(NH_3)_5]^{4+}$ (-··-) at 25 °C. (B) Near infrared spectra (0.01 M DCl/D_2O) of $[(NH_3)_5OspyzOs(NH_3)_5]^{6+}$ (---), $[(NH_3)_5OspyzOs(NH_3)_5]^{5+}$ (—), $[(NH_3)_5OspyzOs(NH_3)_5]^{4+}$ (-··-) and $[(NH_3)_4(N_2)OspyzOs(NH_3)_5]^{5+}$ (···) at 25 °C. Most of the absorbance of the extremely air-sensitive 4+ ion, in the near IR is due to contamination with ~20% of the 5+ ion.

Table I. Cyclic Voltammetry Results for Osmium Pyrazine Complex Ions

complex	$E_f(6+/5+)^a$	$E_f(5+/4+)^a$
$([(NH_3)_5Os]_2pyz)^{n+}$	+0.32	−0.44
$[(NH_3)_4ClOs(pyz)Os(NH_3)_5]^{n+}$	$+0.19^{b,c}$	-0.52^d
$[(NH_3)_4(N_2)Os(pyz)Os(NH_3)_5]^{n+}$	$+1.11^e$	+0.13
$[(NH_3)_5Os(pyz)Rh(NH_3)_5]^{n+}$	+0.25	

[a] $(E_a + E_c)/2$, volts vs. NHE; medium = 0.10 M HCl, Ar, glassy carbon electrode, scan rate = 100 mV s^{-1}. [b] Medium = 0.50 M NaCl, 10^{-3} M HCl. [c] 5+/4+. [d] 4+/3+. [e] $i_c/i_a < 1$, E_a given (100 mV s^{-1}).

The electronic spectrum of the mixed-valence $[(NH_3)_4ClOs(pyz)Os(NH_3)_5]^{4+}$ ion (prepared by reducing the 5+ ion under Ar with $[Ru(NH_3)_6]^{2+}$) is similar to that of the decaammine mixed valence ion, except for a higher energy shift (~500 cm^{-1}) of the IR electronic transitions. The proximity of these bands to the low-energy edge of the near-IR region permitted a solution spectrophotometric titration to be carried out, which showed

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(1) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988–3989.

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(3) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149–193.

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(6) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129–5136.

(7) Lay, P. A.; Magnuson, R. H.; Sen, J. P.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658–7659.

(8) pyz = pyrazine = 1,4-diazine; triflate = trifluoromethanesulfonate = $CF_3SO_3^-$.

(9) $([(NH_3)_5Os]_2pyz)Cl_6 \cdot H_2O$. Anal. ($C_4H_{36}N_{12}Cl_6OOs_2$) C, H, N.[20] The complex exhibited very similar IR spectral properties to those reported for the ruthenium analogue.[2,21]

(10) $([(NH_3)_5Os]_2pyz)(Tos)_5 \cdot H_2O$. Anal. ($C_{39}H_{71}N_{12}O_{16}S_5Os_2$) C, H, N.[20]

(11) This was synthesized by the reaction of $[Rh(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$[12] with $[Os(NH_3)_5pyz](CF_3SO_3)_3$ in sulfolane for 1 day at 60–80 °C and was isolated as the chloride salt, $[(NH_3)_5Os(pyz)Rh(NH_3)_5]Cl_6 \cdot H_2O$. Anal. ($C_4H_{36}N_{12}Cl_6OOsRh$) C, H, N.[20] ($C_4H_{34}N_{12}Cl_6OOsRh$) C, H, N.[20]

(12) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 846–847.

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(16) Bomben, K. D.; Jolly, W. L.; Magnuson, R. H.; Richardson, D. E., to be submitted for publication.

(17) $[(NH_3)_4ClOs(pyz)Os(NH_3)_5]Cl_5$. Anal. ($C_4H_{31}N_{11}Cl_6Os_2$) C, H, N.[20] $[(NH_3)_4(N_2)Os(pyz)Os(NH_3)_5]Cl_5 \cdot H_2O$. Anal. ($C_4H_{33}N_{13}Cl_5OOs_2$) C, H, N.[20]

beyond doubt that the strong bands are associated only with the mixed-valence ions. However, the electronic spectrum of the (μ-pyrazine)-*cis*-(dinitrogen)nonaamminediosmium 5+ ion is dramatically different, approximating a summation of spectral properties of a tetraammine Os(II) coordinated by dinitrogen and pyrazinium ion and a pentaammine Os(III) pyrazinium center.[6,7] Further, the dinitrogen stretching frequency (2075 cm^{-1}) is appropriate for Os(II), and a band with comparable extinction occurs at 1600 cm^{-1}. This band has been previously associated with a ring mode of the pyrazine, which is normally IR inactive for D_{2h} symmetry but becomes allowed when the center of symmetry has been lost, as in localized mixed-valence systems.[18] This 1600-cm^{-1} peak is quite weak in $[(NH_3)_4ClOs(pyz)Os(NH_3)_5]^{4+}$ and is virtually absent in the symmetrical $([(NH_3)_5Os]_2pyz)^{5+}$ ion, in harmony with their delocalized description. A detailed spectra analysis is now in progress[19] to further our understanding of the electronic structures in relation to both a molecular orbital description and the effects of spin-orbital coupling.

Acknowledgment. Support of this work by National Science Foundation Grant CHE79-08633 and National Institutes of Health Grant GM13638-17 is gratefully acknowledged. P.A.L. also acknowledge the receipt of a CSIRO Postdoctoral Fellowship.

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(18) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064–1073.

(19) Lay, P. A.; Magnuson, R. H.; Taube, H., work in progress.

(20) It was necessary to use the Kirsten–Dumas method to obtain satisfactory analytical data for nitrogen. (Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164.) All microanalyses were performed by the Stanford University Microanalytical Laboratory.

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Additions and Corrections

Polymerized Phosphatidylcholine Vesicles. Synthesis and Characterization [*J. Am. Chem. Soc.* **1982**, *104*, 791]. STEVEN L. REGEN,* ALOK SINGH, GÜNTHER OEHME, and MANINDER SINGH.

Page 793: Figure 5 is in error. The turbidity of both polymerized and nonpolymerized vesicles of **5** decreases approximately 30% on going from 0% to 25% ethanol. When 45% ethanol in water is used, nonpolymerized vesicles are completely destroyed (no apparent absorbance at 400 nm) and the polymerized dispersion exhibits a turbidity that is 20% higher than that found in pure water. We presume that this increase in turbidity is due to vesicle aggregation. In addition, phosphorus analysis now reveals a small but detectable extractability ($CHCl_3$) of lipid monomer, oligomer, and/or polymer from aqueous polymerized dispersions of **5**.

Cyclohexaamylose Complexation with Organic Solvent Molecules [*J. Am. Chem. Soc.* **1982**, *104*, 6283–6288]. ROBERT I. GELB, LOWELL M. SCHWARTZ,* MICHAEL RADEOS, ROBERT B. EDMONDS, and DANIEL A. LAUFER.

In our recent paper[1] we regretfully failed to mention a previous publication by Matsui and Mochida[2] which reports studies of some of the same chemical systems. Both papers determine aqueous complexation constants of cyclohexaamylose with ethanol, 2-propanol, 2-methyl-2-propanol, and cyclohexanol. Although the two studies employed entirely different experimental techniques, the sets of equilibrium constant values are in essential agreement.

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(1) Gelb, R. I.; Schwartz, L. M.; Radeos, M.; Edmonds, R. B.; Laufer, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 6283–6288.

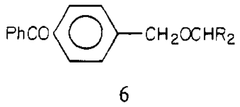
(2) Matsui, Y.; Mochida, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2808–2814.

Reactive Intermediates. Volume 2 [*J. Am. Chem. Soc.* **1982**, *104*, 7394].

First column, second line from the bottom, the sentence starting here should read as follows: An idea of the activity in these various fields is given by the fact that the carbene, free-radical, and silylene chapters are by far the longest, whereas that on arynes is less than a fifth as long as the carbene chapter.

Surface Photochemistry: Deviation of the Course of Reaction in Benzoin Ether Photolysis by Adsorption on Silica Gel [*J. Am. Chem. Soc.* **1982**, *104*, 6824–6825]. PAUL DE MAYO,* AKIRA NAKAMURA, PETER W. K. TSANG, and S. KING WONG.*

Page 6825, Scheme I: Structure **6** should be



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Definitive Evidence for Cycloheptatetraene from Dehydrobromination of Bromocycloheptatrienes [*J. Am. Chem. Soc.* **1982**, *104*, 7329–7330]. JAMES W. HARRIS and W. M. JONES.*

Page 7329: In footnote 3 the date should be 1970 not 1980.

Iron(III)–Porphyrin π-Cation Radical Complexes. Molecular Structures and Magnetic Properties [*J. Am. Chem. Soc.* **1982**, *104*, 6793]. GEORGES BUISSON, ALAIN DERONZIER, EMILE DUEE, PIERRE GANS, JEAN-CLAUDE MARCHON,* and JEAN-RENE REGNARD.

Page 6795, second column, the second paragraph should read: Pertinent bond lengths in the coordination unit of **3** are as follows: Fe–N$_1$, 2.04 (1); Fe–N$_2$, 2.05 (2); Fe–O, 2.13 (1) Å. The equatorial bond length values are consistent with one-electron occupancy of the $d_{x^2-y^2}$ orbital, and therefore they confirm the high-spin Fe(III) state, ...

Kinetics, Thermodynamics, and Mechanism of the Radical Chain Process for Ligand Substitution of Metal Carbonyls [*J. Am. Chem. Soc.* **1983**, *105*, 61–73]. J. W. HERSHBERGER, R. J. KLINGLER, and J. K. KOCHI.*

Page 63: Entry 18 of Table II for $(MeC_5H_4)Mn(CO)_3$ should be corrected to—$E_p^{ox} = 1.15$ V and $(E_p^{ox} + E_p^{red})/2 = 1.10$ V.

Organic Electronic Spectral Data. Volume XVII [*J. Am. Chem. Soc.* **1982**, *104*, 7673].

The third editor of this reviewed book should be H. Feuer.