

Spectroelectrochemistry of aromatic ligands and their derivatives

III*. Binuclear transition metal complexes of Cu^I, Mo⁰, and Re^I with 2,2'-bipyrimidine

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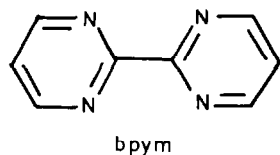
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Abstract

The binuclear complexes [Mo(CO)₄]₂(bpym) (I), [Re(CO)₃Cl]₂(bpym) (II), and [[Cu(PPh₃)₂]₂(bpym)]²⁺ (III) were subjected to one- and (for I, III) two-electron reduction, and the products studied *in situ* by UV-Vis-NIR spectroscopy. The spectra were assigned in terms of a simple Hückel molecular orbital scheme, in which the reduction orbital is ligand π(7), related to π(7) of biphenyl, the transition π(6) → π(7) moves to lower energy on successive reduction, and bands observed in the near IR-visible region are due to transitions from π(7) to higher unoccupied orbitals. Detailed assignments are directly related to those of other singly and doubly reduced azabiphenyls; the bpym dianion has been characterized for the first time.

Introduction

Homo- and heterobinuclear transition-metal complexes of 2,2'-bipyrimidine (bpym) have received increasing attention in recent years [1]. Because bpym can act as a doubly bidentate, bridging ligand with delocalized π bonding it combines the chelating properties of ligands such as 2,2'-bipyridine with the bridging function of ligands such as the 1,4-diazines [2].



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Overton and Connor [1d] prepared mono- and heterobinuclear d^6 metal carbonyl complexes $(\text{CO})_4\text{Mo}-\text{bpym}-\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and reported their electrochemical reduction but did not characterize the products. We report here spectroelectrochemical studies of singly and doubly reduced homobinuclear complexes of $\text{Mo}(\text{CO})_4$, $\text{Cu}(\text{PPh})_2^+$, and $\text{Re}(\text{CO})_3\text{Cl}$ with bpym and compare them with the known anion radical of bpym itself [3]. In contrast to binuclear bpym complexes of $\text{Ru}(\text{bpy})_2^{2+}$ [1a,k] the other ligands of the Mo^0 , Cu^I and Re^I fragments do not give rise to additional low-energy transitions.

Experimental

Materials

The complexes were prepared as described previously [1h,j,4]. "Spectrol" grade dimethylformamide (DMF) as purchased from BDH was stored over molecular sieves. Tetra-*n*-butylammonium tetrafluoroborate (TBABF_4) was prepared from the aqueous acid and hydroxide, recrystallized twice from ethyl acetate/pentane, and washed repeatedly with water.

Instrumentation

Cyclic voltammetry was performed under argon in a Metrohm cell equipped with the cross-section of a 0.1 mm diameter platinum wire as working electrode and a 5 mm length of similar platinum wire as counter-electrode, using a PAR 173 potentiostat and 175 signal generator, results being recorded on a JJ X-Y recorder, Model 151 (the same potentiostat was then used for controlled potential electrolysis in the spectroelectrochemistry experiments). The reference electrode was $\text{Ag}/0.01 \text{ M AgNO}_3 + 0.09 \text{ M TBABF}_4$, but potentials are referred to the ferrocene/ferrocenium⁺ potential obtained under identical conditions. Solutions were 0.005 *M* for cyclic voltammetry and 0.001 *M* for spectroelectrochemistry; for both type of study 0.1 *M* TBABF_4 was used as supporting electrolyte. The Cu complex III was examined in the presence of 0.01 *M* triphenylphosphine to suppress solvolysis. The spectra of the reduced species were recorded on a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrophotometer. Controlled potential reduction for spectroelectrochemistry was carried out in a special 1 mm path quartz cell with platinum gauze working electrode, as described elsewhere [5].

Results and discussion

Electrochemistry

The reduction potentials of the binuclear bpym complexes in DMF solution are collected in Table 1; similar values were reported in other solvents [1h,j,4]. All reductions were reversible one-electron processes except the second reduction of the Re^I complex and of free bpym. However, the oxidation potentials of the compounds could not be determined because of chemical irreversibility. As shown in Table 1, the differences between first and second reductions are only slightly different in the three complexes and are close to the free ligand value. We assign these reductions as ligand-based, the redox active orbital being $\pi(7)$, the lowest π^* orbital of bpym (b_{2u} in idealized D_{2h} symmetry [1h,7], which we use for spectroscopic labeling despite *cis/trans* isomerism of II [1i,4] in solution and intramolecular distortion of III, at

Table 1

Reduction potentials of 2,2'-bipyrimidine and its binuclear complexes in DMF ^a

Compounds	1st reduction	2nd reduction	Difference
bpym ^b	-1.867(0.063) ^c	-2.390(irr) ^d	> 0.56
I	-1.217(0.064)	-1.851(0.070)	0.634
II	-0.950(0.072)	-1.575(0.092) ^e	0.661
III ^f	-1.310(0.064)	-1.950(0.079)	0.640

^a Data by cyclic voltammetry (50–200 mV s⁻¹, PAR 173/175; *iR* compensation), V vs. ferrocene/ferrocenium⁺ in stated solvent at 25 °C. Measurements taken vs. Ag/0.01 M AgNO₃–0.09 M n-tetra-butylammonium tetrafluoroborate (TBABF₄) in stated solvent, but referred to ferrocene/ferrocenium⁺/0.1 M TBABF₄ in solvent/cell combination as used. ^b After ref. 12. ^c $E_{pa} - E_{pc}$ (V) in parentheses. ^d Denotes a chemically irreversible reduction process (cathodic peak potentials given at 200 mV s⁻¹ scan rate). ^e Incompletely chemically reversible, but anodic return wave detected. ^f With 0.01 M triphenylphosphine.

least in the solid [1j]). For a ligand-centered LUMO, stable π radicals may be expected, especially since the ligand itself undergoes reversible reduction. After being singly or doubly reduced, each of the binuclear complexes contains a very stable anion or dianion ligand; this high stability is in part due to a hyperconjugative interaction between the LUMO (π^*) of bpym and the antibonding metal-carbonyl or metal-phosphine σ^* orbitals [8]. The binuclear complexes are considerably easier to reduce than the corresponding mononuclear complexes [1h], no doubt because two electron-withdrawing Lewis acids are attached to a single bpym. This would also explain why the metal-to-ligand charge-transfer absorption bands appear at longer wavelength in the binuclear complexes.

Spectroelectrochemistry

The spectra of I, II, and III, and the corresponding reduced species, between 280 and 1100 nm, are listed in Table 2 and shown in Fig. 1. The electronic absorption spectrum of the parent I in the region between 260 nm and 1000 nm exhibits three main absorption bands. The band at 301 nm is associated with the HOMO \rightarrow LUMO ($\pi \rightarrow \pi^*$) transition of the bridged bpym. However, another two transitions appear in the visible region at approximately 390 nm and 545 nm in DMF solution. Both are assigned to metal-to-ligand charge-transfer transitions from $d\pi$ orbitals of molybdenum to the π^* orbitals of the bridged bpym ligand [7]. In II, the two MLCT transition bands again appear in the visible region at approximately 344 nm and at 457 nm in DMF solution with a tail extending to about 570 nm [1i,4]. Complex III contains a four-coordinate d^{10} metal center from which apparently two intense MLCT transitions occur to unoccupied bpym orbitals [1j]: in chlorinated hydrocarbons there is a shoulder at 440 nm and a maximum at 365 nm. Compared to the corresponding mononuclear complexes [1d,8,9], the MLCT absorption bands are shifted to longer wavelength in the binuclear complexes. The two bands correspond to transfer of an electron to $\pi(7)$ and $\pi(8, 9)$ (a_u, b_{3g}), respectively [7]. This assignment gives a separation of around 7000 cm⁻¹ between the two MLCT bands, in moderate agreement with the 11000 cm⁻¹ energy of $\pi(7) \rightarrow \pi(9)$ in the singly reduced species (see below). Absorption around 390 nm [7] could also arise from M \rightarrow CO charge transfer, as in [(Ph₂P)₂MeN]Mo(CO)₄ [10] or in *trans*-(R₃P)₂Mo(CO)₄ [11].

Table 2

The main absorption maxima of binuclear complexes of bpym as measured in DMF and their assignments [λ/nm (ν) ($\epsilon \times 10^{-3}/\text{l mol}^{-1} \text{cm}^{-1}$)]

Parent	$\pi \rightarrow \pi^*$	MLCT [$d \rightarrow \pi(9)$]	MLCT [$d \rightarrow \pi(7)$]
bpym	262(38170)(17.5) 287(34840)(19.0)		
bpym	292(34250)(18.5)		
I		390 ^b (25640)(10.1)	545(18350)(7.3)
II		344(29070)(7.5)	457(21880)(4.8)
III		312(32050)(23)	405(24690)(6.7)
Parent ¹⁻	$\pi(6) \rightarrow \pi(7)$	$\pi(7) \rightarrow \pi(10)$ ^a	$\pi(7) \rightarrow \pi(9)$ ^a
bpym ⁻ [6]	392(25510)(19.0)	562(17790)(5.9)	880(11360)(3.2)
bpym ⁻ [12]	361(27700)(20.5)	500(20000)(6.5)	800(12500)(3.0)
I ⁻	356(28090)(16.1)	480(20830)(5.2)	819(27100)(3.2)
II ⁻	344(29070)(16.4)	444(22520)(5.3)	775(12900)(3.1)
III ⁻	363(27550)(19.7)	490(20410)(6.2)	817(12240)(3.2)
Parent ²⁻	$\pi(7) \rightarrow \pi(10)$ ^a		
bpym ²⁻ [6]	397(25190)(21.5)		
I ²⁻	390(25640)(14.5)		
III ²⁻	397(25190)(17.2)		

^a Vibrational structure. ^b Includes non-MLCT band.

The electronic absorption spectra of all the singly reduced bimetallic complexes I⁻–III⁻ show characteristic [bpym]⁻ intraligand $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions in the region between 260 nm and 1000 nm. These results are consistent with our earlier demonstration (by ESR) [1g,1j,4] that in complexes of this type the added electron is localized in the π^* orbital of the coordinated bpym. In the neutral ligand, the lowest transition is $\pi(6) \rightarrow \pi(7)$, in the range 260–300 nm. This transition still occurs in the reduced species, in which $\pi(7)$ is half full (Fig. 2), but lower energy transitions from $\pi(7)$ to $\pi(8-11)$ are now available, and are assigned (Table 2) as in our earlier treatment of bpym [12].

The band at around 350 nm which appears with high intensity in each of the singly reduced complexes is assigned to the intraligand $\pi(6) \rightarrow \pi(7)$ transition of the bridged [bpym]⁻ ligand. As previous found for bipyridyl anion radical complexes [5,13] the transition in the reduced species appears lower in energy than the corresponding $\pi(6) \rightarrow \pi(7)$ transition of the neutral ligand in the parents. The band in the visible region with a vibrational structure of approximately 1480 cm^{-1} is assigned to the $\pi(7) \rightarrow \pi(10)$ transition of [bpym]⁻. The vibrational progression of 1480 cm^{-1} is presumably due to the strengthening of the C–C bond between the two pyrimidine rings; a band at 1478 cm^{-1} was observed as major feature in the resonance Raman spectrum of 441.6 nm (MLCT I) excited Ru(bpym)₃Cl₂ [14]. Another band with similar vibrational structure appears in the near infrared region between 700 nm and 900 nm, as expected for the $\pi(7) \rightarrow \pi(9)$ transition of [bpym]⁻ [12]. The $\pi(7) \rightarrow \pi(8)$ transition of [bpym]⁻ is forbidden both in the free ligand and in these bridged complexes. In I–III, the second ligand-based reduction is 0.65 V more cathodic than the first; the slightly lower value for the free ligand is as expected for a chemically irreversible process. If, by analogy with the spacings [15] in species of type $[\text{M}(\text{bpy})_n]^{x+}$, we attribute 0.18 V of this to the general effect of

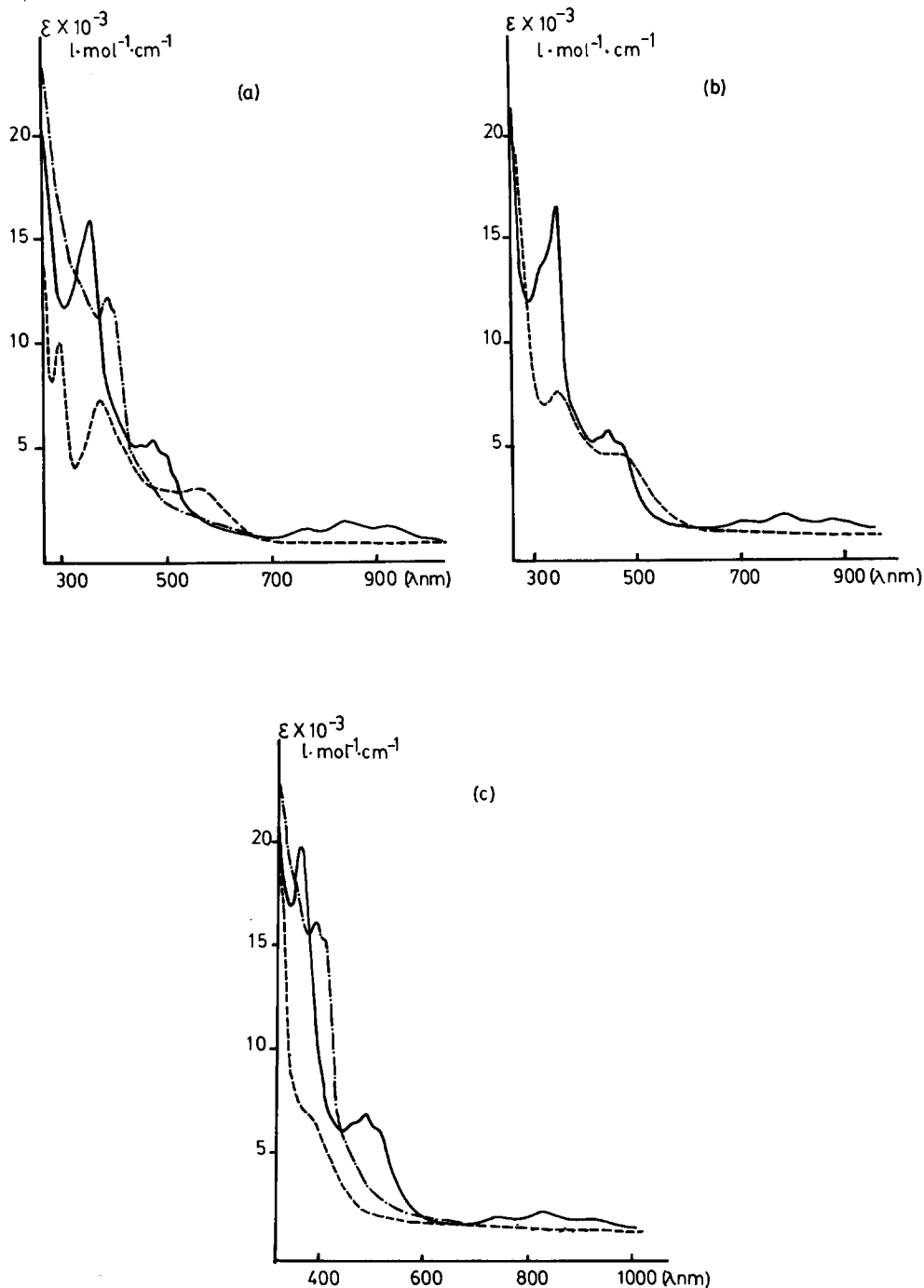


Fig. 1. The electronic absorption spectra of parent and reduced bridged bpm complexes in DMF-TBAPF₄ solution at 25°C [V vs. ferrocene/ferrocenium⁺]. (a) $[\text{Mo}(\text{CO})_4]_2(\text{bpm})^{0/-/2-}$ (I) and reduction products at -1.240 and -1.880 V. (b) $[\text{Re}(\text{CO})_3\text{Cl}]_2(\text{bpm})^{0/-}$ (II) and a reduction product at -0.980 V. (c) $[\text{Cu}(\text{PPh}_3)_2]_2(\text{bpm})^{2+/+/0}$ (III) and reduction products at -1.340 and -1.980 V. Dashed lines: parent; full lines: singly reduced species; dashed/dotted lines: doubly reduced species.

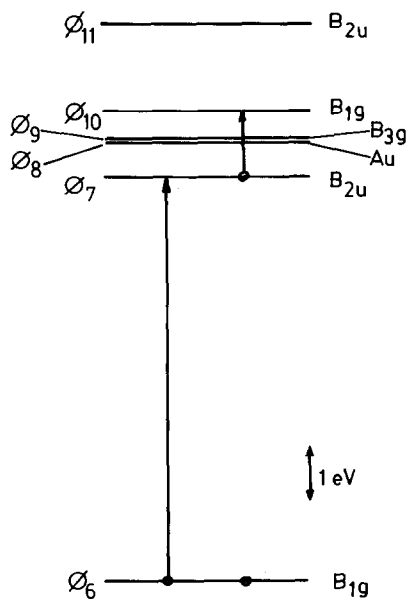
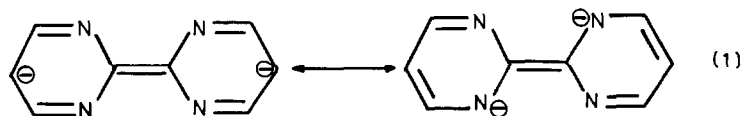


Fig. 2. Orbital scheme of b pym^- .

additional negative charge, then MLCT [$t_{2g} \rightarrow \pi(7)$] should be raised by a one-electron ligand-based reduction by some 0.46 V or 3700 cm^{-1} . In addition, the intensity should be halved; for these two reasons, the MLCT band cannot be separately resolved from the other bands present in the reduced species.

The doubly reduced complex II^{2-} could not be generated because of rapid loss of halide ions [4]. The very slow halide dissociation [3] in the singly reduced form II^- is due to small LUMO orbital coefficients at the coordination centers of b pym [8]. Free $[\text{b pym}]^{2-}$ could not be observed owing to dimerization of the anion radical [12]. $[\text{Bpym}]^{2-}$ is of interest as a ligand, however, in view of its interesting resonance structure. This combines the properties of a 1,2-diaminoethylene grouping with those of a quinoid delocalized system.



Coordinative stabilization of $[\text{b pym}]^{2-}$ occurs in doubly reduced complexes I^{2-} and III^{2-} . In such complexes $\pi(7)$ is full; by analogy with such species as doubly reduced bipyridyl [6] and doubly reduced diquat [12], we can assign the band with vibrational structure at around $25,000 \text{ cm}^{-1}$ to $\pi(7) \rightarrow \pi(10)$ of the ligand. As in these other cases, $\pi(7) \rightarrow \pi(9)$ is symmetry-allowed but for well-understood reasons [6,12] is too weak for us to observe.

The rather small spectral differences among the singly and doubly reduced complexes confirm the ligand-localization of the added electrons. The not very pronounced hypsochromic shift in the series $[\text{b pym}]^-$; III^- ; I^- ; II^- ; reflects the stabilization of $\pi(7)$ by metal centers, especially by $\text{Re}(\text{CO})_3\text{Cl}$ [4]. Even in those

cases where ESR spectra are not immediately conclusive on account of insufficient resolution [4], as well as in the diamagnetic dianions, the spectroelectrochemical data can thus help to clarify the electronic structure of related reduced species

Acknowledgements

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