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Synthesis, electrochemistry and emission spectroscopy in fluid solution of four isomeric (α-diimine)Re(CO)$_3$Hal complexes

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Abstract

Complexes (bdz)Re(CO)$_3$Hal (Hal = Cl or Br) derived from the four isomeric bidiazine (bdz) chelate ligands 3,3′-bipyridazine, 2,2′-bipyrazine, 2,2′- and 4,4′-bipyrimidine have been synthesized from Re(CO)$_5$Hal by thermal substitution. All the complexes were found to show long-wavelength emission at room temperature in chloroform solution after irradiation into the metal-to-ligand charge transfer (MLCT) band. Spectroscopic data and electrochemical reduction potentials confirm the superior polarizing ability of neutral Re(CO)$_3$Hal fragments for α-diimine π system, and the electrochemical and photophysical data can be correlated with the established properties of the free ligands, of their anion radicals, and of other d^6 metal (W^0, Ru^{II}) complexes.

Introduction

The availability of four isomeric bidiazines (1) and their complexes provides a unique opportunity for detailed studies of electronic interactions between metals and ligands [1,2]. In particular, a better understanding of the much studied complexes [3,4] of the related 2,2′-bipyridine (bpy) [5] can be obtained through comparative investigations [1,2,6,7]. The bidiazines exhibit essentially the same structural features as bpy, [5,8,9], but the four isomeric diaza analogues (1) have distinctly different properties in terms of σ-coordinating and π-back-bonding capability [1]. Detailed investigations of the ligands [1], their anion radicals [7], and of their group 6 metal carbonyl [1,10,11] and [Ru(bpy)$_2$]$^{2+}$ complexes [1,2] have illustrated the value of such an approach.

The neutral (η^2-)halotricarbonylrhenium(I) fragments are important d^6 organometallic species and their bpy complexes and derivatives thereof have attracted increasing interest in recent years following reports of their luminescence [12–22], non-linear optical behaviour [23], photo- and electrocatalytic activity [24–30]. After the pioneering work by Wrighton and coworkers on the photophysi-

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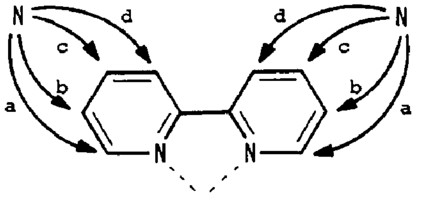


(1)

a : 3,3'-bipyridazine (bpdz) pK_{BH^+} = 3.37 [42]

b : 4,4'-bipyrimidine (bpm) pK_{BH^+} = 1.0 - 1.5 [1,9]

c : 2,2'-bipyrazine (bpz) pK_{BH^+} = 0.45 [43]

d : 2,2'-bipyrimidine (bpym) pK_{BH^+} = 2.2 - 2.6 [2,11]

cal behaviour of these systems [12–19], it was the discovery of CO_2 activation using (bpy)Re$(CO)_3$Hal and light or electrons [24,25] that provoked renewed interest in them [26–30].

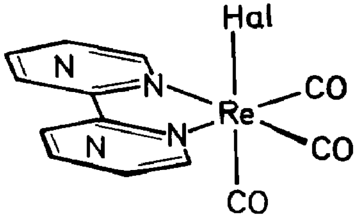
We describe here the synthesis, the absorption and emission spectroscopy, and the electrochemistry of Re$(CO)_3$Hal complexes of the four isomeric ligands (**1**); A. Vogler and Kisslinger have recently reported the solid-state luminescence of the mononuclear bidiazine complex (bpym)Re$(CO)_3$Cl [31]. A very sensitive detector system was used in order to cover a wide range of emission intensities, since luminescence in solution is generally weaker than that in the solid [31], but it is chemically more significant [4].

Results and discussion

Synthesis and electrochemistry

The complexes **2** were obtained from carbonylmetal halides Re$(CO)_3$Hal and the appropriate chelate ligands **1** by thermal replacement of CO. Elemental analyses and carbonyl vibrational frequencies (cf. Experimental) confirmed the composition, the purity, and stereochemistry of the materials; the *fac* configuration **2** was observed as in all other related cases [6,12–33].

(bpdz)Re$(CO)_3$Cl
(bpm)Re$(CO)_3$Cl
(bpm)Re$(CO)_3$Br
(bpz)Re$(CO)_3$Cl
(bpz)Re$(CO)_3$Br
(bpym)Re$(CO)_3$Cl



(2)

Cyclic voltammetry in *N,N*-dimethylformamide(DMF)/0.1 *M* Bu_4NClO_4 gave reversible one-electron reduction waves corresponding to the formation of anion radical complexes (**3**) [34]. That the π^* (α-diimine) orbital is the lowest lying [26] was established recently through ESR studies of the one-electron reduced species $(bpy^{-\cdot})$Re$(CO)_3$Hal [6]; such radical anions have been commonly but misleadingly, referred to as a "Re^0" systems in earlier reports [13,22,25]. ESR spectroscopic data

Table 1

Cyclic voltammetry data for reduction of the complexes (α-diimine)$Re(CO)_3Hal$ [a] and of the free diimine ligands

Complex	$E_{1/2}^{(0/-)}$ (ΔE (mV))	$E_{pc}^{(-/2-)}$	$e_{1/2}^{(0/-)}$ (ligand)
(bpy)$Re(CO)_3Cl$	−1.25 (70)	−1.71	−2.08
(bpy)$Re(CO)_3Br$	−1.24 (90)	−1.65	−2.08
(bpdz)$Re(CO)_3Cl$	−0.90 (70)	−1.42	−1.72
(bpm)$Re(CO)_3Cl$	−0.61 (75)	−1.22	−1.34
(bpm)$Re(CO)_3Br$	−0.59 (70)	−1.16	−1.34
(bpz)$Re(CO)_3Cl$	−0.74 (75)	−1.18	−1.59
(bpz)$Re(CO)_3Br$	−0.74 (100)	−1.25	−1.59
(bpym)$Re(CO)_3Cl$	−0.93 (80)	−1.55	−1.73

[a] Potentials in V vs. SCE; 0.1 *M* Bu_4NClO_4/DMF as electrolyte. ΔE: peak separation for reversible first reduction; E_{pc}: cathodic peak potential for irreversible process at 100 mV/s scan rate.

for the anions of the new complexes **2** and their substitution products will be presented elsewhere.

$$(\alpha\text{-diimine})\mathrm{Re^I(CO)_3Hal} \xrightarrow{+\,e^-} \underset{\textbf{(3)}}{(\alpha\text{-diimine}^{-\bullet})\mathrm{Re^I(CO)_3Hal}} \qquad (1)$$

The midpoint potentials (Table 1) for corresponding chloride and bromide complexes are virtually identical and illustrate that coordination to $Re(CO)_3Hal$ results in very strong anodic shifts $\Delta E_{1/2}$ of more than 0.7 V relative to the values for the free ligands **1** [1,2]. The "polarizing" effect of these metal fragments is thus even stronger (by 0.05–0.2 V) than that of the dipositively charged $[(bpy)_2Ru]^{2+}$ fragment [1,2,6]; the little variation of $\Delta E_{1/2}$ among complexes **2** once again [1,2] reflects the effect of increased basicity in the reduced state, which can be estimated from the Hückel MO electron densities at the coordinating nitrogen centers in the lowest unoccupied molecular orbital (LUMO) [1]. The bpz complexes show the largest shifts $\Delta E_{1/2}$(ligand/complex), and the bipyrimidine systems, especially bpm, the smallest. One consequence of this is that the bpm complexes of $Re(CO)_3Hal$ are only slightly more easily reduced (ca. 0.15 V) than their bpz analogues, whereas for the free ligands there is a reduction potential difference of 0.25 V.

Oxidation of the complexes **2** in DMF proved to be irreversible. Metal-centered oxidation would create a labile 17 electron [35,36] Re^{II} species, which should then easily undergo displacement of carbonyl ligands by solvent molecules [37,38]. Similarly, further electron uptake by already anionic complexes occurs irreversibly in all cases, with potential differences typical of the individual bidiazine anion/dianion couples [1].

Absorption and emission spectroscopy

The complexes (α-diimine)$Re(CO)_3Hal$ owe their colour and initial photochemistry to a symmetry-allowed metal-to-ligand charge transfer (MLCT) transition from filled (d^6) metal orbitals to unoccupied (π^*) orbitals of the "chromophoric" ligand (**4**) [12–33]. Absorption spectra of four systems are shown in Fig. 1, and Table 2

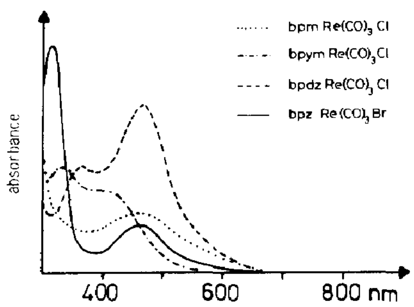


Fig. 1. Electronic absorption spectra of ca. 10^{-4} molar solutions of four bidiazine complexes in chloroform solution (absorbance different for each spectrum).

lists the absorption and emission data.

$$(\alpha\text{-diimine})\text{Re}^{\text{I}}(\text{CO})_3\text{Hal} \xrightarrow{h\nu} {}^{*}[(\alpha\text{-diimine}^{-\cdot})\text{Re}^{\text{II}}(\text{CO})_3\text{Hal}] \tag{4}$$

In terms of the simplified formulation (4), three factors determine the optical absorption energy E_{op} (eq. 1) [39], viz.:

(i) the relative positions of the π^* orbitals, which can be deduced from the electrochemical reduction potentials E_{red};

(ii) the relative positions of filled d orbitals, which can be derived from the oxidation potentials E_{ox} or estimated from the σ donor strength as measured by the $\text{p}K_{\text{BH}^+}$ (1) [1]; and

(iii) the Franck–Condon contributions χ from intra- and intermolecular vibrational interactions [39,40].

$$E_{\text{op}}\ (\text{eV}) = E_{\text{ox}}\ (\text{V}) - E_{\text{red}}\ (\text{V}) + \chi \tag{5}$$

The contribution χ is assumed to be constant and rather small because of the isostructural chelate arrangement for all the systems studied here [39,41]. The differences in the long-wavelength absorption maxima arising from $d \rightarrow \pi^*$ (LUMO) transitions can thus be accounted for in terms of the relative importance of the

Table 2

Photophysical data for the complexes (α-diimine)Re(CO)$_3$Hal in chloroform solution [a]

Complex	Absorption		$\tilde{\nu}_{\text{em}}$ (cm^{-1}) [b]	$\Delta\tilde{\nu}$ (cm^{-1}) [c]	E^{*}_{red} [d]	ϕ_{F} [e]
	$\tilde{\nu}_1$ (cm^{-1})	$\tilde{\nu}_2$ (cm^{-1})				
(bpy)Re(CO)$_3$Cl	25400	34100	16000	9400	0.73	1.5×10^{-3}
(bpy)Re(CO)$_3$Br	25200	33900				
(bpdz)Re(CO)$_3$Cl	21600 (ϵ 3649)	27500	13100 (15300)	8500	0.72	9.8×10^{-5}
(bpm)Re(CO)$_3$Cl	21800	35200	15100	6700	1.26	5.0×10^{-1}
(bpz)Re(CO)$_3$Cl	22200	31300				
(bpz)Fe(CO)$_3$Br	21900 (ϵ 3300)	32300	13300 (14500)	8600	0.87	1.5×10^{-4}
(bpym)Re(CO)$_3$Cl	24900 [f]	30200	13800 (17600)	11100	0.78	1.0×10^{-5}

[a] Emission spectra are corrected; excitation wavelength 436 nm. Extinction coefficients ϵ in M^{-1} cm^{-1}. [b] Solid state data in parentheses; the value for bpym is from ref. 31. [c] $\tilde{\nu}_1 - \tilde{\nu}_{\text{em}}$. [d] In V vs. SCE, calculated from eq. 6. [e] Relative to 1-phenylaminoanthraquinone in toluene ($\phi_{\text{F}} = 1.7\times10^{-4}$). [f] 26950 cm^{-1} in DMSO (ref. 31), 27100 cm^{-1} in methanol, 26300 cm^{-1} in acetonitrile, 25300 cm^{-1} in dioxane.

value of pK_{BH^+} for the ligand and reduction potentials of each complex. The bpy systems absorb at rather high energies because of the high lying LUMO and negative values of E_{red}, while within the series of the four bidiazine systems the bpym species has a relatively high lying LUMO [1]. The other three ligands yield complexes with absorption maxima at longer wavelengths because of high ligand field strength (bpdz) [42] or of a low-lying LUMO (bpm, bpz) [1,43]. Moreover, bpz and bpdz stand out as undergoing a particularly large ligand field increase on going to the reduced state [1].

Differences are noticeable in the absorption spectra of corresponding chlorides and bromides because the optical transition involves a metal centered (d) level [13], which should be more affected by a change of the halide than is the π^* (LUMO) level [38,44]. The complexes display moderate negative [45] solvatochromism, as is usual for MLCT absorption [46–48]. Poor solubility in non-polar solvents has precluded a more detailed study.

The intensities of the MLCT absorption bands are relatively small compared with $M(CO)_4$ [1,43] or the $[(bpy)_2Ru]^{2+}$ complexes [2], but the molar extinction coefficients are still in the range for symmetry-allowed charge transfer transitions [3]. Second symmetry-allowed MLCT bands arising from $d \rightarrow \pi^*$ (SLUMO) transitions are found at higher energies and with intensities characteristic of each individual bidiazine ligand system [1,42]; the bpdz complexes show the smallest [42] and the bpm systems the largest LUMO/SLUMO gap [1].

The complexes (α-diimine)$Re(CO)_3Hal$ have primarily been studied in recent years because of their interesting photophysical properties [12–23,31,49]. All the complexes investigated in this respect show emission of different intensity when irradiated with visible light of 436 nm wavelength in chloroform solution at room temperature (Fig. 2); a comparison with solid state data confirms that luminescence is hypsochromically shifted in the crystal [12,31,49]. Irradiation at $436\ \text{nm} \mathrel{\hat{=}} 23000\ \text{cm}^{-1}$, i.e. into the MLCT bands of the compounds (Fig. 1), should initially lead to an MLCT excited state, and ligand field absorption should occur at distinctly higher energies [50]. An investigation of the luminescence in solution at 293 K seemed to

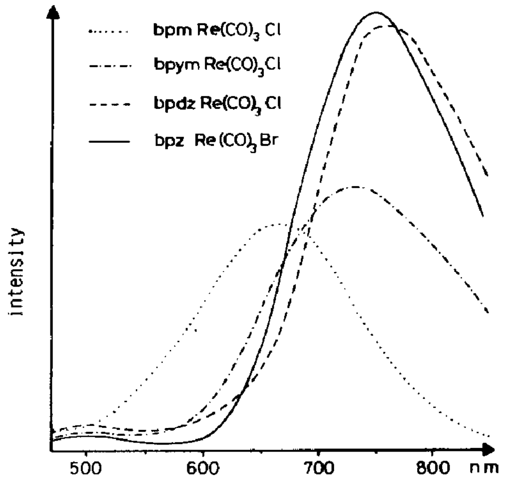


Fig. 2. Corrected luminescence spectra of four bidiazine complexes at 293 K in chloroform solution (excitation wavelength 436 nm, intensities not to scale).

be more relevant for possible applications of such complexes as photosensitizers using visible light [4,25], and the data obtained, including emission maxima and relative quantum yields, are listed in Table 2.

In the case of the emission maxima, examination of the absorption features reveals significant differences for the four isomeric complexes. The largest Stokes shift of 11100 cm^{-1} is found for the bpym system; other features, such as bands widths [1,51], solvatochromism [47], and resonance Raman data [52] previously pointed to considerable structural changes in this ligand upon electron uptake [53]. The smallest Stokes shift $\Delta\tilde{\nu}$ of only 6700 cm^{-1} is noted for the bpm complex: once again previous observations [2], and calculations in connection with ESR studies, have indicated a very even spin distribution, resulting in little geometrical change upon reduction (or MLCT excitation) [7]. Because of this, the emission maxima of bpdz, bpz, and bpym complexes lie in the long-wavelength region (Fig. 2), whereas the complex from the bpm isomer emits at higher energies, albeit very weakly.

Considerable differences in the emission quantum yields were found. The well established [12,18] bpy complex was used as an "internal" reference, and relative to that complex all the bidiazine systems have *lower* values of ϕ. In agreement with results obtained for the potentially photosensitizing complexes $[(bdz)_3Ru]^{2+}$ [2,54], emission is weakest for the bpm derivative and highest for the bpz and bpdz (and bpy) derivatives. The bpdz and bpy ligands display large basicities in the ground state whereas the bpdz and bpz ligands experience an increase of pK_{BH^+} in the MLCT excited state [1,42], however, bpy does not contain additional potentially (solvent)-coordinating, nitrogen centers [41,55].

An important requirement for the use of complexes such as **2** as photosensitizers is the reduction potential in the excited state, which must be sufficient for the sensitized reaction [56], e.g. the reduction of CO_2 [25]. In terms of approximation (**6**) [57], the data in Table 2 indicate similar values of $E^{\star}_{red}$ for the bpy, bpdz, and bpym systems, but significantly higher values for the bpm and bpz complexes. The still acceptable quantum yield for the bpz system makes complexes of this ligand particularly attractive for use in photoreduction processes [25,43].

$$E^{\star}_{red}\ (V) = E_{red}\ (V) + E_{em}\ (eV) \qquad (6)$$

Quenching experiments will have to be carried out to test the suitability of complexes **2**; the calculation based approach [1,2] to the design of ligands for photosensitizing complexes can now be applied to binuclear complexes of the $Re(CO)_3Hal$ fragments [6,22,31,58].

Experimental

Electronic absorption spectra were recorded on a Shimadzu UV 160 spectrometer. Emission spectra were recorded with a mercury super pressure lamp HBO 100 W (Osram) as exciting light source. The exciting and the emission monochromator (Spex) were both equipped with a grating. The emitted light was measured at right angles to the exciting beam and detected by a photomultiplier with a GaAs-Photocathode (RCA C 31034). Further details of the apparatus are available on request [59a,b].

Fluorescence quantum yields were determined relative to that of 1-phenylaminoanthraquinone in toluene ($\phi_F = (1.7 \pm 0.5) \times 10^{-4}$) and corrected for the spectral sensitivity of the detection system as well as for the changes of the refractive index of the solvent. In order to keep the relative error small, the value for 1-phenylaminoanthraquinone was obtained by measurement of a set of anthraquinone derivatives with quantum yields ranging from 3.2×10^{-1} to 2.5×10^{-5} (standard: quinine sulphate in 0.1 *n* H_2SO_4: $\phi_F = 0.52$). Quantum yields up to 10^{-6} ($\pm 3 \times 10^{-7}$) can be measured by this procedure; an exact description of the method is found in [59a,b]. Spectrograde chloroform was used as solvent, and the concentrations for absorption and emission spectroscopy were between 0.1 and 0.01 mmolar.

Cyclic voltammetry was performed with a PAR 363 potentiostat and Bank VSG 72 scan generator. The three-electrode configuration contained a glassy carbon working electrode and a saturated calomel electrode (SCE) as reference. A 0.1 *M* solution of tetrabutylammonium perchlorate in dry, oxygen-free *N,N*-dimethylformamide was used as electrolyte.

Bidiazine ligands [1] not commercially available and complexes $Re(CO)_5Hal$ [6] were prepared by published procedures. For bpm, the synthesis described by Effenberger [60] was found to be preferable to other methods [9,61].

General procedure

A solution of 79 mg (0.5 mmol) of the bidiazine ligand and 181 mg (0.5 mmol) $Re(CO)_5Cl$ (or the appropriate amount of the bromide) in 25 ml toluene was heated for 2 h under reflux. The precipitate formed on cooling was washed with diethyl ether, dissolved in chloroform, and reprecipitated by addition of n-hexane. Yields were between 70 and 80%. IR: $\tilde{\nu}(CO) = 2302 \pm 3$, 1930 ± 3, 1912 ± 5 cm^{-1} (in acetonitrile solution).

Chloride isomers:

$C_{11}H_6ClN_4O_3Re$ (463.85) calc: C, 28.48; H, 1.30; N, 12.08% found: C, 30.74; H, 1.41; N, 12.26 (bpdz isomer) C, 28.47; H, 1.21; N, 12.19 (bpm isomer) C, 28.26; H, 1.22; N, 12.08 (bpz isomer) C, 28.48; H, 1.18; N, 11.98 (bpym isomer)

Bromides:

$C_{11}H_6BrN_4O_3Re$ (508.30) calc: C, 25.99; H, 1.19; N, 11.02% found: C, 25.81; H, 1.25; N, 10.91 (bpm isomer) C, 26.17; H, 1.17; N, 11.10 (bpz isomer)

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