Inorganica Chimica Acta, 181 (1991) 15–21

Electronic structure of heterodinuclear complexes $(bpy)_2Ru^{II}$-(μ-bpym)ML_n; bpy = 2,2′-bipyridine; bpym = 2,2′-bipyrimidine; $ML_n = {}^{+}Cu(PPh_3)_2$, $Mo(CO)_4$, $Re(CO)_3Cl$

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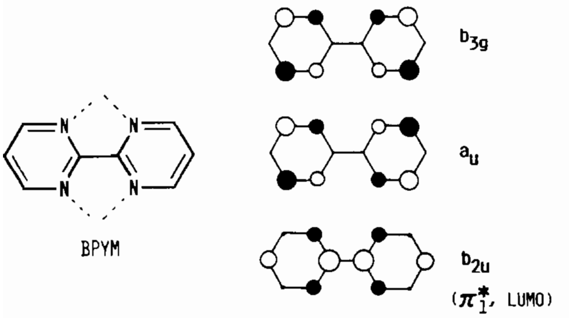
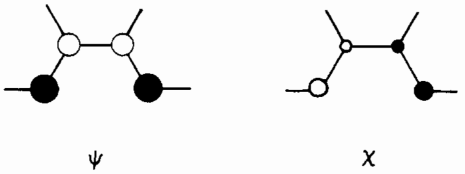
(Received July 16, 1990)

Abstract

The heterodinuclear title complexes were studied by cyclic voltammetry, absorption spectroscopy and by ESR of their singly reduced forms. Comparison with the homodinuclear analogues reveals that the metal-centered occupied d orbitals show relatively little change on coordination of a second metal (weak interaction) whereas the bpym-centered lowest unoccupied MOs π^*_1 and π^*_2 are stabilized by effects coming from both metal fragments. Combinations of metal fragments with different π donor/σ acceptor characteristics give rise to variable charge transfer energies for major transitions d(Ru) → π^*_1, d(M) → π^*_1, d(Ru) → π^*_2, d(M) → π^*_2; the appearance of spectra is further determined by different widths and intensities of individual bands and by solvent dependence.

Introduction





2,2′-Bipyrimidine is a symmetrically tetradentate bis(α-diimine) chelate ligand [1] with some remarkable features. Two metal centers can be positioned at a distance of about 550 ppm [2–4] in a fixed orientation, allowing direct or indirect dπ–dπ interaction [1, 5]. The latter is influenced by the b_{2u} symmetry of the low-lying LUMO (π^*_1) of bpym (in D_{2h}); two other relatively low-lying unoccupied MOs ($\pi^*_{2,3}$) of bpym have a_u and b_{3g} symmetry [1, 5] (designations were interchanged in Chart II of ref. 1). In Orgel's notation [6], the three lowest unoccupied π^* MOs may be designated as $2\psi(b_{2u})$, $2\chi(a_u)$, and $\psi_r-\psi(b_{3g})$. Orbital coefficients at the four potential coordination atoms are not very large in the LUMO [1]; homodinuclear complexes of π-accepting bpym with π-donating metal fragment such as ${}^{2+}[Ru(bpy)_2]$ [7–9], $Mo(CO)_4$ [1, 5, 10–12], $Re(CO)_3Hal$ [13, 14] and ${}^{+}[Cu(PPh_3)_2]$ [4, 15] thus display one broad MLCT absorption band at low energy and another more intense such feature at higher energy. In addition to those often very solvent-sensitive MLCT bands [5, 16]**, there is an intense solvent-insensitive band in most dinuclear bpym complexes in the near ultraviolet region [1, 5, 14], presumably resulting from a mixed d → d transition [11].

Heterodinuclear complexes have been described early in bpym coordination chemistry [17]; more recent examples involving electron-rich transition metal fragments include Ru(II)/Os(II) [18], Ru(II)/Pt(II) [19] and Ru(II)/Re(I) systems [20, 21]. We

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The MLCT absorption maxima for **6 in toluene were in error; the correct values for that little soluble dinuclear complex are 14 560 and 22 170 cm^{-1} which reverses the solvent sensitivities of absorptions MLCT I and MLCT II, cf. ref. 5.

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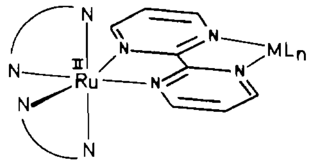


now wish to report the addition of two new $(bpy)_2Ru$-containing heterodinuclear bpym complexes, complex **1** with cationic, moderately electron-rich $^{+}Cu(PPh_3)_2$ (d^{10}) and compound **2** with neutral, more electron-rich $Mo(CO)_4$ (d^6) as the second metal fragment.

Complexes $(ML_n)(\mu\text{-bpym})(ML_n)'$

ML_n	$(ML_n)'$	Compound
$^{2+}[Ru(bpy)_2]$	$^{+}[Cu(PPh_3)_2]$	**1** (as tris(hexafluorophosphate))
$^{2+}[Ru(bpy)_2]$	$Mo(CO)_4$	**2** (as bis(hexafluorophosphate))
$^{2+}[Ru(bpy)_2]$	$Re(CO_3)Cl$	**3** (as bis(hexafluorophosphate))
$^{2+}[Ru(bpy)^2]$	$^{2+}[Ru(bpy)_2]$	**4** (ref. 8)
$Re(CO_3)Cl$	$Re(CO_3)Cl$	**5**
$Mo(CO)_4$	$Mo(CO)_4$	**6**
$^{+}[Cu(PPh_3)_2]$	$^{+}[Cu(PPh_3)_2]$	**7** (as bis(tetrafluoroborate))

Electrochemical data and absorption energies are compared to those of homodinuclear analogues **4–7** in order to provide guidelines for a design of specifically absorbing polynuclear complexes [22]. The ESR spectra and the substitution behaviour of singly reduced species, including that of the previously [20, 21] reported Ru(II)/Re(I) system **3**, should provide further insight into the electronic structure.

Experimental

Instrumentation

UV–Vis–NIR absorption spectrometer: Bruins Instruments model Omega 10. Fluorescence spectrometer: Perkin-Elmer LB 3. IR spectrometer: Perkin-Elmer model 684. ESR spectrometer: Bruker ESP 300 in the X band; electrolytic generation intra muros in a two-electrode cell [9]. Cyclic voltammetry: PAR model 273/175; glassy carbon working electrode, SCE reference electrode, ferrocene/ferrocinium pilot system (+0.31 V versus SCE), 1,2-dichloroethane solutions of 0.1 M Bu_4NClO_4 as electrolyte.

Syntheses

The starting materials $[(bpy)_2Ru(bpym)](PF_6)_2$ [9], (norbornadiene)$Mo(CO)_4$ [23], and the complex **3** as bis(hexafluorophosphate) [20, 21] were prepared according to published procedures.

All syntheses were performed under argon atmosphere and subdued light in purified solvents.

$[(bpy)_2Ru(\mu\text{-}bpym)Cu(PPh_3)_2](PF_6)_3$ (1)

To 100 mg (0.12 mmol) $[(bpy)_2Ru(bpym)](PF_6)_2$ dissolved in a mixture of 16 ml dichloromethane and 4 ml methanol were added 5 mg (0.07 mmol) copper powder, 17 mg (0.07 mmol) copper(II) tetrafluoroborate, and 78 mg (0.30 mmol) triphenylphosphine. After 2 h the reaction mixture was treated with 5 ml of a saturated solution of ammonium hexafluorophosphate in methanol. Insoluble material was filtered off and the red–brown filtrate cooled to −30 °C. Addition of 20 ml diethylether yielded 138 mg (75%) of complex **2**. *Anal.* Calc. for $C_{64}H_{52}CuF_{18}N_8P_5Ru$ (1594.6): C, 48.21; H, 3.29; N, 7.03. Found: C, 47.06; H, 3.18; N, 7.27%.

$[(bpy)_2Ru(\mu\text{-}bpym)Mo(CO)_4](PF_6)_2$ (2)

Solutions of 100 mg (12 mmol) $(bpy)_2Ru$-$(bpym)](PF_6)_2$ in 30 ml DCE and of 40 mg (0.13 mmol) (norbornadiene)$Mo(CO)_4$ in 20 ml DCE were united slowly and stirred for 12 h at ambient temperature. Addition of 20 ml hexane and cooling to −30 °C precipitates dark brown **1**. Yield: 85 mg (66%). IR (nujol): $\tilde{\nu}$(CO) 2020, 1920, 1905sh, 1835 cm^{-1}. *Anal.* Calc. for $C_{32}H_{22}F_{12}MoN_8O_4P_2Ru$ (1069.5): C, 35.94; H, 2.07; N, 10.48. Found: C, 34.97; H, 2.30; N, 9.89%.

Results

The new complexes **1** and **2** were synthesized starting from the robust Ru(II) containing mononuclear bpym complex by addition of the other metal fragment. Anion exchange had to be carried out in order to obtain the trication **1** as tris(hexafluorophosphate) salt. Cyclic voltammetric measurements and absorption studies were performed in 1,2-dichloroethane (DCE), a non-coordinating solvent with relatively high dielectric constant. A typical cyclovoltammogram is shown in Fig. 1. Figures 2 and 3 contain ESR spectra of the electrochemically reduced complexes **2** and **3**, the latter before and after addition of triphenylphosphine. Absorption spectra, including second derivative spectra, are displayed in Figs. 4 and 5. Electrochemical, ESR and absorption spectroscopic data are summarized in Tables 1–3.

Discussion

Apart from differences concerning charge, geometry and d electron configuration, the doubly coordinatively unsaturated transition metal fragments *cis*-$Mo(CO)_4$ and $^{+}[Cu(PPh_3)_2]$ have rather different bonding/backbonding character — especially in relation to *cis*-$^{2+}[Ru(bpy)_2]$ or *fac*-$Re(CO)_3Cl$ [24].

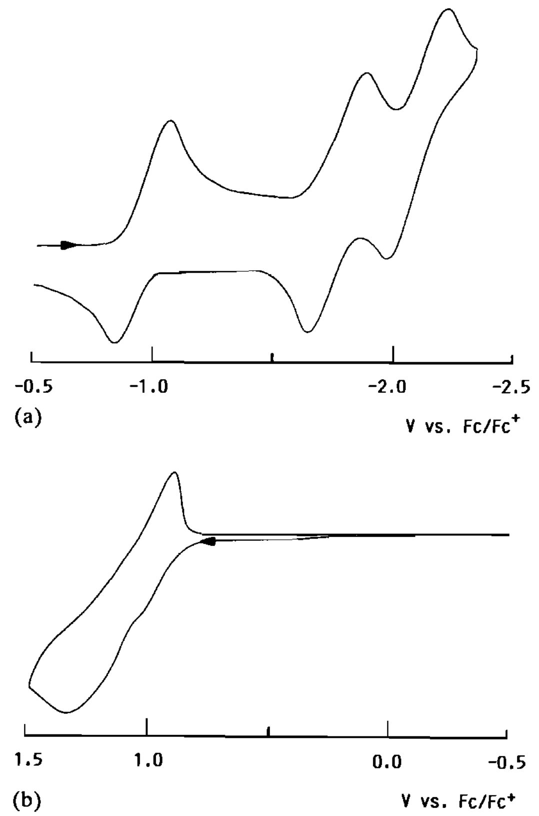


Fig. 1. Cyclovoltammograms of complex **1** in 1,2-dichloroethane–0.1 M Bu_4NClO_4. Reductive scan (a) and oxidative scan (b); scan rate 200 mV/s.

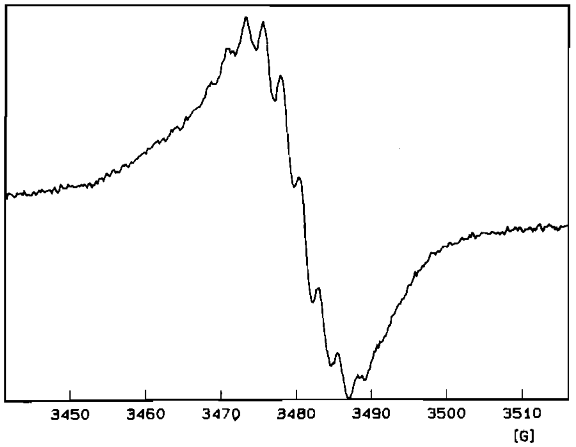


Fig. 2. ESR spectrum of electrolytically reduced **2** in DCE/0.1 M Bu_4NClO_4 (1 G = 0.1 mT).

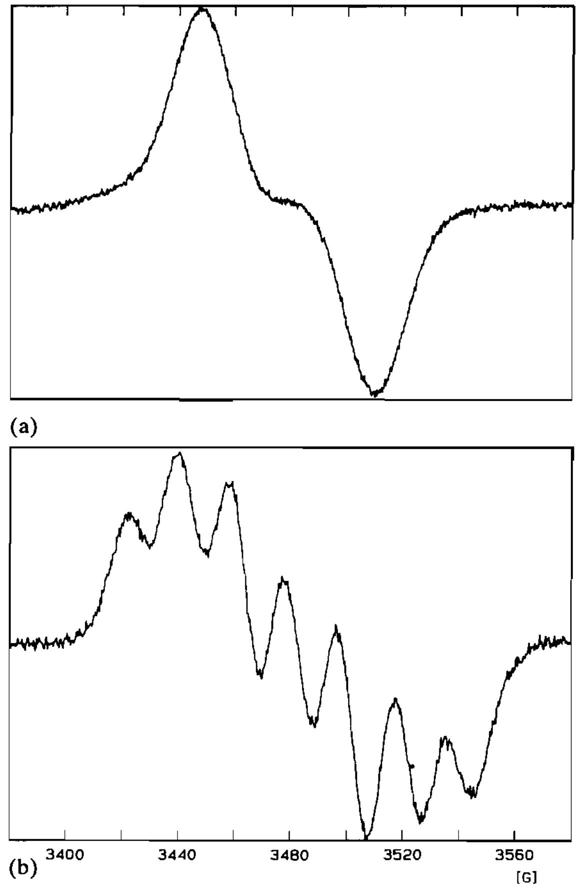


Fig. 3. ESR spectra of electrolytically reduced **3** in DCE/0.1 M Bu_4NClO_4 in the absence (a) and in the presence of excess triphenylphosphine (b).

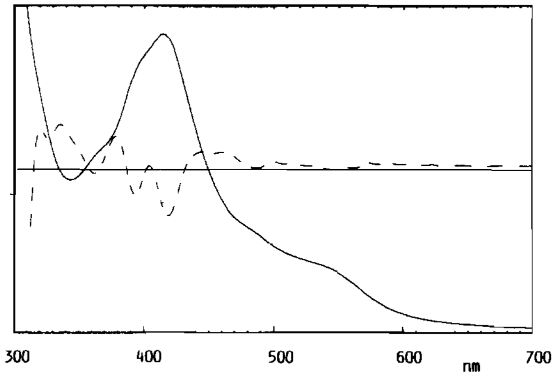


Fig. 4. Absorption spectrum of complex **1** in DCE (——), second derivative spectrum (– – –).

The Mo(0) fragment contains a rather electron-rich metal center which is easily but irreversibly oxidized. The Cu(I) fragment is less electron-rich, only a little more so than the Ru(II) or Re(I) centers in the fragments mentioned above [24]. On the other hand, the ability of these metal fragments to facilitate reduction of σ-coordinated π-acceptor ligands increases along the sequence $Cu(I) \approx Mo(0) < Ru(II) < Re(I)$ [24].

Cyclic voltammetry

The metal fragment characteristics are reflected in the electrochemistry of hetero- and pertinent

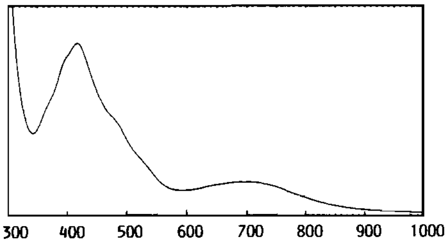
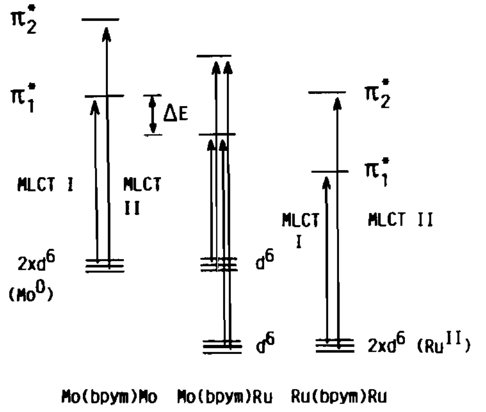


Fig. 5. Absorption spectrum of complex **2** in DCE.



Scheme 1.

homodinuclear systems **1–7** (Table 1), with one important distinction. Whereas the polarization effects of the two metals *combine* to yield an averaged reduction potential of the ligand, the metal-centered oxidation of apparently weakly interacting [25] metal centers occur *separately* in the expected potential range; Scheme 1 illustrates this situation in terms of molecular orbital energies.

Figure 1 shows the cyclic voltammogram of compound **1**. The oxidative scan contains a very irreversible 'shoulder' for Cu(I) oxidation, followed immediately by the Ru(II) oxidation peak. The signal in the reverse scan corresponds to that of mononuclear $[(bpy)_2Ru(bpym]^{2+}$ [26] after copper dissociation. The reductive scan displays two reversible one-electron processes centered on the bpym ligand at less negative potentials before two bpy-centered reductions occur in the usual region [8, 25, 26]. The irreversible oxidation of the Mo(0) center in **2** occurs at rather low potential (Table 1).

ESR results

Stability of the singly reduced state and identity of the singly occupied MO as π^*_1 [1, 12] are evident from ESR studies on electrochemically generated radical complexes [9, 12]. The spectrum of $\mathbf{2}^{\cdot-}$ (Fig. 2) shows the typical hyperfine structure due to coupling with four ^{14}N nuclei (0.24 mT) and two $^{1}H(5,5')$ nuclei (0.48 mT) [12]. While the spectrum of $\mathbf{1}^{\cdot-}$ is broader (7 mT) and less resolved due to additional $^{63,65}Cu$ and ^{31}P hyperfine coupling [4, 15, 27], the new anion radical complex $\mathbf{3}^{\cdot-}$ displays the typical shape (Fig. 3(a)) of an insufficiently resolved sextet from $^{185,187}Re$ nuclei ($I = 5/2$) [28, 29]. The propensity of anion radical complexes of the $Re(CO)_3Cl$ fragments to exhibit enhanced halide/phosphine substitution reactivity [15, 29] was used to generate the radical $[(bpy)_2Ru(\mu\text{-}bpym^{\cdot-})Re(CO)_3(PPh_3)]^{2+}$ with larger $^{185,187}Re$ and additional ^{31}P coupling (Fig. 3(b)). The relatively small rhenium and phosphorus coupling results from spin polarization and hyperconjugative spin transfer from the spin-bearing bpym π system [14] to the metal fragment. Isotropic g factors of reduced species $\mathbf{1}^{\cdot-}$ to $\mathbf{4}^{\cdot-}$ are invariably smaller than 2 (Table 2) because of the presence of low-lying excited states involving unoccupied π^*(bpy) and

TABLE 1. Electrochemical potentials of dinuclear complexes of 2,2'-bipyrimidine[a]

Compound	E_{ox}	E_{red}	$E_{ox1} - E_{red1}$	Solvent[b]
bpym		−2.23, −2.94(i)		DMF
1 (Cu, Ru)	1.2(i), 0.9(sh)	−0.94, −1.70	1.84	DCE
2 (Mo, Ru)	1.2(i), 0.49(i)	−0.92, −1.74	1.41	DCE
3 (Re, Ru)	1.1(i)	−0.88, −1.45	1.98	DCE
	1.45, 1.27	−0.72, −1.41	1.99	AN[c]
4 (Ru, Ru)	1.38, 1.22	−0.72, −1.39	1.94	AN[d]
5 (Re, Re)	1.3(i)	−0.84, −1.52	2.14	AN
	1.17(i)	−0.82, −1.51	1.99	DMF[e]
6 (Mo, Mo)	0.4(i)	−1.13	1.53	DMF
7 (Cu, Cu)	0.9(i)	−1.24, −1.87	2.14	DCE

[a] From cyclic voltammetry at 200 mV/s. Potentials in V vs. ferrocene/ferricinium couple. (i): Irreversible step, peak potential given. [b] DMF: *N*,*N*-dimethylformamide; AN: acetonitrile; DCE: 1,2-dichloroethane; all containing 0.1 M Bu_4NClO_4 as electrolyte. [c] Ref. 21; conversion assuming ferrocene/ferricinium couple with +0.31 V vs. saturated calomel electrode (SCE). [d] Ref. 8; conversion assuming ferrocene/ferricinium couple with +0.31 V vs. saturated calomel electrode (SCE). [e] Ref. 13; conversion assuming ferrocene/ferricinium couple with +0.31 V vs. saturated calomel electrode (SCE).

TABLE 2. ESR data of reduced complexes[a]

Radical	g	a	Reference	Solvent
bpym$^{\bullet -}$	2.0030	^{14}N:0.143 + HFS	12	THF
1$^{\bullet -}$ (Cu, Ru)	1.9952	^{14}N:0.24	this work	DCE
2$^{\bullet -}$ (Mo, Ru)	1.9964	^{14}N:0.24	this work	DCE
3$^{\bullet -}$ (Re, Ru)	1.9953 (1.9944)[b]	^{185,187}Re:1.05 (^{185,187}Rd:1.9[b]; ^{31}P:1.7)[b]	this work	DCE
4$^{\bullet -}$ (Ru, Ru)	1.9890	^{99,101}Ru:0.27; ^{14}N:0.274 + HFS	9	AN
5$^{\bullet -}$ (Re, Re)	2.0005	^{185,187}Re:1.2	14	acetone
6$^{\bullet -}$ (Mo, Mo)	2.0022	^{95,97}Mo:0.105; ^{14}N:0.228 + HFS	12	THF
7$^{\bullet -}$ (Cu, Cu)	2.0017	^{63}Cu:0.646; ^{65}Cu:0.691; ^{31}P:0.691; ^{14}N:0.218 + HFS	4, 15	CH_2Cl_2

[a] Coupling constants a in mT; HFS: additional analyzed hyperfine coupling (see ref.). [b] Substitution product Cl^-/PPh_3.

TABLE 3. Energies E_{max} (eV)[a] at the absorption maxima of dinuclear complexes of 2,2′-bipyrimidine

Complex	Absorption energies	E_{max} (in eV)[a]	Solvent[c]	Reference
1 (Cu, Ru)	2.27sh (Ru $\rightarrow \pi^*_1$) 2.54sh (Cu $\rightarrow \pi^*_1$)	2.99 (Ru $\rightarrow \pi^*_{bpy}$)[d] 3.40sh (Cu $\rightarrow \pi^*_2$)	DCE	this work
2 (Mo, Ru)	1.76 (Mo $\rightarrow \pi^*_1$) 2.35sh (Ru $\rightarrow \pi^*_1$)	2.56sh (Mo $\rightarrow \pi^*_2$) 2.97 (Ru $\rightarrow \pi^*_{bpy}$)[d]	DCE	this work
3 (Re, Ru)	2.15 (Ru $\rightarrow \pi^*_1$)	3.01 (Ru $\rightarrow \pi^*_{bpy}$)[d]	DCE	this work
4 (Ru, Ru)	2.09 (Ru $\rightarrow \pi^*_1$)	3.02 (Ru $\rightarrow \pi^*_{bpy}$)	AN	8
5 (Re, Re)	2.64 (Re $\rightarrow \pi^*_1$)	3.47 (Re $\rightarrow \pi^*_2$)	acetone	14
6 (Mo, Mo)	2.22 (Mo $\rightarrow \pi^*_1$)	3.22 (Mo $\rightarrow \pi^*_2$)	acetone	5
6 (Mo, Mo)	2.07 (Mo $\rightarrow \pi^*_1$)	2.90 (Mo $\rightarrow \pi^*_2$) 3.19[b]	THF	1
6 (Mo, Mo)	1.84 (Mo $\rightarrow \pi^*_1$)	2.82 (Mo $\rightarrow \pi^*$)	CH_2Cl_2	10
7 (Cu, Cu)	2.83sh (Cu $\rightarrow \pi^*_1$)	3.54 (Cu $\rightarrow \pi^*_2$)	$CHCl_3$	4

[a] 1 eV = 8066 cm^{-1}. [b] Separate solvent-independent band (d → d transition). [c] DCE: 1,2-dichloroethane; AN: acetonitrile. [d] High energy shoulder, cf. ref. 30.

d(Ru) orbitals [9]. In addition, rather small g factors relative to that of the free ligand radical anion are typical [12] for one-electron reduced complexes of bpym (Table 2) which can be taken as an indication for close lying excited states, perhaps involving the second lowest unoccupied MO π^*_2.

Electronic absorption spectra

According to Scheme 1 there should be at least four major MLCT transitions possible in a heterodinuclear complex of the kind described here, producing four intense charge transfer bands: d(Ru) $\rightarrow \pi^*_1$, d(M) $\rightarrow \pi^*_1$, d(Ru) $\rightarrow \pi^*_2$, and d(M) $\rightarrow \pi^*_2$. Additional absorption bands in the visible and near ultraviolet region can arise from ligand field (d → d) transitions, from charge transfer transitions d(Ru) $\rightarrow \pi^*$(bpy), and from less overlap-favoured transitions d(M) $\rightarrow \pi^*_{1,2}$ which can appear as shoulders in certain solvents [30, 31].

All these transitions may have different characteristics not only in terms of energy (Scheme 1) but also with respect to relative intensity, typical band width, and solvatochromism. Only some of the expected transitions may thus appear as individual bands with distinct maxima or as shoulders; the spectra of the two different $^{2+}$Ru$(bpy)_2$-containing complexes **1** and **2** (Figs. 4 and 5) are interpreted as follows (cf. Table 3).

Both complexes show a dominating maximum around 415 nm (3.0 eV) which is easily attributed to d(Ru) $\rightarrow \pi^*$(bpy) transitions [7, 8, 21, 26]; the high energy shoulder is quite characteristic for tris(α-diimine)ruthenium(II) complexes [30]. The tetracarbonylmolybdenum complex with its electron rich metal(0) center displays the typical [1, 10, 11] broad band (Fig. 4) from the transition d(Mo) $\rightarrow \pi^*_1$(bpym) at somewhat lower energy than the homodinuclear complex **6** (Table 3); this effect is attributed to ΔE in Scheme 1 which accounts for the stronger lowering of the π^*(bpym) orbitals by the fragment $^{2+}$Ru$(bpy)_2$ relative to $Mo(CO)_4$ [1, 26]. The broad long-wavelength band terminates (0 → 0 transition) at about 900 nm (1.38 eV) which is in excellent agreement with the difference 1.41 V between reduction and oxidation (peak) potentials (Table 1). Two visible shoulders at 528 and 485 nm are attributed to transitions d(Ru)→π^*_1 and d(Mo)→π^*_2, respectively, in agreement with similar values for homodinuclear analogues **4** and **6** (Table 3). The transition d(Ru)→π^*_2 is probably hidden under the intense d(Ru)→π^*(bpy) band; this transition is so intense (lg $\epsilon \approx 4$ [26]) because there are two bpy chromophors with relatively large orbital coefficients at the coordination centers [26].

In contrast to complex **2**, the Cu(I)/Ru(II) system **1** contains two metal centers with closer lying occupied d orbitals [24] as indicated by the cyclovoltammogram (Fig. 1). Furthermore, transitions from $^+Cu(PPh_3)_2$ fragments to α-diimines are less intense than those from $^{2+}Ru(bpy)_2$ [4, 8, 15, 26]. Accordingly, the spectrum of **1** (Fig. 5) lacks the distinct long-wavelength transition of **2**; nevertheless, the two shoulders at 546 and 488 nm are assigned to transitions d(Ru)→π^*_1 and d(Cu)→π^*_1, respectively. The shoulder at 365 nm (3.40 eV) is attributed to the d(Cu)→π^*_2 transition, in agreement with the maximum observed for the homodinuclear compound **7** [4, 15]. The absorption data of complex **3** (Table 3) are similar to those reported by other groups [20, 21]; again, the rather low intensity of Re(I)→π^*(α-diimine) bands (1/3 relative to corresponding $^{2+}Ru(bpy)_2$ complexes [26, 32]) causes d(Ru)→π^* transitions to dominate the spectrum [21]. The apparent solvatochromism of some heterodinuclear complexes of bpym including the remaining combinations Mo(0)/Re(I), Mo(0)/Cu(I) and Re(I)/Cu(I) will be treated in more detail elsewhere [33].

The two new complexes **1** and **2** do not show any strong luminescence on excitation with light of 400 nm wavelength; a similar result was reported for complex **3** [20]. Even mononuclear complexes of bpym are relatively poor emitters when compared to some isomeric bidiazine systems [26, 32]; of the homodinuclear systems **4** [7] and **6** [34] emit very weakly and **5** not at all [20]. The strong luminescence of **7** is the result of a special intra-complex π interaction [4]; such a (P)-Phenyl/bpym overlap is not possible for steric reasons in complex **1**.

Conclusions

It is clear from the results and the model presented in Scheme 1 that for compounds with weakly interacting heterometallic centers and similar coordinating sites at the bridging ligand there can be no 'averaging' of the two spectra of the homodinuclear species in order to arrive at the spectrum of the heterodinuclear system [35]. While the metal d orbitals remain quite separate in their relative energies, the π^* orbitals of the bridging acceptor ligand receive the combined effects from both metal fragments. In addition to their model role for studying inner sphere metal-to-metal electron transfer [36, 37] such heterodinuclear complexes may thus provide a better understanding of electronic structures. A survey of metal fragments binding to α-diimines should help to recognize opportunities for a specific design of heterodinuclear complexes with bpym and related ligands [1].

Acknowledgements

This work was generously supported by Deutsche Forschungsgemeinschaft and Volkswagenstiftung. We also thank Degussa AG for a gift of $RuCl_3$.

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