

spectra are well simulated within the fast-relaxation limit. The fine structure and hyperfine structure parameters derived for 1 and 3 (Table V) agree reasonably well with those found for reduced P450,³⁵ with no significant preference for 1 or 3, besides $\Delta E_Q(T)$ for model compound 3 (as mentioned above), which represents the situation in the reduced enzyme closer than 1 does.

Conclusion

The (ethanethiolato)- and (tetrafluorobenzenethiolato)iron(II) picket-fence porphyrin complexes that we have synthesized and characterized are useful models for the reduced ferrous state of cytochrome P450. The Fe-S bond distance of 2.324 (2) Å in the ethanethiolato derivative, which is in complete agreement with the Fe-S bond length found by EXAFS spectroscopy in the reduced ferrous state of P450, shows together with the Mössbauer results obtained for the derivatives studied here that the cysteinato axial ligand remains bound to iron in the ferrous state of cytochrome P450 and is not protonated when reduction of the ferric to the ferrous state of P450 takes place. Oxygenation of some of these complexes led to models for the oxygenated state of cytochrome P450.^{13,34,37} The comparison of these structures and

Mössbauer properties with the properties of the oxygenated state of P450 led to the conclusion that the cysteinato axial ligand is also bound to iron in the oxy state of the enzyme.^{34,37,38}

Acknowledgment. R.W. is a recipient of an Alexander von Humboldt Award and thanks the Alexander von Humboldt Foundation for financial support.

Registry No. 1, 123411-74-5; 1', 123484-33-3; 2, 123484-31-1; 3, 123535-87-5; [Fe(TP_{pin})Cl], 86107-94-0.

Supplementary Material Available: Thermal parameters for anisotropic atoms (Table SI), hydrogen atom positions (Table SII), a complete set of bond lengths (Table SIII), a complete set of bond angles (Table SIV), and a full set of experimental X-ray data collection parameters (Table SVI) (17 pages); observed and calculated structure factor amplitudes ($\times 10$) for all observed reflections (Table SV) (23 pages). Ordering information is given on any current masthead page.

- (37) Schappacher, M.; Ricard, L.; Weiss, R.; Montiel-Montoya, R.; Bill, E.; Gonser, U.; Trautwein, A. X. *J. Am. Chem. Soc.* **1981**, *103*, 7646.
 (38) Dawson, J. H.; Kau, L. S.; Penner-Hahn, J. E. Sono, M.; Eble, K. S.; Bruce, G. S.; Hager, L. P.; Hodgson, K. O. *J. Am. Chem. Soc.* **1986**, *108*, 8114.

Contribution from the Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, West Germany

Stabilization of Biochemically Interesting Intermediates by Metal Coordination. 6.¹ Charge Transfer in Complexes of 1,3-Dimethylalumazine with Low-Valent Metals

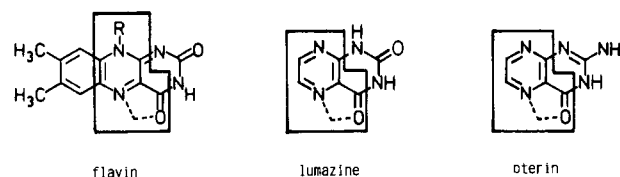
Christian Bessenbacher,² Conny Vogler, and Wolfgang Kaim*

Received March 10, 1989

Chelate complexes between O(4),N(5)-coordinating 1,3-dimethylalumazine and the metal fragments (Ph₃P)₂Cu⁺, (bpy)₂Ru²⁺ (bpy = 2,2'-bipyridine), and (OC)₃ClRe have metal-to-ligand charge-transfer absorption bands in the visible region. Cyclic voltammetry illustrates the thermodynamic and kinetic stabilization of the reduced state in these complexes.

Flavins, lumazines, and pterins (Chart I) are biochemically important molecules that can function as coenzymes by undergoing 1e- or 2e-transfer reactions coupled with (de)protonation.³⁻⁵ All three heterocycles (Chart I) contain a potentially metal-chelating α -carbonylpyrazine coordination site.⁶ In the oxidized form, flavins were found to bind only "soft", electron-rich metal centers⁷

Chart I



- (1) Part 5: Bessenbacher, C.; Ernst, S.; Kohlman, S.; Kaim, W.; Kasack, V.; Roth, E.; Jordanov, J. *J. Chem. Soc., Faraday, Trans. 1*, in press.
 (2) Present address: Department of Chemistry, York University, North York, Ontario, Canada M3J 1P3.
 (3) (a) Hemmerich, P.; Massey, V.; Wood, H. C. S. *Angew. Chem.* **1965**, *77*, 699; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 671. (b) Walsh, C. *Acc. Chem. Res.* **1980**, *13*, 148. (c) Bruce, T. C. *Acc. Chem. Res.* **1980**, *13*, 256. (d) Hemmerich, P.; Massey, V.; Michel, H.; Schug, C. *Struct. Bonding* **1982**, *48*, 93.
 (4) Andondonskaja-Renz, B.; Zeitler, H.-J. *Biochem. Clin. Aspects Pteridines* **1984**, *3*, 295. (b) Zeitler, H.-J.; Andondonskaja-Renz, B. *Ibid.* **1984**, *3*, 313.
 (5) (a) Scrimgeour, K. G. In *Chemistry and Biology of Pteridines*; Pfeleiderer, W., Knappe, W. R., Eds.; de Gruyter: Berlin, 1975; p 731. (b) Dryhurst, G. *Electrochemistry of Biological Molecules*; Academic Press: New York, 1977. (c) Dryhurst, G.; Raghavan, R.; Ege-Serpken, D.; Karber, L. G. *Adv. Chem. Ser.* **1982**, no. 201, 457. (d) Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101.
 (6) Bessenbacher, C.; Kaim, W. *Z. Anorg. Allg. Chem.*, in press.
 (7) (a) Hemmerich, P.; Lauterwein, J. *Inorganic Biochemistry*; In Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1975. (b) Wade, T. D.; Fritchie, C. J., Jr. *J. Biol. Chem.* **1973**, *248*, 2337. (c) Garland, W. T., Jr.; Fritchie, C. J., Jr. *Ibid.* **1974**, *249*, 2228. (d) Yu, M. W.; Fritchie, C. J., Jr. *Ibid.* **1975**, *250*, 946. (e) Selbin, J.; Sherrill, J.; Bigger, C. H. *Inorg. Chem.* **1974**, *13*, 2544. (f) Clarke, M. J.; Dowling, M. G. *Inorg. Chem.* **1981**, *20*, 3506. (g) Dowling, M. G.; Clarke, M. J. *Inorg. Chim. Acta* **1983**, *78*, 153. (h) Clarke, M. J.; Dowling, M. G.; Garafalo, A. R.; Brennan, T. F. *J. Biol. Chem.* **1980**, *255*, 3472. (i) Clarke, M. J. *Comments Inorg. Chem.* **1984**, *3*, 133.

whereas the singly reduced species, the flavosemiquinones, form stable complexes with rather normal metal ions.⁸ Complexes of lumazine (2,4(1*H*,3*H*)-pteridinedione) with divalent metal ions were described earlier,⁹ and the coordination chemistry of pterins¹⁰ has been discussed recently in the light of the discovery of a "molybdopterin" cofactor,¹¹ which apparently contains coordinatively linked pterin and molybdenum fragments.

Since the α -carbonylpyrazine moiety represents a strongly π -accepting chelate arrangement,^{1,6} the ligands (Chart I) are likely to form compounds with electron-rich metal fragments. Complexes of flavins with Ru(II),^{7f-i} Re(I),⁶ Ag(I),^{7b} and Cu(I)^{7c,d} were shown to exhibit structural and spectroscopic effects of

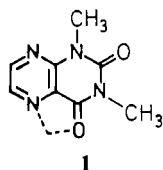
- (8) (a) Müller, G.; Hemmerich, P.; Ehrenberg, A.; Palmer, G.; Massey, V. *Eur. J. Biochem.* **1970**, *14*, 185. (b) Ehrenberg, A.; Müller, F.; Hemmerich, P. *Eur. J. Biochem.* **1967**, *2*, 286. (c) Ehrenberg, A. *Vitam. Horm. (N.Y.)* **1970**, *28*, 489.
 (9) Goodgame, M.; Schmidt, M. A. *Inorg. Chim. Acta* **1979**, *36*, 151.
 (10) (a) Burgmayer, S. J. N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 8310. (b) Kohzuma, T.; Odani, A.; Morita, Y.; Takani, M.; Yamauchi, O. *Inorg. Chem.* **1988**, *27*, 3854.
 (11) (a) Rajagopalan, K. V.; Kramer, S.; Gardlik, S. *Polyhedron* **1986**, *5*, 573. (b) Kramer, S. P.; Johnson, J. L.; Ribeiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* **1987**, *262*, 16357.

Table I. Cyclic Voltammetric Data for 1,3-Dimethylalumazine and Its Complexes in 1,2-Dichloroethane^a

compd	$E_{pc}(red)^b$	$E_{pa}(ox)^c$	$\frac{E_{pa}(ox) - E_{pc}(red)}{\Delta E_{pp}}$
1	-1.43		
[(1)Cu(PPh ₃) ₂](BF ₄)	-0.97	+1.28	2.25
[(1)Ru(bpy) ₂](PF ₆) ₂	-0.58 ^d	+1.46 ^f	2.04
[(1)Re(CO) ₃ Cl]	-0.60 ^e	+1.51	2.11

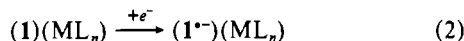
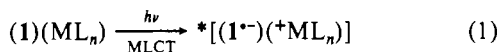
^aPotentials in V vs SCE; 100 mV/s scan rate, 0.1 M solution of Bu₄N⁺ClO₄⁻. ^bCathodic peak potential for reduction; irreversible processes unless noted otherwise. ^cAnodic peak potential for oxidation; irreversible processes unless noted otherwise. ^dQuasi-reversible; $\Delta E_{pp} = 75$ mV, $i_a/i_c = 0.4$. Other reduction processes at -1.45 and -1.77 V. ^eQuasi-reversible; $\Delta E_{pp} = 80$ mV, $i_a/i_c = 0.92$. ^fElectrode adsorption; $\Delta E_{pp} = 120$ mV.

metal-to-ligand charge transfer (MLCT). We now wish to report that the related 1,3-dimethylalumazine (**1**), a "debenzo" derivative



of the isoalloxazine ring system of flavins, forms strongly colored complexes with the differently charged d¹⁰ and d⁶ metal fragments (Ph₃)₂Cu⁺, (bpy)₂Ru²⁺, and (OC)₃ClRe under aprotic conditions (bpy = 2,2'-bipyridine).

Aprotic conditions allow the reactions of electron-rich organometallic compounds with this heterocyclic ligand "of biological origin"¹² and thus help to avoid complicating acid-base or hydrogen-bond interactions. Organometal coordination can facilitate reduction of π -acceptor ligands and even bring about metal-to-ligand electron transfer in the ground state.¹³ We therefore studied the complementary^{2,14,15} processes (eq 1, 2) of the complexes by absorption spectroscopy and cyclic voltammetry in order to understand the thermodynamic and kinetic stabilization of reduced intermediates by metal coordination to such coenzyme models.¹⁶



Experimental Section

Instrumentation. The following instruments were used: ESR, Bruker ESP 300; IR, Jasco A100; UV/vis/near-IR absorption, Shimadzu UV 160; UV/vis emission, Perkin-Elmer LS-3B; cyclic voltammetry, PAR potentiostat 363, Bank ramp generator VSG 72, glassy-carbon working electrode, saturated calomel reference electrode (SCE), 0.1 M solutions of tetrabutylammonium perchlorate in acetonitrile as electrolyte. All measurements were done in an argon atmosphere; rapid dissociation of many complexes in polar solvents required dissolution of solid materials in dry solvents immediately before the measurements.

1,3-Dimethylalumazine (**1**) and its *fac*-Re(CO)₃Cl complex were obtained according to published procedures.^{5,17}

[(1)Cu(PPh₃)₂](BF₄). A 1.0-g (0.83 mmol) sample of tetrakis(triphenylphosphane)copper(I) tetrafluoroborate and 160 mg (0.83 mmol) of **1** were reacted in 20 mL of dichloromethane for 1 h at room temperature. The orange solution was concentrated, and the product was precipitated in 380-mg yield (53%) by addition of *n*-hexane. IR (1,2-dichloroethane solution): $\tilde{\nu}(2-CO) = 1640$ cm⁻¹.

(12) Ioganson, A. A. *Usp. Khim.* **1985**, *54*, 479.

(13) (a) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 176. (b) Gross, R.; Kaim, W. *Angew. Chem.* **1987**, *99*, 257; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 251.

(14) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 776.

(15) (a) Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520. (b) Kaim, W.; Kramer, H. E. A.; Vogler, C.; Rieker, J. *J. Organomet. Chem.* **1989**, *367*, 107. (c) Vogler, C.; Hausen, H.-D.; Kaim, W.; Kohlmann, S.; Kramer, H. E. A.; Rieker, J. *Angew. Chem.*, in press.

(16) Ernst, S.; Hänel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733.

(17) Albert, A.; Brown, D. J.; Cheeseman, G. *J. Chem. Soc.* **1952**, 4219.

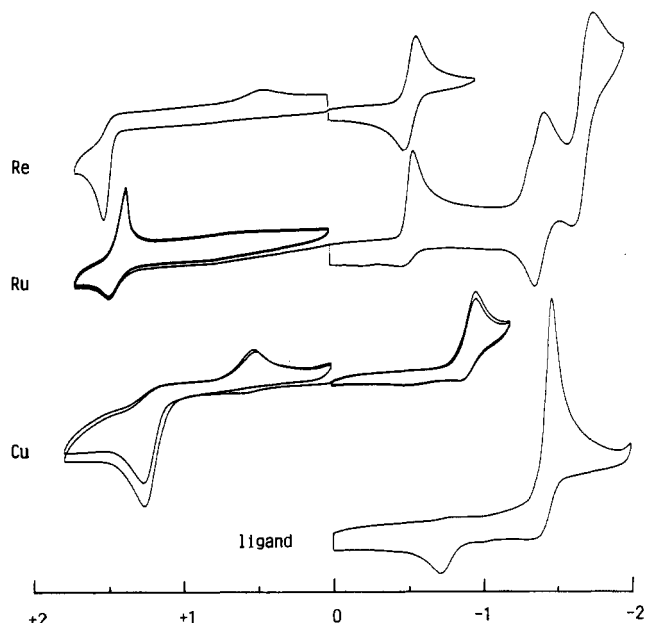


Figure 1. Cyclic voltammograms (separate scans for oxidation and reduction) of complexes [(1)Re(CO)₃Cl], [(1)Ru(bpy)₂](PF₆)₂, and [(1)Cu(PPh₃)₂](BF₄) and of the free ligand **1** in 1,2-dichloroethane/0.1 M Bu₄N⁺ClO₄⁻ (potential in volts vs SCE).

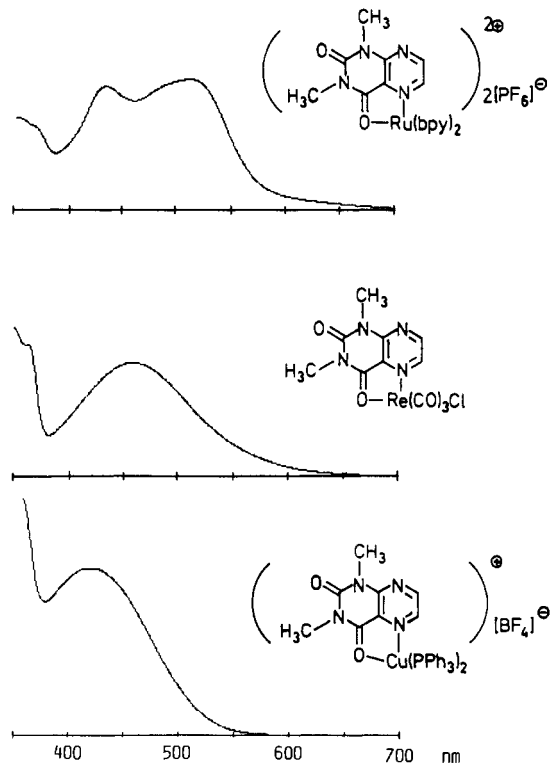


Figure 2. Long-wavelength absorption spectra of complexes in 1,2-dichloroethane (absorbance scale different for each spectrum).

Anal. Calcd for C₄₄H₃₈BCuF₄N₄O₂P₂ (*M*_r 867.1): C, 60.99; H, 4.42; N, 6.47. Found: C, 59.84; H, 4.42; N, 6.24.

[(1)Ru(bpy)₂](PF₆)₂·2H₂O. A 184-mg (0.95 mmol) sample of **1** and 180 mg (0.95 mmol) of bis(2,2'-bipyridine)ruthenium(II) chloride dihydrate were heated to reflux for 30 min in 30 mL of ethylene glycol. Addition of a saturated aqueous solution of KPF₆ to the cooled reaction mixture gave a red precipitate, which was redissolved in acetone and precipitated again by addition of diethyl ether. Yield: 60 mg (20%). IR (1,2-dichloroethane solution): $\tilde{\nu}(2-CO) = 1610$ cm⁻¹.

Anal. Calcd for C₂₈H₂₈F₁₂N₈O₄P₂Ru (*M*_r 931.6): C, 36.10; H, 3.03; N, 12.03. Found: C, 36.92; H, 3.21; N, 11.79.

Results

The chelate complexes of **1** are formed readily via standard procedures.^{2,15,18} Lumazines and pterins are moderately basic

Table II. Charge-Transfer Absorption Maxima of 1,3-Dimethylalumazine Complexes in 1,2-Dichloroethane

complex	λ_{max} , nm (log ϵ)	E_{max} , eV	$[E_{\text{pa}}(\text{ox}) - E_{\text{pc}}(\text{red})] - E_{\text{max}}$
[(1)Cu(PPh ₃) ₂](BF ₄)	421 (3.38)	2.94	0.69
[(1)Ru(bpy) ₂](PF ₆) ₂	511 (3.97)	2.43	0.39
	432 ^a (3.94)	2.87 ^a	
[(1)Re(CO) ₃ Cl]	459 ^b (3.51)	2.70	0.59

^a Transition d(Ru) → π^* (bpy). ^b In acetone, 430 nm \cong 2.88 eV.

ligands,¹⁹ and the complexes with electrophilic metal fragments employed here are rather inert in less coordinating solvents. Both the *fac*-rhenium² and the tris chelate ruthenium centers^{15b,20} are chiral, and it is assumed that pairs of enantiomers are formed. Cyclic voltammograms of the complexes in the nonnucleophilic solvent 1,2-dichloroethane are shown in Figure 1; Table I summarizes the data.

All complexes between π -accepting **1** and the electron-rich metal fragments are highly colored, as illustrated by the absorption spectra in the visible region (Figure 2); wavelengths, extinction coefficients, and energies at the absorption maxima are given in Table II. Although many α -diimine complexes of the three metal fragments employed show strong luminescence,^{15,18} it is only complex [(1)Cu(PPh₃)₂](BF₄) that emits weakly in the solid state at 605 nm.

Discussion

The presence of just one carbonyl stretching band from the 2-CO group in the 1600-1750-cm⁻¹ region of the infrared spectra indicates that the 4-CO group has experienced a low-field shift because it participates in the coordination of back-donating metal centers.^{2,21} Mono and bis chelate complexes of the three Cu(I), Ru(II), and Re(I) metal fragments with α -diimine and α -dicarbonyl ligands and their reduced forms have been described.^{13a,15,18,20,22-24} The α -iminoketo combination as shown in the general chelate redox system (eq 3) has been employed less



frequently²⁵ although the β -azaenolate arrangement is known to form very stable chelate complexes (cf. oxinato complexes).²⁶ In order to ensure the full chelate effect, the metal centers should bind equally well to imino nitrogen and carbonyl oxygen atoms; slow dissociation in coordinating solvents suggests that the bonds of Cu(I) and Ru(II) to carbonyl oxygen atoms are not as inert as those to imine nitrogen centers.

In contrast to the parent heterocycle, pteridine,²⁷ the 1,3-dimethylalumazine ligand **1** is reduced irreversibly at a potential that lies roughly between that of pteridine²⁷ and that of the monocyclic pyrazine.²⁸ Coordination of the Cu(I), Ru(II), and Re(I) fragments does not only facilitate reduction thermodynamically,

as indicated by a positive shift in the potential; the reduction also becomes increasingly reversible in the order given above. While the rhenium complex shows an almost Nernstian wave (Figure 1, Table I), it still does not form an ESR-detectable anion-radical complex^{2,6,13a,29} at room temperature. This series of complexes thus illustrates nicely the 2-fold stabilizing effect of coordinated metal centers for the singly reduced form in a less resonance-stabilized "debenzo" derivative of the isoalloxazine ring of flavins where similar effects had been noted before.⁷

Additional redox processes are evident from Figure 1: The (bpy)₂Ru complex shows reduction waves for coordinated bpy ligands from -1.4 to -1.7 V vs SCE;^{15b,20} metal-centered oxidation processes in the expected range between +1.0 and +1.6 V vs SCE are irreversible for rhenium carbonyl⁶ and distorted tetrahedral copper(I) fragments.^{29,30} The Ru(II) → Ru(III) transition occurring at ca. 1.4 V would correspond to a fairly high pK_{BH^+} of 3.8 according to an established correlation (eq 4);^{15b} the anodic return wave is somewhat distorted (Figure 1) due to electrode adsorption.

$$pK_{\text{BH}^+}(\text{ligand}) = 11.73 - 5.64E_{\text{ox}}(\text{Ru}(\text{bpy})_2 \text{ complex}) \quad (4)$$

Whereas the cathodic peak potentials for reduction may be associated with the LUMO energy (π^* of **1**) and follow the sequence Cu(I) < Re(I) < Ru(II) complex, the anodic peak potentials for irreversible metal-centered oxidation ($d^n \rightarrow d^{n-1}$) increase from the copper to the ruthenium to the rhenium system. If the difference of peak potentials (Table II) is used as a guideline,^{14,15} it may be anticipated that MLCT absorption energies should decrease in the order Cu(I) > Re(I) > Ru(II) complex.

In fact, Figure 2 illustrates that all three complexes show intense ($\epsilon > 2000 \text{ M}^{-1} \text{ cm}^{-1}$) charge-transfer absorption bands in the visible region, the energies of the maxima decreasing as outlined above. Whereas the Cu(I) and Re(I) complexes show only one such band, the (bpy)₂Ru-containing complex clearly exhibits two allowed transitions, viz., from corresponding d orbitals of the filled t_{2g} set to the $\pi^*(\mathbf{1})$ and to the $\pi^*(\text{bpy})$ orbitals.^{15b} The former is assigned to the low-energy band because **1** is far easier to reduce (Table I) than bpy ($E_{\text{red}} = -2.1 \text{ V}$).^{15a} In addition, the shift of that second MLCT absorption maximum from 452 nm for Ru(bpy)₃²⁺ to 432 nm is in agreement^{15b,16} with the lower basicity of **1** in relation to bpy ($pK_{\text{BH}^+} = 4.4$).

A comparison (Table II) between peak potential differences (in volts) and absorption energies (in electronvolts) shows the largest discrepancy for the copper system with its considerable geometry change between tetrahedral Cu(I) and preferably square-planar Cu(II),³⁰ while the ruthenium system expectedly shows a small such difference because of relatively little geometry change between Ru(II) and Ru(III) as formed by oxidation.^{15b,16,31}

While the positions (340-360 nm) and intensities (log $\epsilon = 3.5-3.7$) of low-energy intraligand (IL) absorptions¹⁹ are virtually unchanged for the three complexes, the band intensities of the MLCT bands vary (Table II) as do the absorption maxima. In agreement with earlier observations,^{15a,29} the ruthenium(II) system exhibits rather large extinction coefficients for both MLCT bands, indicating the better overlap of **1** relative to bpy with the metal center.^{15a} This result supports the notion that the "chromophore" of **1** comprises essentially the α -carbonylpyrazine π system.⁸ Overlap between **1** and the rhenium(I) and particularly the copper(I) fragment is apparently smaller, as indicated by significantly lower MLCT band intensities (Table II).

The rhenium tricarbonyl chloride complex shows the negative solvatochromism typical for most MLCT absorption features.³² The use of a more "polar" solvent such as acetone causes a distinct hypsochromic shift (Table II). Such effects were also observed

- (18) Cf.: Kirchoff, J. R.; McMillin, D. R.; Robinson, W. R.; Powell, D. R.; McKenzie, A. T.; Chen, S. *Inorg. Chem.* **1985**, *24*, 3928.
 (19) Pfeleiderer, W. In *Chemistry and Biochemistry of Pterins*; Benkovic, S. J., Blakley, R. L., Eds.; Wiley: New York, 1985; Vol. 2, p 43.
 (20) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.
 (21) (a) Olbrich-Deussner, B.; Kaim, W. *J. Organomet. Chem.* **1989**, *361*, 335. (b) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.
 (22) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 1469.
 (23) Kaim, W.; Kohlmann, S. *Chem. Phys. Lett.* **1987**, *139*, 365.
 (24) Kaim, W.; Ernst, S.; Kohlmann, S.; Welkerling, P. *Chem. Phys. Lett.* **1985**, *118*, 431.
 (25) (a) van Vliet, M. R. P.; Jastrzebski, J. T. B. H.; van Koten, G.; Spek, A. L. *J. Organomet. Chem.* **1983**, *251*, C17. (b) van Vliet, M. R. P.; van Koten, G.; Buysingh, P.; Jastrzebski, J. T. B. H.; Spek, A. L. *Organometallics* **1987**, *6*, 537.
 (26) (a) Umland, F. *Theorie und praktische Anwendung von Komplexbildnern*; Akademische Verlagsgesellschaft: Frankfurt/Main, West Germany, 1971. (b) Firsching, F. H. In *Chelates in Analytical Chemistry*; Flaschka, H. A., Barnard, A. J., Jr., Eds.; Marcel Dekker: New York, 1969; Vol. 2. (c) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1986**, *25*, 3858.
 (27) (a) Bessenbacher, C.; Kaim, W. *J. Organomet. Chem.* **1989**, *362*, 37. (b) *Ibid.* **1989**, *369*, 83.
 (28) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498.

- (29) Kohlmann, S. Ph.D. Thesis, University of Frankfurt, 1988.
 (30) Datta, D.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 1085.
 (31) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61; **1986**, *124*, 152.
 (32) (a) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306. (b) Kaim, W.; Kohlmann, S.; Ernst, S.; Olbrich-Deussner, B.; Bessenbacher, C.; Schulz, A. *J. Organomet. Chem.* **1987**, *321*, 215.

for carbonylmetal (0) complexes of the parent heterocycle of lumazines and pterines, viz., pteridine;^{27b} however, attempts to isolate tetracarbonylmolybdenum and -tungsten chelate complexes of **1** were unsuccessful because of the high lability of M⁰-O bonds.

In summary, organometallic complexes from alkylated derivatives of biochemically relevant molecules can be studied in aprotic media and may serve as starting systems for subsequent studies that involve real coenzymes under physiological conditions.

Acknowledgment. This work was generously supported by grants from the Deutsche Forschungsgemeinschaft and Stiftung Volkswagenwerk. We also thank Degussa AG for donation of chemicals.

Registry No. 1, 13401-18-8; [(1)Cu(PPh₃)₂](BF₄), 124021-09-6; [(1)Ru(bpy)₂](PF₆)₂, 124021-11-0; [(1)Re(CO)₃Cl], 124021-12-1; tetrakis(triphenylphosphine)copper(I) tetrafluoroborate, 34010-82-7; bis-(2,2'-bipyridine)ruthenium(II) chloride, 15746-57-3.

Contribution from the Chemistry Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6119, Biology Division, Oak Ridge National Laboratory, P.O. Box 2009, Oak Ridge, Tennessee 37831-8077, and University of Tennessee-Oak Ridge Graduate School of Biomedical Sciences, Oak Ridge, Tennessee 37831

Preparation and Properties of the Nitrido-Bridged Osmium(IV) Binuclear Complexes [Os^{IV}₂N(NH₃)_{10-n}Cl_n]Cl_{5-n} (n = 2, 3)

Sook-Hui Kim,^{1a} Bruce A. Moyer,^{*,1b} Sarah Azan,^{1c} Gilbert M. Brown,^{1b} Ada L. Olins,^{1d,e} and David P. Allison^{1d}

Received February 8, 1989

The nitrido-bridged osmium(IV) binuclear complexes [Os₂N(NH₃)₈Cl₂]Cl₃·2H₂O (I) and [Os₂N(NH₃)₇Cl₃]Cl₂·H₂O (II) have been shown to be products of the ammonolysis of sodium hexachloroosmate(IV) (Na₂[OsCl₆]) in aqueous ammonia at elevated temperatures. Spectral (infrared and UV-vis) and electrochemical properties of the complexes have been explored. In aqueous solution, I and II undergo aquation reactions involving the chloro ligands, and the resulting aqua complexes of I and II exhibit respectively two and three ionizable protons with pK_a values in the range 3.6-7.3. In purified form, the complexes I and II plus their aquated derivatives were found to be ineffective as DNA-selective, electron-dense stains for electron microscopy, whereas effective staining was observed with unpurified mixtures.

Although polynuclear nitrido-bridged complexes of osmium were first encountered over a century ago, the study of their syntheses and properties has primarily been limited to a small number of bi- and trinuclear compounds.²⁻¹¹ Most of the binuclear examples belong to the series [Os^{IV}₂N(NH₃)_{10-n}X_n]Y_{5-n} when n = 0 and n = 2; a variety of ligands X and counterions Y are possible. Our interest in the nitrido-bridged polynuclear

complexes of osmium has arisen from the need for an electron-microscopy stain having DNA-staining properties improved over those of the ill-defined "osmium ammine" complex^{9,11-15} currently in use. Because of similarities in the preparations of the binuclear complexes⁶ and "osmium ammine",¹³ we have been led to a closer examination of [Os₂N(NH₃)₈Cl₂]Cl₃·2H₂O (I).¹⁶

Experimental Section

Chemicals and General Procedures. All chemicals were of reagent quality and were used without further purification. Water was doubly distilled.

IR and UV-visible spectra were recorded on Digilab FTS-60 FTIR and Cary 219 spectrophotometers, respectively. Cyclic voltammograms were obtained at a carbon-paste working electrode¹⁷ vs a saturated sodium chloride calomel (NaSCE) reference electrode with use of a PAR Model 173 potentiostat and a PAR Model 175 universal programmer; solutions were purged with argon and scanned at 50-500 mV s⁻¹ at ambient temperature (23 ± 2 °C). Solution conductivities (ambient temperature) were determined by using a Type CDM 2d conductivity bridge (The London Co.). Molar conductivities at infinite dilution (Δ_{M,0}) were determined by extrapolation of plots of Δ_M vs C^{1/2} to zero. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

[Os₂N(NH₃)₈Cl₂]Cl₃·2H₂O (I). A sealed, thick-walled glass tube containing Na₂[OsCl₆] (0.5 g, 1.114 mmol) in 5 mL of concentrated

- (1) (a) Postgraduate Research Associate, Oak Ridge Associated Universities, Oak Ridge, TN. Present address: Chemistry Department, Loyola University of Chicago, Chicago, IL 60611. (b) Chemistry Division, Oak Ridge National Laboratory. (c) Student Research Participant, Oak Ridge Associated Universities. (d) Biology Division, Oak Ridge National Laboratory. (e) University of Tennessee-Oak Ridge Graduate School of Biomedical Sciences.
- (2) (a) Griffith, W. P.; Raub, C. J. In *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Swars, K., Ed.; Springer-Verlag: New York, 1980; No. 66, Suppl. Vol. 1, pp 90-283. (b) Griffith, W. P. *The Chemistry of The Rarer Platinum Metals (Os, Ru, Ir and Rh)*; Interscience: New York, 1967; Chapter 3.
- (3) Dwyer, F. P.; Hogarth, J. W. *J. Proc. R. Soc. N. S. W.* **1950**, *84*, 117.
- (4) (a) Belova, V. I.; Syrkin, Ya. K. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1958**, *3*(9), 33. (b) Watt, G. W.; Vaska, L. *J. Inorg. Nucl. Chem.* **1958**, *6*, 246.
- (5) (a) Hewkin, D. J.; Griffith, W. P. *J. Chem. Soc. A* **1966**, 472. (b) Griffith, W. P. *J. Chem. Soc. A* **1965**, 3694.
- (6) (a) Cleare, M. J.; Lever, F. M.; Griffith, W. P. *Adv. Chem. Ser.* **1971**, No. 98, 54. (b) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 1117.
- (7) Kolbin, N. I.; Semenov, I. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1963**, *8*, 1270.
- (8) (a) Watt, G. W.; McMordie, W. C., Jr. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2013. (b) Watt, G. W.; Potrafke, E. M. *J. Inorg. Nucl. Chem.* **1961**, *17*, 248.
- (9) Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410.
- (10) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269-277.
- (11) Cleare, M. J.; Hydes, P. C. *Ger. Offen. DE 2905450*, Aug 30, 1979; *Chem. Abstr.* **1980**, *92*(3), 18403t.

- (12) Allen, D. E.; Perrin, D. D. *Int. Rev. Cytol.* **1979**, *61*, 63.
- (13) Cogliati, R.; Gautier, A. C. R. *Seances Acad. Sci., Ser. D* **1973**, *276*, 3041.
- (14) Gautier, A. *Int. Rev. Cytol.* **1976**, *44*, 113.
- (15) (a) Derenzini, M.; Viron, A.; Puvion-Dutilleul, F. *J. Ultrastruct. Res.* **1982**, *80*, 133. (b) Derenzini, M.; Viron, A.; Puvion, E. *Eur. J. Cell Biol.* **1984**, *33*, 148. (c) Derenzini, M.; Pession, A.; Licastro, F.; Novello, F. *Exp. Cell Res.* **1985**, *157*, 50.
- (16) Olins, A. L.; Moyer, B. A.; Kim, S.-H.; Allison, D. P. *J. Histochem. Cytochem.* **1989**, *37*, 395.
- (17) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 280.