

π^* Molecular Orbital Crossing $a_2(\chi)/b_1(\psi)$ in 1,10-Phenanthroline Derivatives. *Ab Initio* Calculations and EPR/ENDOR Studies of the 4,7-Diaza-1,10-phenanthroline Radical Anion and Its $M(\text{CO})_4$ Complexes ($M = \text{Cr}, \text{Mo}, \text{W}$)

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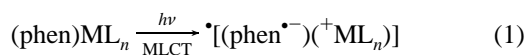
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Ab initio, semiempirical, and HMO perturbation calculations were employed to assess the relative positioning of the closely situated low-lying unoccupied π^* MOs $a_2(\chi)$ and $b_1(\psi)$ in 1,10-phenanthroline (phen) and its 3,4,7,8-tetramethyl (tmphen) and four symmetrical diaza derivatives (*n,m*-dap). Compared to $a_2(\chi)$, the $b_1(\psi)$ π MO is distinguished by markedly higher MO coefficients at the chelating nitrogen π centers in 1,10-positions; eventually, a higher Coulomb integral value at those positions will thus always favor the lowering of b_1 beyond a_2 . Using the Coulomb integral parameter at the chelating 1,10-nitrogen π centers as the HMO perturbation variable, the crossing of both energy levels in terms of decreasing preference for the $a_2(\chi)$ over the $b_1(\psi)$ orbital as the lowest unoccupied MO follows the sequence 5,6-dap > 2,9-dap > 4,7-dap > phen > 3,8-dap. The calculations reveal $a_2(\chi)$ as the LUMO in 5,6-dap for all reasonable perturbation parameters, in agreement with previous observations for ruthenium(II) complexes which reveal a discrepancy between the lowest-lying “redox π^* orbital” (a_2) and the “optical π^* MO” (b_1) to which the most intense low-energy MLCT transition occurs. According to the HMO calculations, the situation is more ambiguous for the 4,7-dap analogue, yet EPR/ENDOR studies clearly show that the one-electron-reduced ligand and its tetracarbonylmethyl(0) complexes (Cr, Mo, W) have the $b_1(\psi)$ orbital singly occupied. Only *ab initio* calculations with double- ζ basis and inclusion of d polarization functions reproduced correctly the experimentally observed orbital ordering for tmphen ($a_2 < b_1$) and for phen and 4,7-dap ($b_1 < a_2$).

Introduction

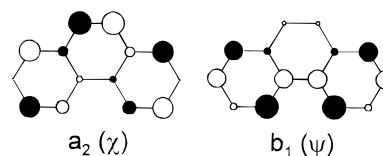
A remarkable dichotomy and uncertainty surrounds both the electronic ground state of the 1,10-phenanthroline anion radical, phen^{•−},^{1,2} and the low-lying metal-to-ligand charge transfer (MLCT) excited states^{3,4} of complexes (eq 1) which, in a first approximation, involve phen^{•−} as a ligand.



M: low-valent metal

In 1,10-phenanthroline and its derivatives, two very close-lying molecular orbitals, $a_2(\chi)$ and $b_1(\psi)$ (Chart 1),^{1–3,5,6} are available to accommodate excess negative charge which is either added from the outside or created by excitation from high-lying

Chart 1



occupied metal-based orbitals (eq 1).^{1–3} Careful high-resolution EPR measurements and their correlation with results from MO perturbation calculations of π -spin populations have allowed an unambiguous identification of phen^{•−} as a ²B₁ species,^{2a} one of the most obvious differences between $b_1(\psi)$ and $a_2(\chi)$ being the distinctly smaller π -spin population on the potentially coordinating (chelating) nitrogen centers in the a_2 orbital.^{1–3}

While the 4,7-dimethyl-1,10-phenanthroline (dmphen) radical anion also exhibits $b_1(\psi)$ as the singly occupied MO (SOMO),^{2a}

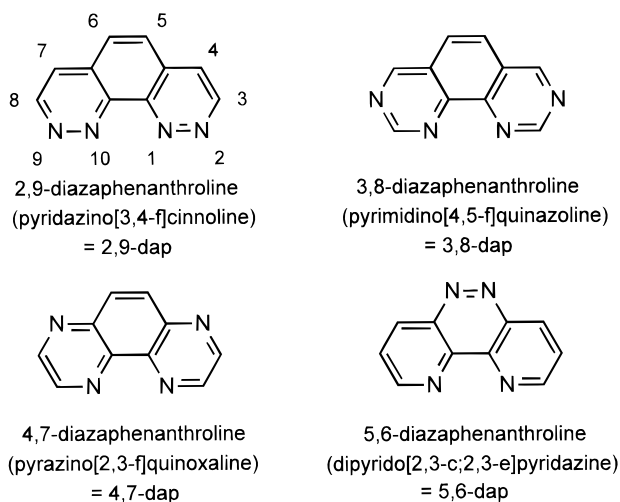
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Chart 2

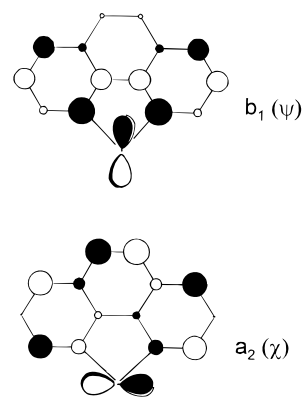


we recently showed by EPR/ENDOR spectroscopy that the one-electron-reduced forms of 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) and of its dimesitylplatinum(II) complex have the $a_2(\chi)$ orbital as the SOMO.^{2b} The reason is the selective destabilization of $b_1(\psi)$ through alkyl substitution at positions 3 and 8, which should leave the $a_2(\chi)$ MO unaffected; $a_2(\chi)$ exhibits almost no π MO coefficients at those positions (Chart 1).

The two π^* orbitals depicted in Chart 1 are also relevant for those compounds of the general formula (α -diimine) ML_n in which the α -diimine ligand (e.g. phen, bpy, 1,4-diazabutadienes)^{3,5-7} is not reduced: The properties of the then lowest unoccupied π MO (LUMO), in particular the π LUMO coefficients at the coordinating nitrogen atoms,⁸ are of considerable interest because these $\pi(N)$ centers represent the “gates” or “interface”⁹ for low-energy charge transfer interactions (eq 1) between the unsaturated π -acceptor ligand and coordinated π -electron-rich metals. In the area of complexes between N-heterocycles and low-valent metals, the value of readily calculated Hückel MO coefficients $c_N^2(\text{LUMO})$ has been demonstrated for interpretations of various physical properties such as NMR shifts,¹⁰ comproportionation constants of mixed-valence dimers,¹¹ EPR π -spin populations,^{8b,d} reduction potential shifts,^{8a,c} reactivity,⁹ MLCT band intensities,^{8a,c} and solvatochromism.¹²

The difference between the $b_1(\psi)$ and $a_2(\chi)$ orbitals is thus responsible for the different MLCT absorption band intensities as resulting from metal d/ligand π^* orbital overlap (Chart 3); obvious qualitative (symmetry)⁷ and quantitative overlap features (MO coefficients; cf. Chart 1) favor the $d_{xz} \rightarrow b_1(\psi)$ transition over the $d_{xy} \rightarrow a_2(\chi)$ absorption, and the latter may thus become difficult to detect even if it represents the transition at lowest energy. The result has sometimes been referred to^{13,14} as a

Chart 3



discrepancy between the lowest-lying “redox π^* orbital” (a_2) and the “optical π^* MO” (b_1) to which the most intense (and only detectable) low-energy MLCT transition occurs.

Employing the delineated approach, the theoretical and experimental characterization and the metal coordination of the four symmetrical diaza-2,2'-bipyridine isomers, the bidiazine ligands,^{8a,b,9} have already been useful in understanding the electronic structure of potentially photosensitizing^{15,16} and photo- and electrocatalytic^{9,17,18} α -diimine complexes. Extending these studies and adding another facet to the “phenanthroline problem”,¹⁻³ we have now applied calculations at various levels¹⁹ and obtained comparative Hückel MO (HMO)^{19a,b} perturbation correlations^{8,20} for the four (C_{2v} -symmetrical) diaza derivatives of 1,10-phenanthroline (phen), the 2,9-, 3,8-, 4,7-, and 5,6-diaza-1,10-phenanthrolines (Chart 2).

While the first two members of that series remain to be synthesized,²¹ the isomers 4,7-dap (1,4,5,8-tetraazaphenanthrene “tap”,^{9,22-24} pyrazino[2,3-f]quinoxaline) and 5,6-dap (“taphen”)¹³ have been employed as ligands in a number of complexes, e.g. with ruthenium(II),^{13,22a-k} chromium(0), molybdenum(0),

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tungsten(0),^{22l,m} rhenium(I),⁹ iron(II),²³ or platinum(II).²⁴ After discussing the calculated data and correlating these with reported experimental properties, we shall particularly focus on the EPR/ENDOR spectroscopy of the anion radical form of 4,7-dap and of its complexes with $M(\text{CO})_4$ fragments ($M = \text{Cr}, \text{Mo}, \text{W}$). This focusing on the 4,7-dap system has been triggered in particular because the calculations do not give unambiguous results regarding the orbital sequence and because coordination-induced switching of the singly occupied MO between $a_2(\chi)$ and $b_1(\psi)$ might be envisaged.²⁵ The HMO perturbation parameter used is the Coulomb integral parameter h_N ^{8,19a,b} at the chelating nitrogen π centers in the 1,10-positions; a higher h_N value reflects increased electronegativity,^{19a,b} caused either by atom exchange $\text{C} \rightarrow \text{N}$ or by σ coordination of an electrophile such as H^+ , R^+ , M^{n+} , or ML_n to an imine N center.^{8,20}

Since previous semiempirical and *ab initio* calculations of 1,10-phenanthrolines have been ambiguous,^{1,3,46} we have set out to clarify these difficulties. Starting with semiempirical (MNDO, AM1) methods, we approached the π^* -orbital ordering for the three experimentally established systems phen, tmphen, and 4,7-dap using eventually high-level *ab initio* procedures.^{19c-e}

The need for a calculation-based development of ligands related to 1,10-phenanthroline derives from a continuing interest in corresponding metal complexes for applications in analytical chemistry,²⁶ for "metallasupramolecular" structuring,²⁷ as active DNA intercalators²⁹ and chemical nuclease mimics,²⁹ in drug development³⁰ and in photochemistry,^{15,31} including photocatalysis.^{17b,31c,d}

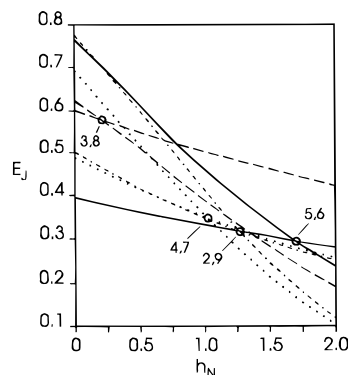


Figure 1. Correlation diagrams from HMO perturbation calculations of LUMO and SLUMO energies E_j of the four symmetrical diaza-1,10-phenanthrolines (Coulomb integral parameter h_N at the chelating nitrogen centers as perturbation variable; $h_N = 0.5$ for nonchelating N centers).

Experimental Section

Materials. The ligand 4,7-dap was used as obtained commercially. The known^{22l,m} tetracarbonylmetal(0) complexes $(4,7\text{-dap})M(\text{CO})_4$ were synthesized using (norbornadiene)Mo(CO)₄ or photogenerated (THF)M(CO)₅ ($M = \text{Cr}, \text{W}$) complexes as activated precursors; the products were identified by UV/vis and IR spectroscopy^{22l} and by C,H,N analysis.

Instrumentation. EPR and ENDOR spectra were recorded in the X band on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter, and an HP 5350B microwave counter. Anion radicals were generated for EPR/ENDOR by reacting THF or 1,2-dimethoxyethane (DME) solutions of the substrate with a potassium or sodium mirror in sealed, evacuated glass capillaries. Infrared spectra were obtained using Perkin-Elmer 684 and 283 instruments; a Shimadzu UV160 spectrophotometer served to record UV/vis spectra.

Standard Hückel MO (HMO) calculation programs for orbital energies^{19a} and π -spin populations^{19b} were used; all resonance integral parameters k were kept at 1.0. MNDO and AM1 calculation methods were used as available. *Ab initio* calculations were performed using the GAUSSIAN92 program package.^{19c} Double- ζ basis sets with d polarization functions proved to be necessary for a correct description of the electronic structures of the 1,10-phenanthroline derivatives. The 6-31G** basis^{19d} and Dunning's^{19e} valence double- ζ sets with polarization functions were used for geometry optimization of all neutral and monoreduced systems within C_{2v} constrained symmetry. The optimized geometries of open-shell systems were calculated using the restricted HF method. Both basis sets used yield almost identical geometries. The EPR spectra simulation program was based on a reported algorithm.³²

Results and Discussion

HMO Perturbation Calculations. Keeping the Coulomb integral parameter h_N at the non-chelating nitrogen π centers constant at a standard value of 0.5,^{19a,c} the variation of h_N at the 1,10-nitrogen chelate centers yielded a crossing between $a_2(\chi)$ and $b_1(\psi)$ orbitals for $0.0 < h_N < 2.0$ for all diaza-1,10-phenanthroline derivatives (Figure 1, Table 1).

The frequently drawn analogy between correspondingly substituted or coordinated phen and 2,2'-bipyridine (bpy) derivatives thus fails not only with regard to the more rigid structures of the former species; in addition, all 1,10-phenanthrolines are distinguished by two close-lying yet very different unoccupied π MOs (Chart 1). Whereas the $b_1(\chi)$ MO is

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Table 1. Squared Hückel MO Coefficients c_N^2 at the Chelating Nitrogen π Centers $N^{1,10}$ in 1,10-Phenanthroline and Diaza Derivatives

ligand	$c_N^2(a_2)^a$	$c_N^2(b_1)^a$	orbital-crossing point (h_N) ^b
phen	0.050	0.157	0.83
2,9-dap	0.073	0.195	1.28
3,8-dap	0.049	0.118	0.20
4,7-dap	0.067	0.174	1.00
5,6-dap	0.029	0.155	1.70

^a Coulomb integral parameters $h_N = 0.5$ for all nitrogen π centers.

^b From perturbation calculations (Figure 1).

essentially the same as the unequivocal LUMO of bpy and the bidiazines,^{8a} the $a_2(\chi)$ π^* MO is the LUMO of the phenanthrene π system.

Although the HMO method cannot provide absolute energy values, the trends obtained from the perturbation approach (Figure 1) should allow us to interpret experimental results and, by comparison, predict the behavior of hitherto unknown systems. As may be anticipated, the 3,8-dap isomer with the additional nitrogen centers in "4,4'-bipyridine" positions strongly prefers as LUMO the $b_1(\psi)$ orbital with its high MO coefficients at those centers (Chart 1). For all reasonable h_N parameters, $b_1(\psi)$ thus lies below $a_2(\chi)$ in 3,8-dap and the orbital-crossing point lies at a small h_N value (Table 1).

The situation is less clear for phen, 4,7-dap, and 2,9-dap (Table 1): Considering the limited accuracy of the HMO approach, the orbital crossing at h_N values around 1.0 leaves open whether the actual systems have the $a_2(\chi)$ or the $b_1(\psi)$ MO as LUMO. EPR/ENDOR studies show that the singly occupied MO (SOMO) of phen^{-2a} and 4,7-dap⁻ is the $b_1(\psi)$ orbital (see below), which leaves the yet unknown 2,9-dap isomer with its still higher orbital-crossing point at 1.28 as a most promising candidate for a coordination-induced orbital switching.²⁵

With an orbital-crossing point calculated at 1.70 (Table 1), the 5,6-dap ligand should have the $a_2(\chi)$ orbital below $b_1(\psi)$. In fact, a correlation between reduction potentials and detectable first absorption maxima for the complexes [(taphen)_nRu(bpy)_{3-n}]²⁺ ("taphen" = 5,6-dap)¹³ has exhibited the uncommon phenomenon¹⁴ of a discrepancy between the "redox π^* orbital" (i.e. the LUMO, here $a_2(\chi)$) and the "optical π^* orbital" (here SLUMO, $b_1(\psi)$) to which the intense long-wavelength MLCT transitions occur. Even with coordinated metal centers (which corresponds to an increased h_N value),^{8,20} the 5,6-dap π system clearly differs from the other dap ligands.

Yet in all phenanthroline derivatives, the $a_2(\chi)$ and $b_1(\psi)$ π^* orbitals are lying close to each other, which raises the question as to whether both⁷ overlap-allowed transitions $d_{xz} \rightarrow b_1$ and $d_{xy} \rightarrow a_2$ can be observed by absorption spectroscopy. The latter transition is disfavored not only by the different type of overlap from the d-orbital set but also by small c_N^2 values (Charts 1 and 3, Table 1) at the metal/ligand interface. Even in the optimistic approximation that those c_N^2 values are proportional to the band intensity^{8a} for both transitions, the $d_{xy} \rightarrow a_2$ absorption band should play a minor role in comparison to that for $d_{xz} \rightarrow b_1$ and may thus be obscured easily by that latter band. The largest ratio $c_N^2(b_1)/c_N^2(a_2) = 5.34$ was calculated for the 5,6-dap system, which thus offers the poorest opportunity to observe the $d_{xy} \rightarrow a_2$ MLCT transition next to $d_{xz} \rightarrow b_1$; better chances can be expected for complexes of the 4,7-dap isomer, where that ratio is only 2.59. Yet considering the presence of other low-intensity d \rightarrow π^* MLCT transitions,⁷ the unambiguous detection of $d_{xy} \rightarrow a_2$ transitions in complexes of 1,10-phenanthroline derivatives may require sophisticated tech-

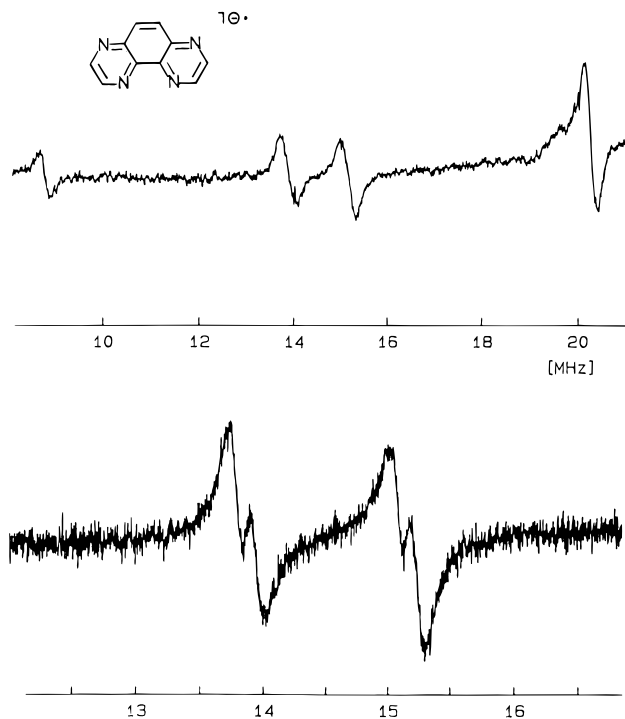


Figure 2. ENDOR spectra of (4,7-dap⁻)(K⁺) at 180 K in THF with 100 kHz (top) and 35 kHz modulation depth (bottom); 60 mW microwave power, 315 W radiofrequency power.

niques.³³ Of course, the energy difference between the transitions $d_{xz} \rightarrow b_1$ and $d_{xy} \rightarrow a_2$ depends also on the relative positioning of d_{xz} and d_{xy} ; octahedral d^6 , square-planar d^8 , and tetrahedral d^{10} metal centers may well differ in that respect.^{24b,34}

Ab Initio Calculations. Semiempirical calculations (MNDO, AM1) and *ab initio* calculations without polarization functions for the optimized geometries of phen and tmphen show two close-lying a_2 (LUMO) and b_1 unoccupied orbitals. Semiempirical calculations and *ab initio* methods using a limited basis thus failed in reproducing the experimental results.²

Using the 6-31G** basis including d polarization functions, however, we correctly obtained b_1 as the LUMO of phen and a_2 as the LUMO of tmphen after geometry optimization. For phen, the b_1/a_2 separation is 0.036 eV, and for tmphen the a_2/b_1 gap is 0.091 eV. Applying the same basis to 4,7-dap, the *ab initio* calculations yielded two virtually energy-degenerate a_2 and b_1 MOs. Restricted HF level calculations of the spin densities at the chelating nitrogen centers in anion radicals yielded values of 0.1011 for phen⁻ (²B₁ ground state), 0.0221 for tmphen⁻ (²A₂ ground state), and 0.1486 for 4,7-dap⁻ (²B₁ state). The spin density at the nonchelating N centers in 4,7-dap⁻ is 0.0557. Translating these values into EPR coupling constants by using a McConnell-type proportionality factor of 2.3 mT^{19b} (cf. Table 2), we obtain calculated $a(^{14}\text{N})$ hyperfine splitting constants of 0.233 mT for phen⁻, 0.051 mT for tmphen⁻, and 0.342 and 0.128 mT for 4,7-dap⁻. A comparison with the experimental data from Table 2 exhibits quite good agreement, confirming the orbital assignment; for the ²A₂ state of 4,7-dap⁻, on the other hand, the calculated $a(^{14}\text{N})$ values are 0.083 and 0.195 mT.

EPR/ENDOR Spectroscopy of 4,7-dap⁻ Systems. Prior to this work it was only known that the phen anion radical is a ²B₁ species.^{2a} Since 4,7-dap was calculated with a higher orbital-crossing point than phen (Table 1), the question arose as to whether 4,7-dap⁻ still has the $b_1(\psi)$ orbital as the SOMO

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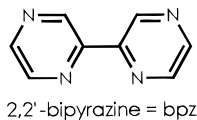
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Table 2. EPR Hyperfine Coupling Constants of Anion Radicals

anion radical	coupling constants (mT)					g	ref
	$a_1(\text{N})$	a_2	a_3	a_4	a_5		
phen ^{•-}	0.280 ^a	0.041	0.360	0.280	0.041	2.0030	2a
tmphen ^{•-}	0.073 ^a	0.417	n.o.	0.336 (Me)	0.449	2.0027	2b
4,7-dap ^{•-} (² A ₂) ^b	0.155	0.236	0.072	0.307	0.244		this work
4,7-dap ^{•-} (² B ₁) ^b	0.380	0.080	0.277	0.203	0.001		this work
4,7-dap ^{•-} ^c	0.340 ^a	0.051	0.390	0.164 ^a	0.051	2.0034	this work
4,7-dap ^{•-} ^d	0.344	0.051 ^e	0.409	n.o.	0.041 ^e		this work
bpz ^{•-} ^f	0.370	0.020 ^e	0.480	0.100	0.012 ^e	2.0033	8b
(OC) ₄ Cr(4,7-dap ^{•-})		insufficiently resolved hyperfine structure				2.0023	this work
(OC) ₄ Mo(4,7-dap ^{•-}) ^g	0.425	n.o.	0.405	0.155	n.o.	2.0021	this work
(OC) ₄ W(4,7-dap ^{•-})		insufficiently resolved hyperfine structure				2.0005	this work
(OC) ₄ Cr(bpz ^{•-})	0.482	0.020 ^e	0.469	0.093	0.044 ^e	2.0024	8b
(OC) ₄ Mo(bpz ^{•-}) ^{f,h}	0.468	0.016 ^e	0.452	0.101	0.033 ^e	2.0026	8b
(OC) ₄ W(bpz ^{•-})	0.46	n.o.	0.46	0.105	n.o.	2.0032	8b

^a For *ab initio* calculated values of $a(\text{N})$, see text. ^b Calculated via HMO from the McConnell equation $a = \rho_x \cdot Q = c^2 \cdot Q$; $Q = 2.3$ mT, $h_{\text{N}} = 0.89$.^{19b} ^c From EPR at 300 K in THF. ^d From ENDOR at 240 K (¹⁴N ENDOR) or 180 K (¹H ENDOR) in THF. ^e Assignment a_2/a_5 uncertain. ^f Numbering following the phenanthroline chart. ^g $a_x \pm 0.02$ mT; in all other cases the uncertainty of a_x is ± 0.005 mT. ^h $a(^{95,97}\text{Mo}) = 0.22$ mT.

and, if not, whether a coordination-induced orbital switching²⁵ could be accomplished. Recent results on organometallic platinum(II)²⁴ and rhenium(I) complexes⁹ of 4,7-dap and the formally related bidiazine analogue bpz (bpz = 2,2'-bipyrazine)



showed a close similarity in absorption and emission spectroscopy, cyclic voltammetry, and EPR spectroscopy of one-electron-reduced forms,^{9,18,24} suggesting that the $b_1(\psi)$ MO lies below $a_2(\chi)$ in these 5d-element complexes.

We therefore start with an EPR and ENDOR study of the anion radical of the ligand, which should unequivocally show the character of the SOMO. Reduction of 4,7-dap with potassium or sodium in THF yields radical ion pairs (4,7-dap^{•-})-(M⁺) which show hyperfine contribution from the metal ions only below 240 K (220 K: $a(^{39}\text{K}) = 0.012$ mT; $a(^{23}\text{Na}) = 0.019$ mT). Although the EPR spectra are rather well resolved, they do not allow an unequivocal assignment of all hyperfine coupling constants and hence an absolutely safe identification of the SOMO. Electron nuclear double resonance (ENDOR)³⁵ usually provides better resolution and an assignment of coupling constants to different kinds of nuclei; the observed signals must fulfil the ENDOR resonance condition (2).

$$\nu(\text{ENDOR}) = |\nu_x \pm a_x/2| \quad (2)$$

$$\nu(^1\text{H}) = 14.90 \text{ MHz}; \quad \nu(^{14}\text{N}) = 1.08 \text{ MHz}$$

$$1 \text{ mT} = 28 \text{ MHz}$$

The ENDOR measurements on an EPR-saturated sample of (4,7-dap^{•-})(K⁺) in THF were performed at different temperatures and modulation depths (Figure 2). Whereas the optimum conditions³⁵ for the ¹H signals were found at 180 K, one of the ¹⁴N signals could be identified at 240 K; applying eq 2, the high-frequency position at 5.90 MHz translates to 0.344 mT. The other ¹⁴N ENDOR signals occur at lower frequencies and could not be identified with the same certainty.

Variation of the modulation depth revealed the presence of three ¹H coupling constants, *one large* and *two small* splittings. This observation effectively rules out the ²A₂ alternative for

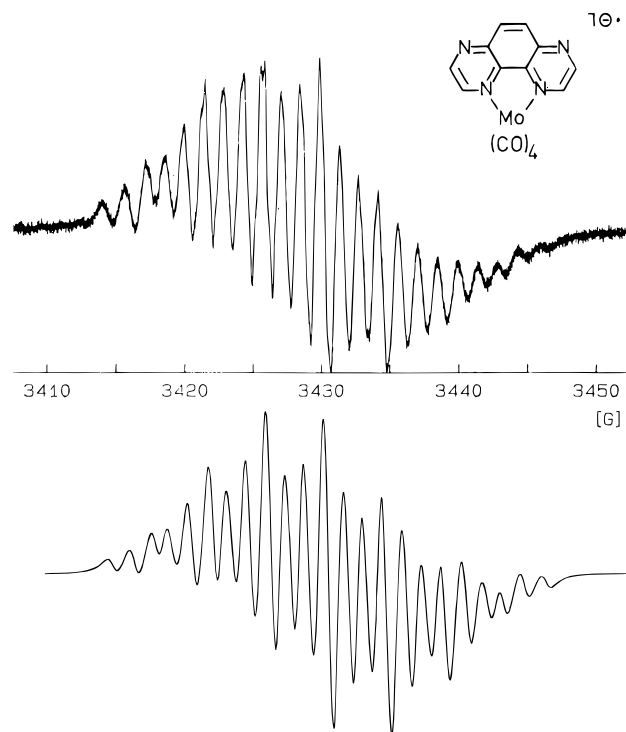


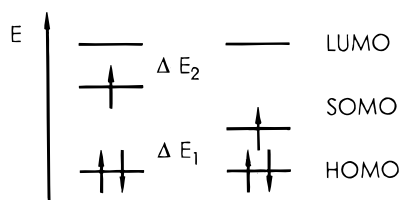
Figure 3. EPR spectrum of [(4,7-dap^{•-})Mo(CO)₄](K⁺) at 300 K in DME; experimental spectrum (top) and computer simulation (bottom).

this radical anion because *one small* and *two large* ¹H couplings would be expected in such a case (Chart 1, Table 2). By employment of the ENDOR data, the EPR spectrum could be reproduced with all relevant coupling constants and in complete agreement with the spin distribution calculated for a ²B₁ species (Table 2).

In an attempt to maintain the necessary EPR resolution for the assignment of coupling constants and, therefore, the identification of the SOMO, we chose to study one-electron-reduced tetracarbonylmetal(0) complexes for our further studies. For the bidiazine series, such complexes have provided resolved EPR spectra and useful information concerning the effect of metal coordination on the spin distribution.^{8b} Starting from known neutral precursors (4,7-dap)M(CO)₄ (M = Cr, Mo, W),^{22l,m} the reduction with potassium in 1,2-dimethoxyethane (DME) yielded paramagnetic complexes [(4,7-dap^{•-})M(CO)₄](K⁺). Unfortunately, the EPR transitions in those compounds could not be sufficiently saturated for ENDOR measurements under fluid-solution conditions, and furthermore, the EPR

(35) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH: Weinheim, 1988.

Chart 4



spectra of the chromium and tungsten complexes were not sufficiently well resolved to analyze the hyperfine splitting. However, the isotropic g factors could be determined at $g = 2.0023$ (Cr complex) and 2.0005 (W complex).

The tetracarbonylmolybdenum complex gave a sufficiently resolved EPR spectrum which could be simulated with the data from Table 2. Although the small coupling constants a_2 and a_5 and the $^{95,97}\text{Mo}$ hyperfine splitting could not be determined due to the residual line width, the other values are compatible (i) with the occupation of $b_1(\psi)$ by the unpaired electron and (ii) with the coordination of $\text{Mo}(\text{CO})_4$ which typically increases the $^{14}\text{N}(\alpha\text{-diimine})$ coupling constant.^{8b,d20} Just as the ligand anion radical $4,7\text{-dap}^{\bullet-}$, the molybdenum(0) complex shows great similarity with the bpz analogue (Table 2),^{8b} supporting the $^2\text{B}_1$ assignment.

While the coordination of $\text{Mo}(\text{CO})_4$ to $4,7\text{-dap}^{\bullet-}$ leaves the spin distribution little changed, there is a remarkable effect of coordination on the g values. In contrast to the anion radical complexes $(\text{bpz}^{\bullet-})\text{M}(\text{CO})_4$, which all have $g > g(\text{electron}) = 2.0023$,^{8b} the tetracarbonylmetal complexes of $4,7\text{-dap}^{\bullet-}$ exhibit $g \leq g(\text{electron})$. In each case, the tetracarbonyltungsten derivative exhibits the most extreme value (2.0032 and 2.0005 , respectively), in accordance with the high spin-orbit coupling factor ζ of that 5d metal;³⁷ similar results were obtained for rhenium(I) complexes.⁹ According to the MO model-based approximation $\Delta g = k \cdot \zeta (1/\Delta E_1 - 1/\Delta E_2)$ (Chart 4) for g factor shifts where $\Delta g = g - g(\text{electron})$,^{20,36} a low g factor indicates close-lying unoccupied MOs in the vicinity of the SOMO; the admixture of low-lying excited states with nonnegligible orbital angular momentum affects the deviation from the spin-only g value of the radical species with the spin-orbit coupling constant ζ serving as a proportionality factor.³⁷ We may thus speculate for the $^2\text{B}_1$ species $(4,7\text{-dap}^{\bullet-})\text{M}(\text{CO})_4$ that the presence of the low-lying unoccupied $a_2(\chi)$ orbital is responsible for the observed low g factors.

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Summary

The reproduction of the correct ordering of the unusually close-lying unoccupied π^* molecular orbitals in 1,10-phenanthroline derivatives requires fairly high-level *ab initio* calculations. Semiempirical and *ab initio* methods without polarization functions failed to predict the correct MO sequence, and the HMO perturbation approach allowed only a comparative discussion between various derivatives.

We have unambiguously shown by EPR/ENDOR that the $4,7\text{-dap}^{\bullet-}$ π system has the unpaired electron situated in the $b_1(\psi)$ MO, like that of $\text{phen}^{\bullet-}$. Accordingly, $4,7\text{-dap}$ is not a candidate for coordination-induced orbital switching.²⁵ Assuming the same situation $E(\chi) > E(\psi)$ for the neutral compound and its complexes within a one-electron approximation, we would then also predict that no discrepancy arises between optical and redox π^* orbitals in corresponding complexes—a result different from that for the isomeric $5,6\text{-dap}$ (“taphen”) species.¹³ Nevertheless, the calculations and EPR results suggest that $a_2(\chi)$ lies rather close to $b_1(\psi)$ in $4,7\text{-dap}$ systems, a result which ought to be considered for excited state chemistry.

Considering the wide and growing applications of 1,10-phenanthroline complexes,^{15,22g-k,26–32} a systematic modification of the phen ligand remains worthwhile. Of the yet unknown dap isomers, the $3,8$ -derivative should strongly prefer the $b_1(\psi)$ orbital as the LUMO over the $a_2(\chi)$ orbital (Figure 1). Since $3,8\text{-dap}$ is related to $4,4'$ -bipyrimidine in the bidiazine series,^{8a,b} one may expect a similar³⁸ reactivity such as the enhanced electrophilic addition e.g. of R^+ at the $3,8$ - (“ $4,4'$ -bipyridine”-) centers of the chelating ligand which would couple α -diimine coordination with “methylviologen”-type redox functionality.³⁹ On the other hand, the $a_2(\chi)/b_1(\psi)$ energy gap should be particularly close in $2,9\text{-dap}$ systems, rendering that hitherto unknown ligand as an attractive synthetic target.

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