

## Design and Evaluation of Conjugated Bridging $\pi$ Systems. Molecular Orbital Characterization and Electrochemical Determination of the $W(CO)_5$ Binding Site in Two New Ambidentate Ligands

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Insertion of the strongly  $\pi$ -accepting tetrazine and azo groups between the molecular halves of 4,4'-bipyridine produces the ambidentate nonchelating ligands 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4,4'-bptz) and 4,4'-azopyridine (4,4'-apy).  $\pi$  molecular orbital calculations reveal high orbital coefficients at the N=N  $\pi$  centers in the LUMO of both ligands. 4,4'-bptz is distinguished by a virtually N(tetrazine) localized LUMO ( $a_u$ ) with a nodal plane through the pyridyl substitution centers 3 and 6; however, there exists another very low-lying unoccupied MO ( $b_{1u}$ ) with appreciable LUMO contribution from the pyridyl rings. The ligands and their bis(pentacarbonyl tungsten) complexes were studied by carbonyl vibrational spectroscopy and cyclic voltammetry. These data as well as the ESR results of the singly reduced species can be correlated with the  $\pi$  MO calculations, indicating coordination of the  $W(CO)_5$  groups at the less  $\pi$ -accepting, yet more basic and sterically unhindered pyridyl nitrogen centers. A correlation between calculated LUMO electron densities and the reduction potential differences between the complexes and the free ligands is derived for a number of dimers ( $\mu$ -L)[ $W(CO)_5$ ]<sub>2</sub>. The potential use of the two new systems in electron-transfer and mixed-valence chemistry is discussed.

Bridging N-heterocyclic ligands that contain a planar conjugated  $\pi$  system and thus allow interaction between  $\sigma$  coordinated electrophiles have received increasing attention in various areas of chemistry. While free ligands of this kind and their N,N'-dialkylated derivatives have been used as electron-transfer mediators<sup>2</sup> for large or heterogeneous entities such as redox proteins,<sup>3a</sup> micellar systems,<sup>3b</sup> or semiconductor surfaces,<sup>4</sup> the dinuclear metal complexes derived from such ligands are widely studied in mechanistic<sup>5</sup> and mixed-valence<sup>6</sup> coordination chemistry and in the search for low-dimensional magnetic,<sup>7</sup> electrically conducting,<sup>8</sup> energy-transferring,<sup>9</sup> photo-<sup>10</sup> and redox-active materials.<sup>11</sup>

One major class of such nonchelating ligands containing two or more heteroatoms in (condensed) ring systems (Chart I) related to pyrazine<sup>11a</sup> was described recently.<sup>11b,c</sup> Another way to arrive at such new systems is to insert  $\pi$ -conjugating groups such as (poly)enes<sup>6b,10,12,13</sup> or (poly)yines<sup>5b,14</sup> between the two pyridines

Chart I

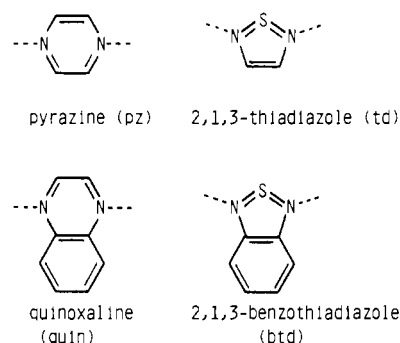


Chart II

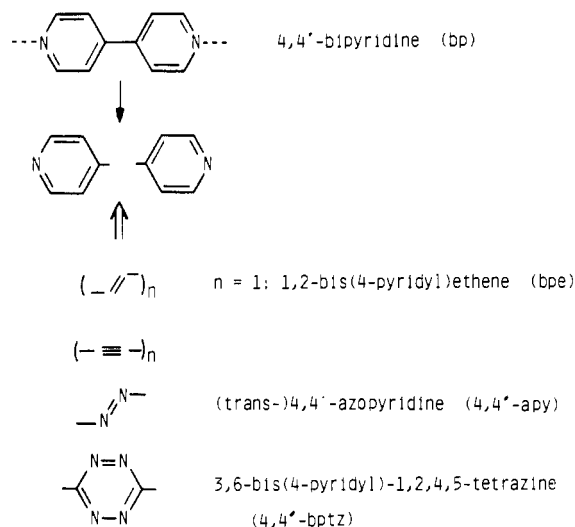
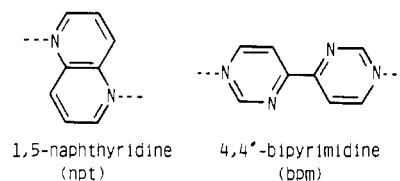


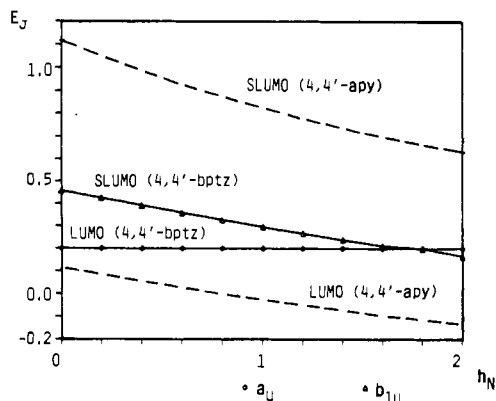
Chart III



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of 4,4'-bipyridine (Chart II); the electron-transfer properties of some dinuclear complexes have been reported very recently.<sup>5b,6b</sup>

Within a concept of HMO calculation-assisted ligand design<sup>11,15,16</sup> we have now studied those cases (Chart II) where the



**Figure 1.** Correlation diagram for the LUMO and SLUMO energies of 4,4'-bptz (—) and 4,4'-apy (---) depending on the pyridine N Coulomb integral parameter  $h_N$  ( $h_{N(\text{azo})} = 0.8$ , all  $k = 1.0$ ).

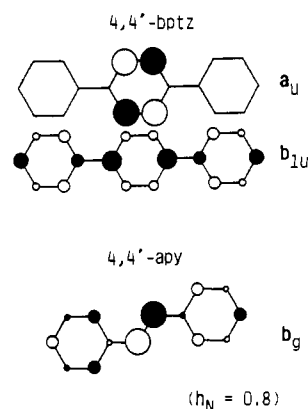
difunctional nitrogen-containing  $\pi$  components  $-\text{N}=\text{N}-$  (azo group) and  $\text{C}_2\text{N}_4$  (1,2,4,5-tetrazine) are inserted between the pyridines of 4,4'-bipyridine. Previous studies on the bischelating ligands resulting from insertion of azo and tetrazine moieties into the single bond of 2,2'-bipyridine have shown the extraordinary coordinating properties of such ligands;<sup>16</sup> both inserted moieties provide very low-lying  $\pi^*$  orbitals for back-donation from low-valent metal centers, but on the other hand, they also offer additional, albeit weakly basic,  $\sigma$  coordination sites for metal electrophiles.

Following an assessment of the properties of the hitherto not employed ligands 4,4'-azopyridine (4,4'-apy) and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4,4'-bptz) as based on MO calculations and comparisons with related systems (Charts I–III), we report the synthesis of dinuclear pentacarbonyltungsten complexes in order to compare these compounds with analogues containing other bridging ligands (Charts I–III).<sup>10c,11–13,15,17–19</sup> The nontrivial problem of coordination site determination, viz., 4-pyridyl or azo coordination, proved possible to solve with a combination of MO calculated data and experimental techniques, especially electrochemistry and ESR spectroscopy of one-electron-reduced forms.<sup>11c,13,20,21</sup> Electronic absorption and emission spectroscopy of these systems will be discussed elsewhere.<sup>22</sup>

## Experimental Section

**Instrumentation.** The following procedures and instruments were used: ESR, Varian E9 in the X-band and calibration of spectra with the perylene anion radical in 1,2-dimethoxyethane;<sup>23</sup> ESR spectra computer simulation, adaptation of a published program;<sup>24a</sup> IR, Jasco A100; cyclic voltammetry, programmer Bank-Wenking VSG 72 and PAR 363 potentiostat. A three-electrode configuration with a glassy-carbon working electrode and an SCE reference system was used. A 0.1 M solution of purified and dried tetrabutylammonium perchlorate in *N,N*-dimethyl-

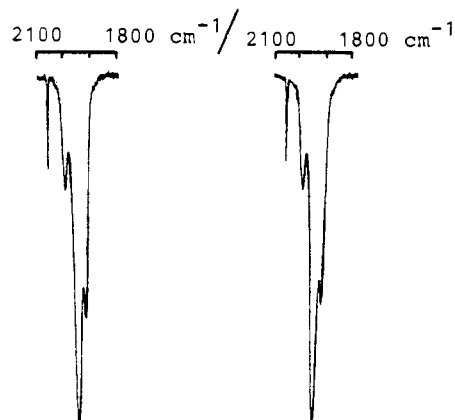
**Chart IV**



**Table I.** LUMO and SLUMO Squared Hückel MO Coefficients  $c_N^2$  at the Coordinating Centers of N-Heterocyclic Dinucleating Ligands<sup>a</sup>

ligand	$c_N^2$		ligand	$c_N^2$	
	LUMO	SLUMO		LUMO	SLUMO
td	0.307	0.157	bp	0.134	0
pz	0.268	0	bpm <sup>b</sup>	0.103	0.019
btd	0.232	0.051	bpe	0.093	0.126
quin	0.217	0	4,4'-bptz <sup>c</sup>	0	0.079
npt	0.136	0	4,4'-apy <sup>c</sup>	0.067	0.130

<sup>a</sup> Parameters (cf. ref 24b,c):  $h_N = 0.8$ ,  $h_c = 0.0$ ,  $h_s = 1.2$ ,  $k_{NS} = 0.7$ . <sup>b</sup> N(1,1') as coordination centers. <sup>c</sup> 4-Pyridyl coordination centers, values of  $c_N^2$  (LUMO) of the azo nitrogen atoms are 0.250 for 4,4'-bptz and 0.2674 for 4,4'-apy.



**Figure 2.** Carbonyl vibrational spectra of (4,4'-apy)[W(CO)<sub>5</sub>]<sub>2</sub> (left) and (4,4'-bptz)[W(CO)<sub>5</sub>]<sub>2</sub> (right) in THF solution (identical scale).

formamide (DMF) was used as electrolyte. Hückel MO perturbation calculations were performed by using standard programs.<sup>24b,c</sup>

**Materials.** Tungsten hexacarbonyl and commercially available organic chemicals were used without further purification. The ligands 4,4'-bptz<sup>25</sup> and 4,4'-apy<sup>26</sup> were obtained by following conventional organic synthesis. All manipulations involving organometallics were carried out in dried solvents under argon atmosphere.

**( $\mu$ -4,4'-bptz)[W(CO)<sub>5</sub>]<sub>2</sub>.** A 250-mg (0.71-mmol) sample of W(CO)<sub>6</sub> was irradiated in 70 mL of THF for 3 h to yield the yellow solvate (THF)W(CO)<sub>5</sub>. This solution was then allowed to react with 60 mg (0.25 mmol) of 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine to form an orange-red solution. After the mixture was stirred for 3 h at room temperature, the solvent was removed in vacuo, the remaining W(CO)<sub>6</sub> was sublimed off at 40 °C (0.1 Torr), and the red-brown product was recrystallized from THF/hexane (1:1 v/v). Yield: 100 mg (45%). IR (CH<sub>2</sub>Cl<sub>2</sub> solution):  $\nu(\text{CO})$  2070 (w), 1980 (m), 1930 (vs), 1910 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>8</sub>N<sub>6</sub>O<sub>10</sub>W<sub>2</sub>: C, 29.89; H, 0.91; N, 9.51. Found: C, 29.07; H, 1.16; N, 8.53.

**( $\mu$ -4,4'-apy)[W(CO)<sub>5</sub>]<sub>2</sub>.** A 625-mg (1.78-mmol) sample of W(CO)<sub>6</sub> was irradiated in 70 mL of THF for 3 h. The yellow solvate (THF)W-

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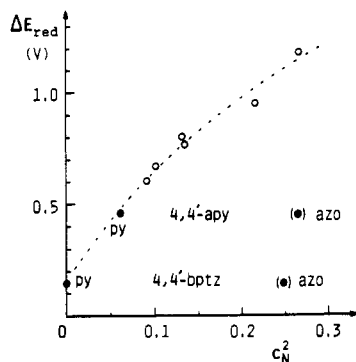
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**Table II.** Reduction Potentials (V vs SCE) of Conjugated Symmetrically Bridging Ligands and their Bis(pentacarbonyl tungsten) Complexes<sup>a</sup>

ligand	$E_{\text{red}}(\text{ligand})$	$E_{\text{red}}(\text{complex})$	$\Delta E_{\text{red}}$	solvent
pz	-2.17	-0.99	1.18	CH <sub>3</sub> CN
quin	-1.62	-0.68	0.94	DMF
npt <sup>b</sup>	-1.72	-0.95	0.77	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>
bp	-2.1 <sup>c</sup>	-1.30	≈0.8	CH <sub>2</sub> Cl <sub>2</sub>
bpm <sup>d</sup>	-1.34	-0.67	0.67	DMF
bpe	-1.8 <sup>c</sup>	-1.20	≈0.6	CH <sub>2</sub> Cl <sub>2</sub>
4,4'-bptz	-0.60	-0.46	0.14	DMF
4,4'-apy	-0.75 <sup>e</sup>	-0.29	0.46	DMF

<sup>a</sup> From cyclic voltammetry,<sup>10c,11b,c,15</sup> all solutions contain 0.1 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. <sup>b</sup> Reference 11c. <sup>c</sup> Cathodic peak potential for irreversible process.<sup>10c</sup> <sup>d</sup> Reference 15. <sup>e</sup> -0.80 V reported in ref 39.

**Figure 3.** Correlation between calculated LUMO electron densities  $c_N^2$  at coordination centers (Table I) and reduction potential differences  $\Delta E_{\text{red}}$  between various N-heterocyclic bridging ligands and their bis(pentacarbonyl tungsten) complexes (Table II).

(CO)<sub>5</sub> was then allowed to react with 150 mg (0.81 mmol) of 4,4'-azopyridine to form a purple solution. After overnight stirring at room temperature, the solvent was removed in vacuo, the remaining W(CO)<sub>6</sub> was sublimed at 40 °C (0.1 Torr), and the dark blue product was recrystallized from THF/hexane (2:3 v/v). Yield: 390 mg (58%). IR (CH<sub>2</sub>Cl<sub>2</sub> solution):  $\nu(\text{CO})$  2070 (w), 1980 (m), 1935 (vs), 1905 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>8</sub>N<sub>4</sub>O<sub>10</sub>W<sub>2</sub>: C, 28.87; H, 0.97; N, 6.73. Found: C, 28.32; H, 1.29; N, 6.01.

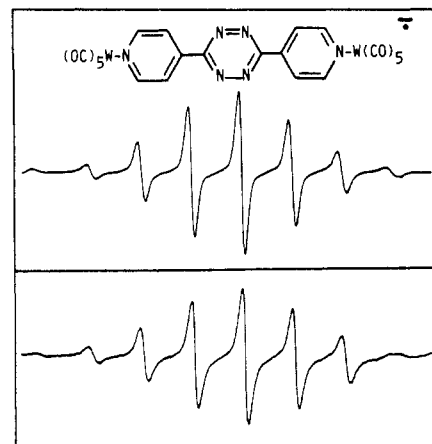
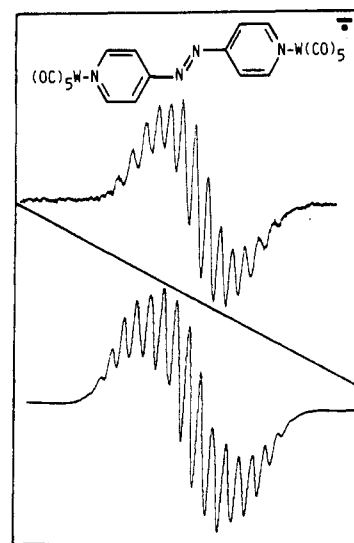
## Results

Hückel MO perturbation calculations were carried out for the two ligand systems with the following established<sup>16a</sup> set of parameters:  $k_{\text{CN}} = k_{\text{NN}} = 1.0$ ;  $h_{\text{N(azo)}} = 0.8$ ,  $0.0 < h_{\text{N(py)}} < 2.0$ . The correlation with the energies of the two lowest-lying molecular orbitals is shown in Figure 1; for  $h_{\text{N}} = 0.8$ , the corresponding squared orbital coefficients  $c_N^2$  for LUMO and SLUMO ( $\psi_{\text{MO}} = \sum_{\mu} c_{\mu} \Phi_{\mu}$ )<sup>15,16</sup> are depicted in Chart IV and compared with values for other bridging ligands in Table I.

Dinuclear W(CO)<sub>5</sub> complexes of 4,4'-apy and 4,4'-bptz were obtained from reactions of the ligands with photogenerated (THF)W(CO)<sub>5</sub> without the problems encountered with related heterocyclic systems;<sup>11b,27</sup> i.e., even in THF, the equilibrium lies sufficiently to the side of the dinuclear complex. Carbonyl vibrational spectra of both complexes are very similar, as shown in Figure 2.

Reduction potentials as obtained from cyclic voltammetry are summarized for the free ligands and the complexes in Table II; for determination of the coordination site, it has been useful to correlate these data, especially the potential differences  $\Delta E_{\text{red}}$  between ligands and complexes, with  $c_N^2$  (LUMO) values (Figure 3).

While electrochemical oxidation of these complexes occurs irreversibly around +1.1 V vs SCE,<sup>10c,15</sup> the reversible one-electron uptake allowed an ESR investigation of the anion radical complexes formed. Figures 4 and 5 show ESR spectra of the complexes and of the 4,4'-bptz ligand anion radical (Figure 4); Table III contains the ESR data for the 4,4'-apy system.

**Figure 4.** ESR spectra of the 4,4'-bptz anion radical (bottom) and its bis(pentacarbonyl tungsten) complex (top) as obtained by cathodic reduction in dichloromethane/0.1 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. Outer lines are reduced in intensity because of anisotropic line broadening.  $a(^{14}\text{N}) = 0.493$  mT and  $g = 2.0041$  for the ligand radical, and  $a(^{14}\text{N}) = 0.488$  mT and  $g = 2.0039$  for the complex.**Figure 5.** Top: ESR spectrum of electrolytically generated (4,4'-apy)•-[W(CO)<sub>5</sub>]<sub>2</sub> in dichloromethane. Bottom: Computer simulation with the data from Table III and a line width of 0.2 mT.**Table III.** HMO-McLachlan Spin Populations  $\zeta_{\text{ML}}^a$  and ESR Parameters<sup>b</sup> of the 4,4'-Azopyridine Anion Radical and Its Bis(pentacarbonyl tungsten) Complex

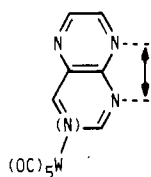
radical	$\zeta_{\text{ML}}$	$a_{\text{H}}$	$a_{\text{N(py)}}$	$a_{\text{N(azo)}}^c$	$g$
4,4'-apy <sup>•-</sup>	0.081 (H(3,5)) -0.016 (H(2,6)) 0.079 (N(py)) 0.310 (N(azo))	0.21 (H(3,5))	0.21	0.55	2.0038
(4,4'-apy <sup>•-</sup> )- [W(CO) <sub>5</sub> ] <sub>2</sub>		0.23 (H(3,5))	0.23	0.55	2.0051

<sup>a</sup>  $h_{\text{N}} = 0.8$ ;  $k = 1.0$ ; McLachlan parameter  $\lambda = 1.224^c$  <sup>b</sup> From electrochemically reduced species in dichloromethane, coupling constants  $a$  in mT. <sup>c</sup> Estimated from total spectral width.

## Discussion

**Ligand Characterization.** In their coplanar conformations, i.e. allowing full  $\pi$  conjugation, the ligands have  $D_{2h}$  (4,4'-bptz),  $C_{2h}$  (*trans*-4,4'-apy) or  $C_{2v}$  symmetry (*cis*-4,4'-apy). If metal coordination occurred at the azo nitrogen atoms, the coplanar conformations could not be maintained because of steric interference; however, metal pentacarbonyl complexes have been reported for *cis*-azobenzene<sup>28</sup> and unsubstituted 1,2,4,5-tetrazine.<sup>18,20d</sup> Co-

Chart V



ordination at the certainly quite basic pyridine nitrogen centers,<sup>29</sup> on the other hand, would not by itself result in nonplanarity.

Hückel MO calculations (Figure 1, Table I) illustrate that the 4,4'-apy ligand has a lower lying LUMO ( $b_g$ ) but a higher lying SLUMO than the bptz system—a situation that is reminiscent of the bischelating 2,2'-analogues.<sup>16</sup> The 4,4'-bptz ligand even shows a crossing of the two lowest lying unoccupied MOs for high values of  $h_{N(py)}$ ; such phenomena have previously been recognized in 2,7-diazapyrene<sup>30</sup> and in 1,10-phenanthroline and its diaza analogues.<sup>31</sup>

The origin of this peculiar effect can be rationalized by looking at the corresponding MO representations (Chart IV). The  $a_u$  orbital is an N(tetrazine)-localized orbital, the nodal plane running through 3,6-positions prevents the 4-pyridyl substituents from acquiring LUMO participation, and a perturbation at the pyridine nitrogens thus does not affect the orbital energy (Figure 1). On the other hand, the  $b_{1u}$  orbital can be described as a combination between the 4,4'-bipyridine LUMO and the second lowest unoccupied MO (SLUMO) of tetrazine, it is clear that this MO must be considerably stabilized by increase of  $h_{N(py)}$ .

A comparison of LUMO orbital energies and squared LUMO/SLUMO coefficients  $c_N^2$  at the (presumably) coordinating pyridine N centers reveals that the 4,4'-apy ligand exhibits some LUMO contributions of these centers; however, the value is similarly small as for the SLUMO of 4,4'-bptz (Table I). From these results, we would expect,<sup>15,16</sup> e.g., small shifts of  $\Delta E_{red} = E_{red}(\text{complex}) - E_{red}(\text{ligand})$  (Table III, Figure 3), low intensities of first CT bands, small ESR coupling constants  $a_{N(py)}$ ,<sup>20d</sup> short lifetimes of MLCT excited states<sup>16b</sup> and small stability constants of mixed valence dimers bridged by these ligands<sup>32</sup>—some of these predicted consequences will be confirmed here while others remain to be verified.

**Carbonyl Vibrational Spectra.** The complexes  $(CO)_5W-L-W(CO)_5$ ,  $L = 4,4'$ -apy and 4,4'-bptz display virtually identical infrared spectra, corresponding to a slightly perturbed  $C_{4v}$  symmetry in the CO stretching region (Figure 2, Experimental Section).<sup>17</sup> The close similarity of these spectra with those of other 4-pyridyl-coordinated pentacarbonyltungsten complexes<sup>10b,c,17,20c,f</sup> already suggests 4-pyridyl coordination in both dinuclear systems. Since <sup>1</sup>H-NMR studies of such 4-pyridyl-containing complexes could not be expected to provide conclusive answers to the question of coordination, we have resorted to an alternative, hitherto not yet employed electrochemical method of determination of the coordination site.

**Cyclic Voltammetry—Discussion of Coordinative Preference.** The unencumbered formation of the dinuclear complexes, their stability in rather polar solvents, and the IR spectra already suggest that the two ambidentate ligands use the sterically unhindered,<sup>15</sup> basic<sup>29</sup> pyridine nitrogen atoms and not the sterically less accessible, less basic<sup>29</sup> azo nitrogen centers for coordination of the carbonylmetal fragment. Recent examples involving unsymmetrical polyazanaphthalines (Chart V)<sup>11c</sup> have demonstrated that there may be only slight energy differences for low-valent metal fragments such as  $W(CO)_5$  between the coordination to a basic, less  $\pi$ -accepting site and the binding to a less basic but strongly  $\pi$ -accepting coordination center. Since there are also examples

of mono- and dinuclear pentacarbonylmetal complexes of azobenzene reported in the literature,<sup>28</sup> we have used a correlation of electrochemical data to further confirm the coordination sites.

The reduction potentials of some N-heterocyclic  $\pi$ -conjugated bridging ligands (Table II) show that the two new ligands have indeed very low-lying unoccupied MOs. Coordination of the organometallic electrophiles further stabilizes the LUMO as evident from positively shifted reduction potentials;<sup>21</sup> however, the extent of this shift is very variable (Table II). We have previously noted that this shift  $\Delta E_{red}$  correlates with the squared orbital coefficients  $c_N^2$  (LUMO) at the coordination site,<sup>15,16</sup> the LUMO being singly occupied during one-electron reduction. Such a correlation is now shown here for dinuclear  $W(CO)_5$  complexes of symmetrically bridging ligands (Charts I–III), the alternatives for the coordination being indicated.

First, this correlation clearly shows the effect of  $a_u$  being the LUMO in the 4,4'-bptz system (Figure 3); a  $c_N^2$  (LUMO) of virtually zero results in a very small shift of the reduction potential on coordination. For the 4,4'-apy case, the value corresponding to pyridine coordination is much more in agreement with the correlation (Figure 3) than the value for the azo nitrogen centers; we therefore conclude also from the electrochemical shifts a pyridine coordination of  $W(CO)_5$  fragments. Although such a correlation seems far-fetched at first, its apparent success for a number of closely related complexes (Figure 3) is in agreement with the generally good results from the Hückel method for the perturbation approach towards planar  $\pi$  systems.

The relatively small (Figure 3)  $\Delta E_{red}$  and  $c_N^2$  values for the two ligands at hand mean that the dinuclear complexes are not that much better to reduce than complexes of some other bridging ligands (Table II). Nevertheless, both dinuclear systems are reduced so easily that an attempt was made to characterize the products by ESR.<sup>11,13,15,20,21,33</sup>

**ESR Spectroscopy.** The spin distribution in the singly occupied MO of an anion radical can with some precautions (one-electron approach!) be related to the squared orbital coefficients  $c^2$  (LUMO) of the non-reduced compound.<sup>21</sup> Both dinuclear complexes form ESR-active species on electrolytic reduction, Figure 4 shows the spectrum of the 4,4'-bptz ligand anion radical and its complex; Figure 5 shows the ESR spectrum of (4,4'-apy)<sup>-</sup>- $[W(CO)_5]$  together with a computer-simulated spectrum which is based on HMO-McLachlan-calculated<sup>24c</sup> spin densities (Table III).

Figure 4 illustrates that the singly occupied molecular orbitals of the ligand anion radical 4,4'-bptz<sup>-</sup> and its bis(pentacarbonyltungsten) complex are very similar. Both systems show a nine-line spectrum resulting from four equivalent tetrazine <sup>14</sup>N centers; the outer lines are reduced in intensity due to anisotropic line broadening (insufficient averaging of  $a$  and  $g$  tensors).<sup>34</sup> The coupling constants of both paramagnetic species are almost identical within the experimental error of  $\pm 0.002$  mT; the very small decrease of  $a(^{14}N)$  is compatible with some very minor spin delocalization through  $W(CO)_5$  coordination.<sup>13</sup> The  $g$  values ( $\pm 0.0001$ ) also exhibit just the slightest of differences, which again signifies<sup>20d,35</sup> the virtual absence of spin transfer to the heavy tungsten(0) atoms with their spin-orbit coupling constant of 2089  $cm^{-1}$ .<sup>36</sup> Accordingly, a <sup>183</sup>W isotope coupling ( $I = 1/2$ , 14.3% natural abundance)<sup>13</sup> is not observed. All these results indicate that it is the  $a_u$  orbital with the nodal plane through the pyridine N and tungsten centers which is singly occupied, signifying a relatively small perturbation by the  $W(CO)_5$  fragments. Addition of positively charged electrophiles such as  $R^+$  to the pyridine nitrogen centers of 4,4'-bptz results in very different, line-rich ESR

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spectra upon reduction (occupation of the  $b_{1u}$  orbital; cf. Chart IV); complete analyses of these complicated spectra will be reported elsewhere.<sup>37</sup>

In agreement with the MO calculations (Table I), the dinuclear anion radical complex  $(4,4'\text{-apy}^{\cdot-})[\text{W}(\text{CO})_5]_2$  displays a more complex ESR spectrum because the unpaired electron is now distributed over more nonequivalent CH and N  $\pi$  centers (Chart IV). The inherently broad lines of  $\text{W}(\text{CO})_5$ -containing anion radicals<sup>13,20a,d,35</sup> and the generally very strong anisotropic line broadening of outer ( $m_N \pm 2$ ) azo nitrogen ESR components<sup>34</sup> have impaired the hyperfine analysis; Table III summarizes the data as obtained from computer-simulated spectra (Figure 5) that are compatible with the HMO-McLachlan-calculated<sup>24c</sup> spin populations. This type of calculation does not take into account the nonequivalence of CH(pyridyl) centers that results from the slow rotation around the "single" bonds between azo and aromatic groups;<sup>34</sup> the bond order increase of such single bonds connecting coplanar  $\pi$  systems is a common phenomenon.<sup>13</sup>

A large LUMO/SLUMO energy difference (Figure 1), considerable spin density at the  $\text{W}(\text{CO})_5$ -coordinating pyridine nitrogen centers (Chart IV, Tables I and III), and the large spin-orbit coupling factor of  $\text{W}(0)$ <sup>36</sup> combine to cause a significant increase of  $g$  upon coordination of the carbonylmetal fragments to the 4,4'-apy anion radical (Table III).<sup>11c,13,20d,35</sup> The <sup>183</sup>W coupling constant should be around 0.09 mT according to an established<sup>20d</sup> relation  $a(^{183}\text{W}) = 0.333a(^{14}\text{N}) + 0.013$  mT for

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similar systems; such a small isotope splitting could not be detected here because of the complexity of the spectrum and the broadness of individual lines.

**Outlook.** According to their MO characteristics and basic experimental data, the two new conjugated bridging ligands differ markedly from the systems used hitherto (Charts I-III). Although these two new systems offer very low-lying  $\pi^*$  levels for back donation and reduction, the small or even vanishing 4,4'-bptz LUMO coefficients  $c_N^2$  at the basic, sterically unhindered pyridine coordination centers should result, e.g., in small  $E_{\text{com}}$  values for mixed-valence systems<sup>32</sup> and relatively low intensities of MLCT absorption bands.<sup>15</sup> The small amount of spin density transferred to the metal fragments should also reduce the substitutional labilization of carbonyl ligands upon reduction<sup>33b</sup> because the  $\delta$  in the  $(18 + \delta)$  valence electron formulation for the anion radical complexes is now very small and the absolute reduction potentials are not too negative.<sup>38</sup> Coordination-induced orbital crossing  $a_u/b_{1u}$  remains a possibility to be explored for the 4,4'-bptz system; this special situation and the effects of the additional azo coordinating centers on the excited state properties are currently being studied.<sup>22</sup>

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## Plutonium(IV) Polymers in Aqueous and Organic Media

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The structures of Pu(IV) hydrous polymers were measured by small-angle neutron scattering (SANS) in aqueous media and after solvent extraction in organic phases. The scattering data from polymers occurring as aqueous colloidal suspensions indicate long, thin, rodlike particles. Pu(IV) hydrous polymers formed in the presence of uranium were shorter than those produced in the absence of uranium; this is consistent with earlier observations that uranium reduces the rate of Pu(IV) polymer formation. The Pu(IV) polymers were extracted into  $\text{C}_6\text{D}_6$  solutions by alkyl esters of phosphoric acid. The extractant-Pu polymer geometries were shorter than those in the aqueous media; their radii were increased by the lengths of the extended alkyl substituents of the extractants. Comparable extractions of Pu(IV) monomers were also examined. X-ray scattering measurements exhibit well-defined Bragg diffraction lines for the Pu polymer in both the aqueous and organic phases. All of the lines could be identified with those of  $\text{PuO}_2$ . Spectrophotometric measurements monitored the polymeric nature of the aqueous and organic suspensions.

### Introduction

The hydrolysis of metal cations has been a subject of interest in numerous reports. The text by Baes and Mesmer<sup>1</sup> summarizes the status of the work up to the present decade and demonstrates the extensiveness of this phenomenon across the periodic table. As many of these metal cations hydrolyze, there is often a tendency for them to aggregate through hydroxyl bridges and form simple dimers and trimers (such as with the uranyl ion)<sup>2</sup> or extensive polymeric networks, which can reach colloidal dimensions and exist as colloidal suspensions. As metastable species, these exhibit varying degrees of stability, but often with time or at elevated temperatures, they condense (with the associated loss of water) or otherwise undergo a conversion from hydroxyl-bridged to oxygen-bridged polymeric species. This chemistry (which includes the behavior of the free metal ion and the extensively oxide-bridged polymeric aggregate) has been studied in various stages and is

summarized in texts such as that by Gimblett,<sup>2</sup> which establishes that these hydrous polymers, either hydroxyl- or oxy-bridged, are a commonly occurring phenomenon observed in many systems.

Ultimately, the stable metal oxide can be produced by precipitation of the hydrous polymer and further drying. Indeed, many reprocessing operations utilize this chemistry to produce the pure oxides. However, if the desire is to keep the metal cation in solution at a relatively high pH (e.g., for maximizing liquid/liquid extraction coefficients under some conditions), one is often confronted with the unwanted hydrolysis/polymerization side reaction. Within this scheme, the polymeric form of the hydrolyzed cation (regardless of whether it is a hydroxide-bridged or an oxygen-bridged polymer species, a simple species, or a

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