# Diquaternized Heterocycles with Strong Electronic Coupling between a Metal-chelating Site and a Methylviologen-type Redox Function: EPR/ENDOR Detected Coordination of Metal Ions and Complexes by Radical Cation Intermediates

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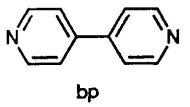
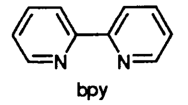
Calculated (MNDO, AM1) and experimental results from electrochemistry and EPR/ENDOR spectroscopy are reported for the diquaternized heterocyclic systems 1,1′-dialkyl-4,4′-bipyrimidinium ($1^{2+/\bullet+/0}$), 4,4′-dimethyl-2,2′-bipyrazinium ($2^{2+/\bullet+/0}$) and 1,1′-dimethyl-3,3′-bipyridazinium ($3^{2+/\bullet+/0}$) which exhibit simultaneously features of the methylviologen two-step redox system, $MV^{2+/\bullet+/0}$, and an α-diimine chelate site for metal coordination. While metal-free species $2^{n+}$ and $3^{n+}$ could not be synthesized as pure compounds, the 'diazamethylviologen' system $1^{n+}$, a hybrid structure between $MV^{n+}$ and 2,2′-bipyridine, was studied especially as the radical cation intermediate (*n* = 1) in the presence of potentially coordinating electrophiles such as $Zn^{2+}$, $Cu^{+}$, $In^{n+}$, $Tl^{+}$, $Mo(CO)_4$, $[Re(CO)_3(PPh_3)]^{+}$ or $[Ru(bpy)_2]^{2+}$. The different character of the metal centres in terms of charge, ligand preference and the ability to back-donate electrons into the singly occupied π* orbital of the cationic radical ligand determine the variable extent of ion-pair association *via* the EPR/ENDOR-detectable spin transfer. System $2^{n+}$ which may be described as a 3,3′-coupled *N*-methylpyrazinium dimer could be isolated only in coordinated form, bound to $[Ru(bpy)_2]^{2+}$ or $Re(CO)_3Cl$, both complexes showing a rather irreversible second reduction due to the non-classical (non-Kekulé) electronic structure as predicted from the calculations for $2^0$ and $3^0$.

Bipyridines are among the most extensively studied heterocycles because the two prominent species, the 2,2′- and 4,4′-isomers, are popular components in supramolecular and materials-oriented chemistry.[1,2] While 4,4′-bipyridine (bp) is a good π conjugated bridging ligand,[3] the 2,2′-bipyridine (bpy) isomer is an excellent metal chelate ligand with low-lying π* orbitals for π back-donation.[1,4] The most prominent forms of the 4,4′-isomer are the *N,N′*-dialkylated (diquaternized) derivatives,[5] the 'methylviologens', which serve as widely used electron mediators or redox indicators with an intensely coloured radical intermediate of the underlying two-step redox system.[5–7]



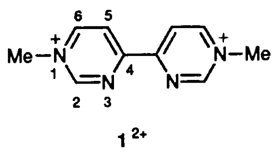
bp



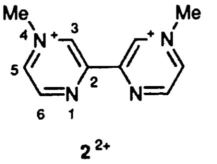
bpy

Bidiazines[8] such as bipyrimidines, bipyridazines and bipyrazines were studied to a much lesser extent because of their less convenient synthesis although the presence of two nucleophilic nitrogen centres in each aryl ring allows for polyfunctional behaviour in terms of metal chelate coordination and *e.g.* quaternization by alkyl groups[9,10] or other coordination.[11] Using three of the potentially metal chelating symmetrical bidiazine isomers[8] we now present calculations and, as available, experimental results for the diquaternized bidiazine redox systems 1,1′-dialkyl-4,4′-bipyrimidinium ($1^{2+/\bullet+/0}$),[9,10] 4,4′-dimethyl-2,2′-bipyrazinium ($2^{2+/\bullet+/0}$) and 1,1′-dimethyl-3,3′-bipyridazinium ($3^{2+/\bullet+/0}$).

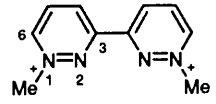
There have been several reports of molecules in which the bpy chelate function and the $MV^{n+}$ two-step redox capability were combined by covalently linking derivatives of bpy and $MV^{2+}$,[12–14] however, an intimate coupling of both functions in one and the same biaryl π system has only been achieved in system $1^{n+}$.[9,10] System $2^{n+}$, on the other hand, may be regarded as two *N*-methylpyrazinium molecules coupled in the 3,3′-position for π conjugation and metal chelating purposes; the *N*-methylpyrazinium cation/radical redox system represents a very unusual monodentate ligand for π donor transition metal centres.[15–17] In this work we give a full account of the three systems 1–3 with emphasis on the electronic structures as evident from EPR/ENDOR spectroscopy of the paramagnetic intermediates and with calculation results on the unusual π electron situation of the neutral forms. Several different kinds of metal species such as $Zn^{2+}$, $Cu^{+}$, $In^{n+}$, $Tl^{+}$, $Mo(CO)_4$, $[Ru(bpy)_2]^{2+}$ or $[Re(CO)_3X]^{n+}$, X = Cl and *n* = 0, X = $PPh_3$ and *n* = 1, were offered for coordination in order to stabilize paramagnetic intermediates and also to probe the very unusual[10,18] situation that a cationic radical can form complexes with positively charged, or at least electrophilic, metal species.



$1^{2+}$



$2^{2+}$



$3^{2+}$

While the $Re^{I}$ and $Ru^{II}$ metal complex fragments were chosen because corresponding 'polypyridine' complexes are being used for purposes of catalytic $CO_2$ activation[19] or photosensitized electron transfer,[20] the zinc, copper, indium and thallium metals were used to reduce electron deficient $1^{2+}$, yielding (solvated) atomic ions with different charge and 'hardness'. The favourable nuclear isotope properties of Cu, In and Tl should allow us to obtain EPR information about a possible ion pairing between metal cations and the cation radical ligand, such charge-disfavoured interactions being virtually unknown[10] in contrast to classical radical ion pairs[18] between metal cations and anion radical ligands.[21]

## Experimental

*Materials and Procedures.*—All reactions and spectroscopic studies were carried out under an argon atmosphere in dried solvents. Syntheses of the 'diazamethylviologen' $(1^{2+})(BF_4^-)_2$ and its complexes with $Re(CO)_3Cl$ or $[Ru(bpy)_2]^{2+}$ have been reported previously.[9,10] Compound $[(2^{2+})Ru(bpy)_2](BF_4^-)_4$ was obtained analogously to the $PF_6^-$ salt of the 4,4'-diethyl derivative.[9]

$[(2^{2+})Re(CO)_3Cl](BF_4)_2$ was obtained as a dark purple complex by slowly adding 100 mg (0.22 mmol) of $(bpz)Re(CO)_3Cl$ (bpz = 2,2'-bipyrazine)[22] in 30 $cm^3$ of 1,2-dichloroethane to 36 mg (0.24 mmol) of $(Me_3O)(BF_4)$ in the same volume of solvent. After heating to reflux for 2 h the complex began to precipitate in the cold; it was filtered off, washed with 1,2-dichloroethane and dried under vacuum to yield 58 mg (38%) of the very sensitive but analytically (C, H, N) pure complex.

Repeated attempts to obtain isolable compounds of $(2^{2+})(BF_4)_2$ from Meerwein alkylation of bpz produced viscous colourless precipitates which rapidly decomposed into a black material even in the absence of air, moisture or light. Rapid reduction of the freshly precipitated compound with zinc in acetonitrile or in deaerated aqueous carbonate solution[10] led to a coloured radical ($\lambda_{max}$ = 620 nm) with an EPR spectrum: $g$ = 2.0032, several lines with 0.3 mT spacing, no central line.

*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 a HP 5350B microwave counter. The various reactions leading to radical formation are described in the main text. Cyclic voltammetry was carried out in acetonitrile–0.1 mol $dm^{-3}$ $Bu_4NPF_6$ using a three-electrode configuration (glassy carbon working electrode, platinum wire counter electrode, saturated calomel reference) and a PAR 273/175 potentiostat and function generator. The ferrocene/ferrocenium ($Fc^{0/+}$) couple was used for internal calibration.

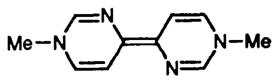
*Calculations.*—Because of the unknown geometry of diquaternized bidiazine ligands in their different oxidation states the Austin model (AM1) method[23] was used for geometry optimization and calculation of rotational barriers. The MNDO method[24] was then used to calculate bond orders.

## Results and Discussion

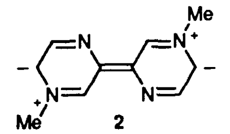
*Calculations of Oxidation States.*—The electronic structures of the diquaternized bidiazine chelate ligands **1**–**3** and of the non-quaternized parent systems 4,4'-bipyrimidine (bpm), 2,2'-bipyrazine (bpz) and 3,3'-bipyridazine (bpdz) were calculated using the semiempirical methods AM1 and MNDO.[23,24] In order to find the preferred conformation of the systems **1**–**3** we used the AM1 program to calculate rotational barriers around the interannular single bonds of the oxidized forms. Although MNDO is fairly reliable with respect to bond distances and angles, the AM1 procedure is better suited to reproduce conformational preferences (torsional angles).[25] Previous *ab initio* calculations have shown an essentially planar *trans* arrangement of the non-quaternized molecules as an energy minimum, in agreement with some experimental data from gas phase studies.[26]

Assuming planar six-membered rings, the potential energy dependence of the interannular dihedral angle $\theta$ was calculated for dications $1^{2+}$–$3^{2+}$, yielding an essentially coplanar *trans* conformation as the only energy minimum in all instances; the energy minima of $2^{2+}$ and $3^{2+}$ were rather flat between $\theta$ = 150 ° and 180 °. The *cis*/*trans* energy differences were obtained as 39.9 kJ $mol^{-1}$ for $2^{2+}$, 33.0 kJ $mol^{-1}$ for $1^{2+}$ and 8.0 kJ $mol^{-1}$ for the $N\overset{\cdot\cdot}{-}N^+(R)$ bond-containing $3^{2+}$, reflecting different contributions from steric and electrostatic interactions. For the radical cation intermediates there are two energy minima for the *cis* and *trans* coplanar forms, the *trans* arrangement lying lower by about 10 kJ $mol^{-1}$ for $1^{\cdot+}$ and $3^{\cdot+}$ and by about 40 kJ $mol^{-1}$ for $2^{\cdot+}$. With a typical value of 56 kJ $mol^{-1}$ for *trans*-$1^{\cdot+}$ the barriers to rotation are significantly higher for the radical cations relative to the dications, in agreement with the increased bond order (Table 1).

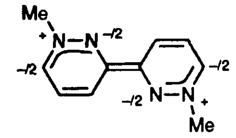
The bond orders as calculated by the MNDO method for the non-reduced species show the aromatic rings connected *via* a single bond. On reduction, this interannular bond order increases in the direction of a double bond corresponding to a quinonoid structure,[27] however, such an arrangement can be formulated without problems only for system **1** (and its parent, bpm). The two other diquaternized bidiazines show a different alternation of nitrogen centres and coupling sites in the biaryl π system which requires unfamiliar formulations, especially for the doubly reduced forms of the diquaternized systems **2** and **3**. Representations derived from the calculated bond orders of these species are shown in structures **1**–**3**. Such 'non-Kekule' structures[9,28] are usually associated with high reactivity, we therefore set out to try and generate these forms by electrochemical reduction.



**1**



**2**



**3**

*Synthesis and Electrochemistry.*—Of the metal-free diquaternized systems only compound $(1^{2+})(BF_4^-)_2$ could be prepared as a fairly stable species *via* Meerwein alkylation.[9,10] Analogous reactions of $(Me_3O)(BF_4)$ in acetonitrile or 1,2-dichloroethane with bpz or bpdz instead of bpm resulted in ill-defined products which rapidly decomposed into dark materials even after exclusion of moisture, air and light. Attempts immediately to reduce $2^{2+}$ to $2^{\cdot+}$ with Zn gave a paramagnetic species with typical[9,29] long-wavelength absorptions at 1030(sh), 910(sh) and 620 nm, however, the absence of a central line in the EPR spectrum is incompatible with a symmetrical species $2^{\cdot+}$. The $g$ factor of 2.0032 and the appearance of about 30 lines with 0.3 mT spacing suggests the formation of a stable 1,4-disubstituted 1,4-diazinium radical cation.[29]

In order to circumvent this problem we took advantage of the π back donation in complexes of $Re^I$ or $Ru^{II}$ with the corresponding non-quaternized π acceptor ligands.[8,22,30,31] The known complexes $(L)(ML'_n)$, L = bpm or bpz, $ML'_n$ = $Re(CO)_3Cl$ or $[Ru(bpy)_2]^{2+}$, could thus be dimethylated much more easily than the metal-free ligands, the increase in π electron density at the peripheral nitrogen centres being due to the effect of metal-to-ligand back donation *via* high-lying d(π) orbitals.

**Table 1** Calculated bond orders[a] for different oxidation states of bidiazines and diquaternized derivatives

| | Bond[b] | | | | | | |
|---|---|---|---|---|---|---|---|
| Compd. | 1–2 | 2–3 | 3–4 | 4–5 | 5–6 | 6–1 | Interannular |
| bpm | 1.359 | 1.415 | 1.373 | 1.393 | 1.359 | 1.449 | 0.974 |
| $\mathrm{bpm}^{\bullet -}$ | 1.306 | 1.505 | 1.205 | 1.158 | 1.516 | 1.325 | 1.207 |
| $\mathrm{bpm}^{2-}$ | 1.233 | 1.624 | 1.041 | 1.019 | 1.663 | 1.221 | 1.631 |
| $\mathbf{1}^{2+}$ | 1.188 | 1.486 | 1.355 | 1.368 | 1.406 | 1.276 | 0.972 |
| $\mathbf{1}^{\bullet +}$ | 1.104 | 1.619 | 1.169 | 1.176 | 1.589 | 1.104 | 1.197 |
| **1** | 1.013 | 1.774 | 1.038 | 1.023 | 1.795 | 1.006 | 1.641 |
| bpz | 1.384 | 1.329 | 1.426 | 1.449 | 1.314 | 1.469 | 0.984 |
| $\mathrm{bpz}^{\bullet -}$ | 1.227 | 1.142 | 1.551 | 1.323 | 1.271 | 1.536 | 1.204 |
| $\mathrm{bpz}^{2-}$ | 1.057 | 1.006 | 1.674 | 1.222 | 1.220 | 1.632 | 1.596 |
| $\mathbf{2}^{2+}$ | 1.337 | 1.411 | 1.241 | 1.348 | 1.269 | 1.515 | 0.975 |
| $\mathbf{2}^{\bullet +}$ | 1.146 | 1.257 | 1.338 | 1.089 | 1.213 | 1.540 | 1.198 |
| **2** | 1.052 | 1.058 | 1.432 | 1.142 | 1.156 | 1.688 | 1.547 |
| bpdz | 1.492 | 1.344 | 1.364 | 1.430 | 1.393 | 1.368 | 0.972 |
| $\mathrm{bpdz}^{\bullet -}$ | 1.556 | 1.179 | 1.183 | 1.553 | 1.274 | 1.319 | 1.204 |
| $\mathrm{bpdz}^{2-}$ | 1.643 | 1.023 | 1.032 | 1.684 | 1.178 | 1.264 | 1.612 |
| $\mathbf{3}^{2+}$ | 1.224 | 1.537 | 1.220 | 1.516 | 1.349 | 1.341 | 0.974 |
| $\mathbf{3}^{\bullet +}$ | 1.125 | 1.203 | 1.215 | 1.481 | 1.279 | 1.340 | 1.186 |
| **3** | 1.306 | 1.081 | 1.018 | 1.765 | 1.097 | 1.332 | 1.572 |

[a] From MNDO calculations of AM1-optimized structures. [b] See structures $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ for numbering of positions.

**Table 2** Electrochemical data[a] of compounds

| Compound (isolated form) | $E_{\mathrm{red1}}$ | $E_{\mathrm{red2}}$ | $E_{\mathrm{ox}}$ |
|---|---|---|---|
| $\mathbf{1}^{2+}$ | −0.38(70) | −0.87(90) | — |
| $[(\mathbf{1}^{2+})\mathrm{Ru(bpy)_2}]^{4+}$ | +0.14(80) | −0.32(70) | +1.45(i) |
| $[(\mathbf{1}^{2+})\mathrm{Re(CO)_3Cl}]^{2+}$ | +0.19(80) | −0.31(i) | +1.68(i) |
| $[(\mathbf{2}^{2+})\mathrm{Ru(bpy)_2}]^{4+}$ | −0.19(70) | −0.79(i)[b] | +1.5(i) |
| $[(\mathbf{2}^{2+})\mathrm{Re(CO)_3Cl}]^{2+}$ | −0.05(130) | −0.64(i) | +1.70(200)[c] |

[a] From cyclic voltammetry at 100 mV $s^{-1}$ in acetonitrile–0.1 mol $dm^{-3}$ $Bu_4NPF_6$. Potentials in V *vs.* $Fc^{0/+}$, peak potential differences in mV (in parentheses). (i): irreversible process (peak potentials given). [b] At 3000 mV $s^{-1}$: −0.82(130). [c] At 500 mV $s^{-1}$, partially reversible.

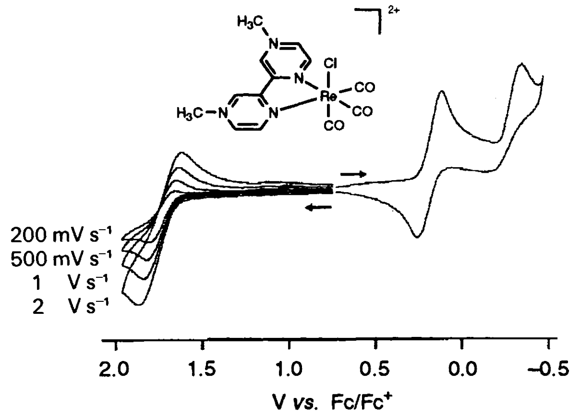


Fig. 1 Cyclic voltammogram of complex $[(\mathbf{2})\mathrm{Re(CO)_3Cl}]^2$ in acetonitrile–0.1 mol $dm^{-3}$ $Bu_4NPF_6$. Reduction at 100 mV $s^{-1}$, oxidation at variable scan rates

The cyclic voltammetric results for the stable species are summarized in Table 2, Fig. 1 shows a typical cyclovoltammogram for one of the complexes.

Despite their ability to donate π electrons to the π* orbitals of the acceptor ligands the $Re^I$ and $Ru^{II}$ complex fragments still behave as net electron-withdrawing groups[32] to the diquaternized ligands as evidenced from anodically shifted reduction potentials. Complexes of $\mathbf{1}^{2+}$ are thus reduced at positive potentials *versus* the ferrocene/ferrocenium couple and the first reduction of complexes with $\mathbf{2}^{2+}$ is also very easy. Although the differences are small, the facilitated reduction of $Re^I$ *vs.* $Ru^{II}$ complexes and bpm *vs.* bpz systems is in agreement with previous experience;[8,22,30] the same holds for the higher potentials for irreversible or only partially reversible (Fig. 1) oxidation of the $Re^I$ systems relative to the $Ru^{II}$ complexes.[31,33]

Whereas the second reduction is still reversible for $\mathbf{1}^{2+}$ and its $Ru^{II}$ complex, the compound with $Re(CO)_3Cl$ loses chloride after that second one-electron reduction, a typical reaction.[22,31,34] The $Ru^{II}$ complex of system $\mathbf{2}^{n+}$ exhibits an irreversible second reduction at normal cyclovoltammetric scan rates; only on rapid scanning at 3 V $s^{-1}$ is the anodic counterpeak visible, indicating a short lifetime of $\mathbf{2}^0$ despite the stabilization by the coordinated metal complex fragment.

*EPR Spectra of Radical Intermediates.*—According to the electrochemical results, the stable complexes of rhenium and ruthenium can be conveniently reduced to paramagnetic species. However, the unusual situation that a methylviologen-derived dication can be reduced very easily to a potentially metal-chelating radical cation invited additional attempts to use various metal electrophiles as coordination partners. Normally, only neutral ('free') or especially anionic radicals can bind metal species in radical complexes or 'ion pairs'.[18,21]

Since the free ligand $(\mathbf{1}^{2+})(BF_4^-)_2$ is stable and reduced at about the potential of the saturated calomel electrode there are several metals conceivable which should be able to reduce $\mathbf{1}^{2+}$ and form potentially ligand-binding cations. We used copper, zinc, thallium and indium for that purpose, the results are described in the following and the data are summarized in Table 3.

In the absence of metallic electrophiles, chemical or electrolytic reduction of $\mathbf{1}^{2+}$ in various solvents yields the stable cation radical $\mathbf{1}^{\bullet +}$, presumably in the *trans* conformation; the best resolution was observed in protic solvents like water or methanol.[10] The EPR/ENDOR derived coupling constants were analysed and assigned according to previously reported HMO/McLachlan calculations;[10] semiempirical spin density calculations (UHF-AM1)[35] gave essentially similar results with very little difference between *cis* and *trans* configurations. Attempts to reduce $\mathbf{1}^{2+}$ by copper or thallium metal in acetonitrile solution were successful and yielded highly resolved EPR spectra, however, the virtually unchanged EPR spectra relative to free $\mathbf{1}^{\bullet +}$ [10] and the absence of any metal hyperfine

**Table 3** EPR data[a] of complexes ($1^{\cdot+}$)($ML_n$)

| $ML_n$ | $g$ | $a$<br>$N^1$ | $CH_3$ | $H^2$ | $N^3$ | $H^5$ | $H^6$ | EPR linewidth[b] | Solvent |
|---|---|---|---|---|---|---|---|---|---|
| —[c] | 2.0031 | 0.378 | 0.378 | 0.048 | 0.078 | 0.128 | 0.252 | 0.020 | MeOH |
| ($Cu^+$)[d] | 2.0031 | 0.378 | 0.378 | 0.050 | 0.078 | 0.128 | 0.252 | 0.010 | MeCN |
| ($Tl^+$)[d] | 2.0030 | 0.378 | 0.378 | 0.054 | 0.071 | 0.126 | 0.250 | 0.015 | MeCN |
| $In^{+}$[d] | 2.0000 | [e] | | | | | | 0.94 | MeCN |
| ($In^{III}$)[f] | 2.0031 | 0.378 | 0.378 | 0.050 | 0.070 | 0.125 | 0.250 | 0.050 | $CH_2Cl_2$ |
| $Zn^{2+}$[d,g] | 2.0029 | 0.342 | 0.359 | 0.016 | 0.129 | 0.113 | 0.306 | 0.005 | MeCN |
| $Mo(CO)_4$ | 2.0021 | 0.364 | 0.364 | < 0.015 | 0.14 | 0.14 | 0.240 | 0.032 | $Me_2CO$ |
| $Mo(CO)_4$[h] | | 0.360 | 0.370 | < 0.005 | < 0.2 | 0.135 | 0.245 | | $Me_2CO$ |
| $[Re(CO)_3X]^{+}$[i] | 2.0013 | 0.34 | 0.34 | < 0.08 | 0.17 | 0.17 | 0.22 | 0.17 | MeCN |
| $[Ru(bpy)_2]^{2+}$ | 1.9963 | [j] | | | | | | | MeCN |

[a] Coupling constants $a$ and linewidths in mT. Numbering of $^1H$ and $^{14}N$ centres according to structures $1^{2+}$–$3^{2+}$. [b] From computer-simulated spectra. [c] Electrochemically reduced $1^{2+}$, values from EPR and ENDOR spectra. [d] Obtained by reduction of (1)($BF_4$)$_2$ with the metal (see the text). [e] $a(^{115}In) = 0.59$ mT. [f] After reduction of $1^{2+}$ with indium in acetonitrile and replacement of the solvent by $CH_2Cl_2$. [g] Values from EPR and ENDOR spectroscopy at 293 K. [h] Values from EPR and ENDOR spectroscopy at 245 K. [i] X = $PPh_3$ (ref. 10); $a(^{185,187}Re) \approx a(^{31}P) \approx 0.9$ mT. [j] Insufficiently resolved spectrum.

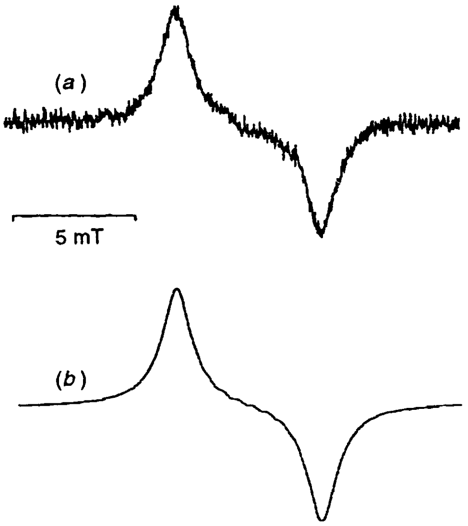


Fig. 2 EPR spectrum of the product from the reduction of (1)($BF_4$)$_2$ by indium metal in acetonitrile [experimental (*a*) and computer-simulated (*b*) spectra]

coupling indicate that there are no close contacts between metal cations and the radical cation ligand, implying solvent-separated ion pairs. Both copper ($^{63,65}Cu$, $I = \frac{3}{2}$) and thallium ($^{203,205}Tl$, $I = \frac{1}{2}$) are composed of isotopes with large nuclear magnetic moments and usually large coupling constants in corresponding radical complexes.[36,37] We attribute this lack of interaction to the low charge of the resulting monovalent ions and to their preferential coordination with the solvent (Scheme 1).

$$1^{2+} + M \xrightarrow{\text{MeCN}} 1^{\cdot+} + [M^{I}(MeCN)_n]^+$$

**Scheme 1**

Using indium in acetonitrile we observe a poorly resolved EPR signal (Fig. 2) the appearance of which suggests interaction of the unpaired electron with $^{113,115}In$ ($I = \frac{9}{2}$). The metal isotope coupling constant of about 0.6 mT is typical for a radical complex, *i.e.* a very small amount of spin transfer from the radical ligand to the coordinated and ionized metal centre.[38] We assume the coordination of solvated $In^+$ because of its electron-rich nature[39] and thus higher affinity to a cationic acceptor ligand as opposed to the more alkali-metal-like $Tl^+$. Removal of acetonitrile and addition of dichloromethane resulted in a better resolved spectrum which could be simulated exclusively with the $^1H$ and $^{14}N$ coupling constants of free $1^{\cdot+}$. Indium(I) is known to be oxidized by halogenated hydrocarbons,[39] we therefore assume the formation of indium(III) species, presumably chloride complexes. While the EPR results do thus exclude any significant interaction between the 'hard' metal ion and the radical cation, the large EPR linewidth in comparison to those solutions with $Cu^+$ or $Tl^+$ present suggests an indirect (electrostatic) effect of metal–ligand interaction *via* diminished mobility in solution. We interpret our findings in Scheme 2.

$$1^{2+} + In \xrightarrow{\text{MeCN}} [(1^{\cdot+})(In^{I})(MeCN)_n]^{2+} \xrightarrow{CH_2Cl_2} (1^{\cdot+})\cdots In^{III}$$

**Scheme 2**

Zinc metal reduces $1^{2+}$ to yield a paramagnetic species which exhibits a well resolved EPR spectrum (Fig. 3) that is clearly different from that of the free ligand radical cation. Although a metal hyperfine coupling could not be detected due to the small nuclear magnetic moment of $^{67}Zn$ ($I = \frac{5}{2}$) and its low natural abundance of 4.1%,[40] an additional ENDOR spectrum gave clear evidence for the coupling constants and their assignments to $^1H$ or $^{14}N$ π centres (Table 3).

We assume that the divalent zinc ion formed in the reduction process coordinates to (*cis*-configurated) $1^{\cdot+}$, however, it is not clear at this point whether the EPR/ENDOR signals are due to a partially solvated complex $[(1^{\cdot+})Zn^{II}(MeCN)_n]^{3+}$ or, less likely, to a compound $[(1^{\cdot+})_2Zn^{II}]^{4+}$ with perpendicularly arranged radical cation ligands.

Not only elemental metals but also organometallic complexes with zerovalent metal centres can reduce $1^{2+}$ to the (metal-coordinated) radical intermediate state. One such example is (nbd)$Mo(CO)_4$, nbd = norbornadiene, which reacts with ($1^{2+}$)($BF_4^-$)$_2$ in acetone to yield EPR and ENDOR-detectable $[(1^{\cdot+})Mo^0(CO)_4]^+$ (Fig. 4, Table 3).

The isolable complexes of $Re(CO)_3Cl$ and $[Ru(bpy)_2]^{2+}$ with $1^{2+}$ and $2^{2+}$ could be reduced electrochemically (Table 2) in order to obtain the complexes of the corresponding radical cations. However, the tendency of $Re(CO)_3Cl$ rapidly to lose chloride after acquiring excess negative charge prompted us to offer a better ligand for replacement (Scheme 3), in particular for better EPR resolution[31] and additional information *via* the coupling of the unpaired electron with the $^{31}P$ nucleus. Addition of excess triphenylphosphine to the dicationic complexes $[(L^{2+})Re^{I}(CO)_3Cl]^{2+}$ was sufficient to generate the

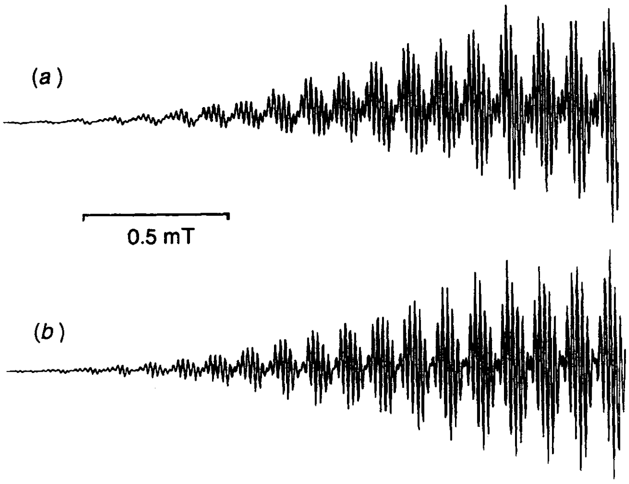


Fig. 3 EPR spectrum (low-field section) of the product from the reduction of $(\mathbf{1})(BF_4)_2$ by zinc in acetonitrile [experimental (*a*) and computer-simulated (*b*) spectra]

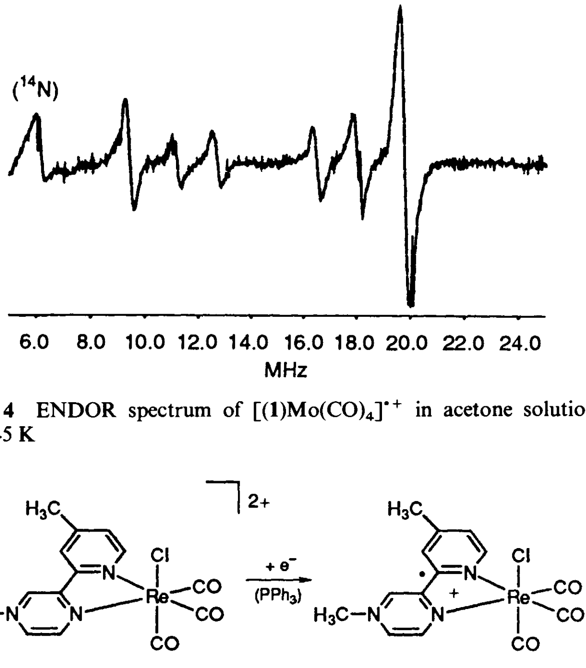
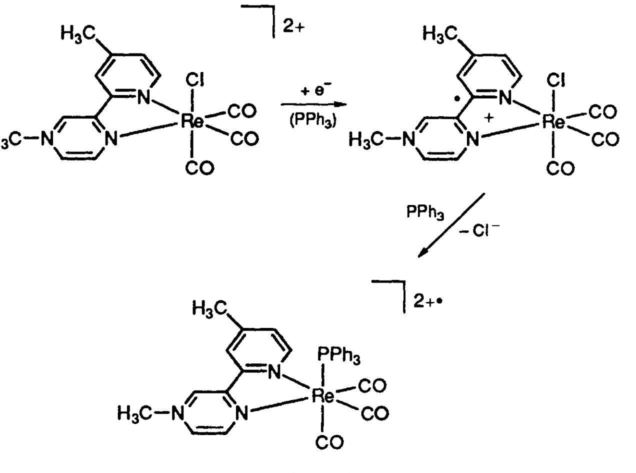


Fig. 4 ENDOR spectrum of $[(\mathbf{1})Mo(CO)_4]^{\bullet +}$ in acetone solution at 245 K



**Scheme 3**

$PPh_3$-substituted radical complexes $[(L^{\bullet +})Re^{I}(CO)_3(PPh_3)]^{\bullet +}$, L = **1**,**2**. Whereas the complex with L = **1** gave a well-resolved but very line-rich EPR spectrum,[10] the radical $[(\mathbf{2}^{\bullet +})Re(CO)_3(PPh_3)]^{2\bullet +}$ showed only an approximate septet splitting (Fig. 5) resulting from the interaction with the $^{185,187}Re$ isotopes ($I = \frac{5}{2}$, $a$ = 4.5 mT) and one $^{31}P$ nucleus ($I = \frac{1}{2}$, $a$ = 3.1 mT).[41]

The much smaller metal and $^{31}P$ coupling of the complex with $\mathbf{1}^{\bullet +}$ is in broad agreement with the different π spin populations calculated for the coordination sites of the parent radical ions, bpz$^{\bullet -}$ and bpm$^{\bullet -}$.[34,42] However, the metallated and diquaternized isomers $[(L^{\bullet +})Re(CO)_3(PPh_3)]^{2\bullet +}$ differ to an unusually large extent in their ability to transfer spin to the coordinated metal as evidenced not only from the factor of five between the metal hyperfine splittings but also from the much lowered *g* factor of 1.9958 for the complex with L = **2** in comparison to *g* = 2.0013 for the compound with L = **1**.

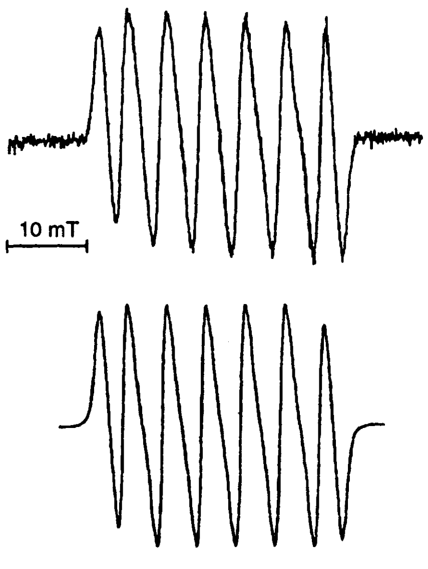


Fig. 5 EPR spectrum of the product from the reduction of $[(\mathbf{2})Re(CO)_3Cl](BF_4)_2$ by triphenylphosphine in acetonitrile (experimental and computer-simulated spectra)

A similarly remarkable decrease of the isotropic *g* factor is observed in the series of complexes $[(L^{\bullet +})Ru^{II}(bpy)_2]^{3+}$ where *g* = 1.9963 for L = **1** but *g* = 1.9834 for L = **2**. These figures indicate an unusually high metal contribution to the singly occupied MO in complexes $(\mathbf{2}^{\bullet +})ML'_n$ which results from the diquaternization in the *para* position to the coordinating chelate atoms. From another point of view, the system $\mathbf{2}^{n+}$ may be regarded as the result of coupled *N*-methylpyrazinium cations or radicals which are known effectively to bind and transfer much spin to low-valent metal centres.[15-17]

## Conclusion

We have shown that the diquaternized bidiazines ($\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$) are unusual molecules which combine the facile interconversion between two or three accessible redox states with the ability to bind metals *via* their α-diimine chelate function. A very diverse response was observed in the interaction between these remarkable radical cation chelate ligands towards different metal species; in particular, the ability to back-donate electron density from the metal seems to favour a tight coordination to the cationic ligand. Whereas the EPR results allowed us to note fine differences between separated (Cu, Tl), loosely coupled ($In^{III}$) or tight ionic complexes ($In^{I}$, Zn, Mo, Ru, Re) with $\mathbf{1}^{\bullet +}$, the absorption spectra of the typically coloured complexes were less informative, showing essentially unchanged transitions of the corresponding 'viologen' chromophor.[9] Theoretical and experimental results confirmed that the system $\mathbf{1}^{n+}$ is still a classical ligand with (semi)quinonoid features in the reduced forms; the $\mathbf{2}^{n+}$ components, on the other hand, may be formulated as coupled *N*-methylpyrazinium species and exhibit fairly unusual properties due to a less conventional electronic structure. It will be challenging to pursue this system further and try to obtain compounds of system $\mathbf{3}^{n+}$.

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## References

1 F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1993.

2 P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vincent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193.

3 G. H. Lee, L. D. Ciana and A. Haim, *J. Am. Chem. Soc.*, 1989, **111**, 2535.

4 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.

5 S. Hünig and H. Berneth, *Top. Curr. Chem.*, 1980, **92**, 1.

6 C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, 1981, **10**, 49.

7 P. M. S. Monk, R. D. Fairweather, M. D. Ingram and J. A. Duffy, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2039.

8 S. Ernst and W. Kaim, *J. Am. Chem. Soc.*, 1986, **108**, 3578.

9 W. Kaim and W. Matheis, *Chem. Ber.*, 1990, **123**, 1323.

10 W. Matheis and W. Kaim, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3337.

11 (*a*) E. S. Dodsworth, A. B. P. Lever, G. Eryavec and R. J. Crutchley, *Inorg. Chem.*, 1985, **24**, 1906; (*b*) H. E. Toma and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 176; (*c*) H. E. Toma, P. R. Auburn, E. S. Dodsworth, M. N. Golovin and A. B. P. Lever, *Inorg. Chem.*, 1987, **26**, 4257.

12 K. Bierig, R. J. Morgan, S. Tysoe, H. D. Gafney, T. C. Strekas and A. D. Baker, *Inorg. Chem.*, 1991, **30**, 4989.

13 C. K. Ryu, R. Wang, R. H. Schmehl, S. Ferrere, M. Ludwikow, J. W. Merkert, C. E. L. Headford and C. M. Elliott, *J. Am. Chem. Soc.*, 1992, **114**, 430.

14 E. H. Yonemoto, R. L. Riley, Y. I. Kim, S. J. Atherton, R. H. Schmehl and T. E. Mallouk, *J. Am. Chem. Soc.*, 1992, **114**, 8081.

15 D. R. Eaton, J. M. Watkins and R. J. Buist, *J. Am. Chem. Soc.*, 1985, **107**, 5604.

16 (*a*) J. F. Wishart, A. Bino and H. Taube, *Inorg. Chem.*, 1986, **25**, 3318; (*b*) W. Bruns, H.-D. Hausen, W. Kaim and A. Schulz, *J. Organomet. Chem.*, 1993, **444**, 121.

17 J. Poppe, W. Kaim, A. Ben Altabef and N. E. Katz, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2105.

18 J. H. Sharp and M. C. R. Symons, in *Ions and Ion Pairs in Organic Reactions*, ed. M. Szwarc, Wiley, New York, 1972, vol. 1, p. 177.

19 J. Hawecker, J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990.

20 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

21 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.

22 W. Kaim, H. E. A. Kramer, C. Vogler and J. Rieker, *J. Organomet. Chem.* 1989, **367**, 107.

23 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

24 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899 and 4907.

25 W. M. F. Fabian, *J. Comput. Chem.*, 1988, **9**, 369.

26 V. Barone, C. Minichino, S. Flisear and N. Russo, *Can. J. Chem.*, 1988, **66**, 1313.

27 S. Zalis and V. Drchal, *Chem. Phys.*, 1987, **118**, 313.

28 W. T. Borden, H. Iwamura and J. A. Berson, *Acc. Chem. Res.*, 1994, **27**, 109.

29 (*a*) F. Hilgers, W. Kaim, A. Schulz and S. Zalis, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 135; (*b*) M. Krejcik, S. Zalis, M. Ladwig, W. Matheis and W. Kaim, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2007; (*c*) H.-D. Hausen, A. Schulz and W. Kaim, *J. Chem. Soc., Perkin Trans. 2*, 1993, 343.

30 S. D. Ernst and W. Kaim, *Inorg. Chem.*, 1989, **28**, 1520.

31 W. Kaim and S. Kohlmann, *Inorg. Chem.*, 1990, **29**, 2909.

32 W. Bruns, W. Kaim, M. Ladwig, B. Olbrich-Deussner, T. Roth and B. Schwederski, in *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*, ed. A. J. L. Pombeiro and J. McCleverty, Kluwer, Dordrecht, 1993, p. 255.

33 C. Vogler and W. Kaim, *Z. Naturforsch., B. Chem. Sci.*, 1992, **47**, 1057.

34 C. Vogler, A. Klein and W. Kaim, manuscript in preparation.

35 S. F. Nelsen, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1005.

36 (*a*) W. Kaim and M. Moscherosch, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3185; (*b*) J. Rall and W. Kaim, *J. Chem. Soc., Faraday Trans.*, in press.

37 H. B. Stegmann, K. B. Ulmschneider, K. Rieke and K. Scheffler, *J. Organomet. Chem.*, 1976, **118**, 259.

38 W. Kaim, *Z. Naturforsch., B. Chem. Sci.*, 1981, **36**, 677.

39 J. Weidlein, *Organoindium Compounds 1*, in *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th edn., Springer-Verlag, Berlin, 1991, pp. 151, 152; see also D. G. Tuck, *Chem. Soc. Rev.*, 1993, 269.

40 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606.

41 K. A. M. Creber, T. I. Ho, M. C. Depew, D. Weir and J. K. S. Wan, *Can. J. Chem.*, 1982, **60**, 1504.

42 W. Kaim and S. Ernst, *J. Phys. Chem.*, 1986, **90**, 5010.

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