the error calculation. We do not wish to claim that a better fit is necessarily proof for a particular electronic assignment, but we do note that a major reason for the larger error for Güdel's assignment was that the splitting of the $^4A_{2g} \rightarrow {}^4T_{2g}$ band was calculated to be too large. The optimized value of ψ in this case was 5.2°, predicting a nearly eclipsed orientation. The assignment of the doublet states to D_4^* eigenfunctions was similar to Güdel's,[3] in that the lowest two lines were derived from the $^2T_{1g}$ state. However, our analysis assigns the lowest state to $^2A_2$ ($^2T_{1g}$) rather than a ^2E ($^2T_{1g}$) component.

Conclusions. The ligand field asymmetry caused by the strong anisotropic π-interaction with hydroxide ion in $[Cr(NH_3)_5OH](ClO_4)_2$ causes the five sharp-line components of the $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ transitions to split to such an extent that the association with the octahedral parents is practically unrecognizable, certainly not from the distribution of energy levels and only with caution from an eigenfunction analysis.

Forster has attempted to identify Cr(III) complexes whose lowest, luminescent excited state is derived from the octahedral $^2T_{1g}$ state by an unusually broad phosphorescence in solution.[9,10] A theoretical basis for this is an orbital analysis in the C_{4v} point group, showing that the tetragonal ^2E state derived from O_h $^2T_{1g}$ is the only one of the group $\{^4A_{2g}, {}^2E_g, {}^2T_{1g}\}$ to have a different configuration than the ground state.[7] The present analysis for $[Cr(NH_3)_5OH](ClO_4)_2$ shows no tetragonal ^2E character for the luminescent state, although it is one of the complexes found to exhibit a broad phosphorescence.[8] This does not necessarily contradict Forster's conclusions, since the effective electronic symmetry is not really tetragonal. An orbital population analysis of the type used by Ceulemans[28] yields a configuration of $(xy)^{0.98}(xz)^{0.76}(yz)^{1.23}$ for the lowest doublet state ($^2A_1$). The difference between that and the nearly pure $(xy)(xz)(yz)$ of the ground state could be a source of the broadening. However, it is also possible that hydroxo complexes will exhibit luminescence broadening due simply to the large perturbations in the transition energy, as seen in Figure 1, caused by the zero-point torsional motion of the hydroxide, as long as the luminescent state is one showing oscillatory behavior.

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Synthesis, Absorption Spectra, and Photochemical Behavior of Mono- and Dinuclear Ruthenium(II) Complexes

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Syntheses, characterization, absorption spectra (including their solvent dependence), and photochemical behavior of some novel mono- and dinuclear ruthenium(II) complexes containing 2,3-dpp and 2,5-dpp as bridging ligands (dpp = bis(2-pyridyl)pyrazine) are reported. The complexes are $[Ru(2,n\text{-dpp})(\eta^6\text{-}C_6H_6)Cl]PF_6$ (**1**, $n = 3$; **2**, $n = 5$), $[(\mu\text{-}2,n\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2](PF_6)_2$ (**3**, $n = 3$; **4**, $n = 5$), and $[Cl(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}2,n\text{-dpp})Ru(CO)_2Cl_2]PF_6$ (**5**, $n = 3$; **6**, $n = 5$). For comparison purposes, the same properties of some closely related mono- and dinuclear ruthenium(II) complexes are also reported. The absorption spectra of all the complexes show intense ligand-centered (LC) bands in the UV region and broad, moderately intense, metal-to-ligand charge-transfer (MLCT) bands in the visible region. In the heteroligated dinuclear complexes two different MLCT transitions are expected, but only one absorption maximum is present in the spectra because the metal fragments exhibit similar chromophoric properties. The energy position of the MLCT band is practically unaffected by solvent polarity in the complexes that do not contain carbonyl ligands, whereas for the other complexes a small red shift is observed in low-polarity solvents. The two heteroligated complexes are strongly photosensitive in fluid solution, with release of a CO ligand. Quantum yields for the reactant disappearance are 0.2 and 0.01 for 2,3-dpp and 2,5-dpp complexes, respectively. The differences in the quantum yields are attributed to intramolecular energy transfer from the reactive $Ru(CO)_2Cl_2$ to the unreactive $Ru(\eta^6\text{-}C_6H_6)Cl$ moiety, which competes with the photoreaction in the 2,5-dpp complex.

Introduction

Photophysical and photochemical properties of N-heterocyclic ruthenium(II) complexes have been the object of extensive investigations in the last 15 years because of their outstanding interest for theoretical purposes and potential applications. In particular, Ru(II)–polypyridine complexes have been used as reactants and/or mediators in light-induced and light-generating electron-transfer processes.[2-4] In recent years there has been a further growth of interest in these complexes[5-13] because they can be used as building blocks to design (i) more complex systems capable of performing useful light-induced functions ("photochemical molecular devices"[14]) and (ii) multielectron-transfer catalysts.[11-16]

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Table I. Selected IR Absorption Maxima[a] of the Novel Complexes

no.	compd	ν(C=C) and ν(C=N)	ν(Ru—Cl)	ν(CO)
1	$[Ru(2,3\text{-dpp})(\eta^6\text{-}C_6H_6)Cl]PF_6$	1590 (m), 1572 (m), 1555 (m), 1548 (m), 1520 (w)	292 (2)	
2	$[Ru(2,5\text{-dpp})(\eta^6\text{-}C_6H_6)Cl]PF_6$	1602 (m), 1580 (m), 1562 (m), 1510 (w)	288 (2)	
3	$[(\mu\text{-}2,3\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2](PF_6)_2$	1605 (m), 1512 (w)	316 (m)	
4	$[(\mu\text{-}2,5\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2](PF_6)_2$	1600 (m), 1508 (w)	282 (m)	
5	$[Cl(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}2,3\text{-dpp})Ru(CO)_2Cl_2]PF_6$	1590 (m)	329 (m), 282 (w)	2075 (vs), 2015 (vs)
6	$[Cl(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}2,5\text{-dpp})Ru(CO)_2Cl_2]PF_6$	1600 (m), 1510 (w)	329 (m), 285 (w)	2077 (vs), 2015 (vs)

[a] cm^{-1}; KBr pellets.

Table II. 300-MHz ^1H NMR Data [δ (ppm)] for New Complexes[a]

no.	$H_{6'}/H_{6''}$[b]	$H_{5'}/H_{5''}$	$H_{4'}/H_{4''}$	$H_{3'}/H_{3''}$	H_6/H_x[c]	C_6H_6
1	9.40 d/8.60 d	7.61 m/7.59 m	8.09 m/7.76 m	7.95 d/7.02 d	9.46 d/8.84 d	6.10 s
2	9.43 d/8.84 d	7.74 m/7.60 m	8.24 m/8.08 m	8.50 d/8.47 d	9.53 s/9.52 s	6.11 s
3[d]	9.64 d	7.91 m	8.14 m	8.54 d	9.74 s	6.30 s
4	9.50 m	7.87 m	8.36 m	8.80 m	10.02 s/10.00 s	6.22 s/6.18 s
5	9.53 d/9.42 d	7.89 m/7.77 m	8.60 m/8.32 m	8.18 d/7.97 d	9.31 d/9.22 d	6.16 s
6	9.49 d/9.30 d	7.95 m/7.85 m	8.43 m/8.31 m	8.96 d/8.72 d	10.19 d/9.85 d	6.21 s

[a] In CD_3CN. [b] Hydrogen numbers refer to positions quoted in Figure 1. In mononuclear complexes, $H_{6'}$ is the hydrogen nearest the metal-ligating pyridyl nitrogen. In binuclear complexes **5** and **6**, $H_{3'}$–$H_{6'}$ are on the side of the $Ru(C_6H_6)$ moiety. [c] $x = 3$ for 2,5-dpp; $x = 5$ for 2,3-dpp. [d] In DMSO-d_6.

A key role in determining the properties of oligonuclear complexes is played by the bridging ligands, since the interactions between the bridged metal fragments depend on the size, shape, and electronic nature of the bridge.[11,16] The 2,3- and 2,5-isomers of bis(2-pyridyl)pyrazine (dpp, Figure 1) are useful bischelating bridging ligands for polymetallic complexes;[8,9,17-21] an important difference between such isomeric ligands is that the 2,5-isomer can be planar in dinuclear chelate complexes, whereas the 2,3-isomer is highly distorted from planarity because of steric hindrance.[21] Such a difference is expected to be critical for some properties of isomeric dinuclear complexes containing 2,3-dpp or 2,5-dpp as bridging ligands. To examine the communication ability of the metal fragments across the two types of isomeric bridges, we have studied the absorption spectra (including their solvent dependence), luminescence properties, and photochemical behavior of two new bimetallic complexes containing different ruthenium(II) moieties (heteroligated Ru dimers) with 2,3-dpp and 2,5-dpp as bridging ligands, as well as of their parent mononometallic and homoligated Ru(II) bimetallic complexes.[22]

Experimental Section

Materials and Methods. 2,3-Bis(2-pyridyl)pyrazine,[23] 2,5-bis(2-pyridyl)pyrazine,[24] and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$[25] were prepared according to literature methods. The complexes $Ru(2,n\text{-dpp})(CO)_2Cl_2$ ($n = 3, 5$) were prepared as previously reported.[17] All reactions were carried on under inert atmosphere. All reactions and manipulations involving carbonyl compounds were carried out strictly in the dark. The following solvents of the best commercial grade were used as supplied: acetonitrile (AN), methanol (MeOH), ethanol (EtOH), dichloromethane (CH_2Cl_2), butyronitrile (BN), tetrahydrofuran (THF), dimethylformamide (DMF), chloroform ($CHCl_3$), toluene. The absorption spectra in the UV and visible region were recorded with a Kontron Uvikon 860 spectrophotometer. For infrared spectra Perkin-Elmer 682 and 1330 spectrophotometers were used. ^1H NMR spectra were obtained on a Bruker AW 300 spectrophotometer. Elemental analyses were performed on a Carlo Erba 1106 apparatus. For conductivity measurements (approximately 10^{-3} mol dm^{-3} light-protected solutions in nitromethane) an LKB 5300B Conductolyzer was employed. Luminescence experiments were performed with a Perkin-Elmer LS-5B spectrofluorimeter. The photochemical behavior was studied by irradiating the solutions with a Bausch-Lomb SP 200 mercury lamp equipped with a Bausch-Lomb high-intensity monochromator; irradiation wavelengths ranged from 405 to 505 nm. The light intensity incident in the reaction cell (1×10^{-6} einstein/min at 405 nm, 3×10^{-7} einstein/min at 505 nm) was measured under dilute or concentrated conditions with a ferrioxalate actinometer.[26]

Synthesis of $[Ru(2,n\text{-dpp})(\eta^6\text{-}C_6H_6)Cl]PF_6$ (1, $n = 3$; 2, $n = 5$). In a typical preparation a suspension of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (50 mg, 0.099 mmol) and the appropriate ligand (molar ratio 1:4) in 5 mL of methanol was stirred at room temperature for 1 h. Some decomposition product was filtered off and washed with small portions of methanol until this passed colorless. The filtrates and the reaction liquor were unified, and a 10-fold excess of solid NH_4PF_6 was added. Yields: **1**, mustard yellow crystals, 80%; **2**, yellow microcrystals, 40% after several purifications from acetonitrile–ethanol.

Anal. Calcd for $C_{20}H_{16}ClF_6N_4PRu$: C, 40.45; H, 2.71; N, 9.28. Found for **1**: C, 39.89; H, 2.65; N, 9.32. Found for **2**: C, 39.81; H, 2.63; N, 9.28. Conductivities: **1**, $\Lambda = 88\ \Omega^{-1}\ mol^{-1}\ cm^2$; **2**, $\Lambda = 83\ \Omega^{-1}\ mol^{-1}\ cm^2$.

Synthesis of $[(\mu\text{-}2,n\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2](PF_6)_2$ (3, $n = 3$; 4, $n = 5$). The complexes were prepared by following the same procedure as above, but by using a precursor:ligand molar ratio of 1:2. Yields: **3**, greenish yellow microcrystals, 85%; **4**, red microcrystals, 90%.

Anal. Calcd for $C_{26}H_{22}Cl_2F_{12}N_4P_2Ru_2$: C, 32.75; H, 2.32; N, 5.87. Found for **3**: C, 32.96; H, 2.13; N, 5.81. Found for **4**: C, 33.03; H, 2.44; N, 6.01. Conductivities: **3**, $\Lambda = 165\ \Omega^{-1}\ mol^{-1}\ cm^2$; **4**, $\Lambda = 144\ \Omega^{-1}\ mol^{-1}\ cm^2$.

Synthesis of $[Cl(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}2,n\text{-dpp})Ru(CO)_2Cl_2]PF_6$ (5, $n = 3$; 6, $n = 5$). In a typical preparation, a suspension of $Ru(2,n\text{-dpp})(CO)_2Cl_2$ (40 mg, 0.086 mmol) and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (22 mg, 0.043 mmol) in 15 mL of methanol was stirred for 28 h at room temperature. After filtration to separate some decomposition product (which was washed with little methanol), 10-fold excess of solid NH_4PF_6 was added to the mother and washing liquors. The precipitate was washed with little methanol and with diethyl ether and was vacuum-dried. Yields: **5**, yellow powder, 65%; **6**, orange-yellow powder, 80%.

Anal. Calcd for $C_{22}H_{16}Cl_3F_6N_4O_2PRu_2$: C, 32.03; H, 1.96; N, 6.81. Found for **5**: C, 31.62; H, 2.03; N, 6.45. Found for **6**: C, 32.03; H, 1.93; N, 6.48. Conductivities: **5**, $\Lambda = 87\ \Omega^{-1}\ mol^{-1}\ cm^2$; **6**, $\Lambda = 75^{-1}\ mol^{-1}\ cm^2$.

Results

Uncomplexed or monocomplexed 2,n-dpp easily react at room temperature in methanol with the halogen-bridged species $[Ru(C_6H_6)Cl_2]_2$, giving rise to the compounds **1**–**6**. The mononuclear complexes are obtained by using an excess of ligands. This

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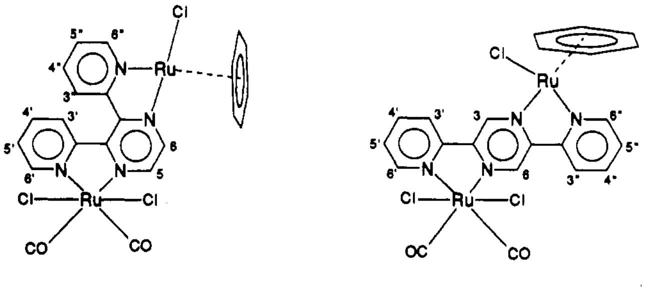
Table III. Absorption Data and Photochemical Quantum Yields

no.	complex	absorption[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	photochemistry[b] Φ
1	$Ru(2,3\text{-dpp})(\eta^6\text{-}C_6H_6)Cl^+$	400 (1600)	
2	$Ru(2,5\text{-dpp})(\eta^6\text{-}C_6H_6)Cl^+$	408 (1500)	
3	$(\mu\text{-}2,3\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2^{2+}$	441 (8000)	
4	$(\mu\text{-}2,5\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2^{2+}$	461 (6700)	
5	$Cl_2(CO)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$	437 (5600)	0.20
6	$Cl_2(CO)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$	457 (5700)	0.01
7	$Ru(2,3\text{-dpp})(CO)_2Cl_2$	385 (2500)	0.65[c]
8	$Ru(2,5\text{-dpp})(CO)_2Cl_2$	405 (1600)	0.60[c]
9	$(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]_2$	410 (4500)	0.20[c]
10	$(\mu\text{-}2,5\text{-dpp})[Ru(CO)_2Cl_2]_2$	448 (4600)	0.20[c]

[a] In AN solution. The maxima reported are relative to the lowest energy MLCT band. Errors: ±2 nm. [b] Quantum yields for CO loss in AN solution (unless otherwise noted), measured by the disappearance of the reactants. λ_{exc} = 405 nm. Errors: 10%. [c] Quantum yields in MeOH; data from ref 17.



5 6

Figure 1. Schematic structural formulas of the N-heterocyclic bridging ligands.

procedure does not prevent, in the case of 2,5-dpp, the formation of the bimetallic species even by using a 1:10 precursor:ligand ratio, in agreement with the tendency of 2,5-dpp to behave as a more effective binucleating ligand than 2,3-dpp. The better yields in the preparations of the homo- and heteroligated diruthenium species of 2,5-dpp compared to the analogous species of 2,3-dpp confirm this effect, which can be connected with different steric[8,9] and electronic[19b] properties.

The IR and NMR data of the new complexes are reported in Tables I and II, respectively.

The NMR spectrum of the homoligated complex **3** accounts for a single, highly symmetrical species with the two benzene rings either in cis or in trans relationship with respect to the pyrazine plane of 2,3-dpp. The spectrum of complex **4** is more complicated, showing unsymmetrical multiplets for all the hydrogens of 2,5-dpp, except H_3 and H_6. These, as well as the benzene hydrogens, give two distinct singlets of intensity about 1:2. These data are in agreement with the presence of two cis and trans isomers. The NMR spectra of the heteroligated complexes **5** and **6** are consistent with the presence of only one isomer. The chemical shifts and the IR data, compared with those of complexes **1**–**4** and with those already reported[17] for their precursor $Ru(2,n\text{-dpp})(CO)_2Cl_2$, are consistent with the highly symmetrical structure of the *cis*-dicarbonyl-*trans*-dichloro arrangement around a ruthenium atom. The schematic structural formulas of **5** and **6** are shown in Figure 1.

All the complexes studied are thermally stable in the dark in each solvent employed for at least 24 h, as indicated by the lack of changes in their absorption spectra.

The absorption spectrum of each complex exhibits a band of medium intensity (ϵ = 1600–8600 M^{-1} cm^{-1}) in the visible region (400–465 nm) and a more intense band at higher energy. Below 300 nm, other bands are present, with ϵ in the 10^4–10^5 range. Figure 2 shows the absorption spectra of $Cl_2(CO)_2Ru(\mu\text{-}2,n\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ (n = 3, 5). Table III reports the energy and the extinction coefficient of the maximum in the visible region for the complexes studied and for some closely related complexes.[22] It can be noted that the absorption spectra of the heteroligated Ru dinuclear complexes are not the mere superimposition of the spectra of the homoligated Ru parents, as shown by Figure 3, where the "expected" (obtained from the summation of the spectra of the homoligated dimers divided by two) and experimental absorption spectra of $Cl_2(CO)_2Ru(2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ are reported.[27]

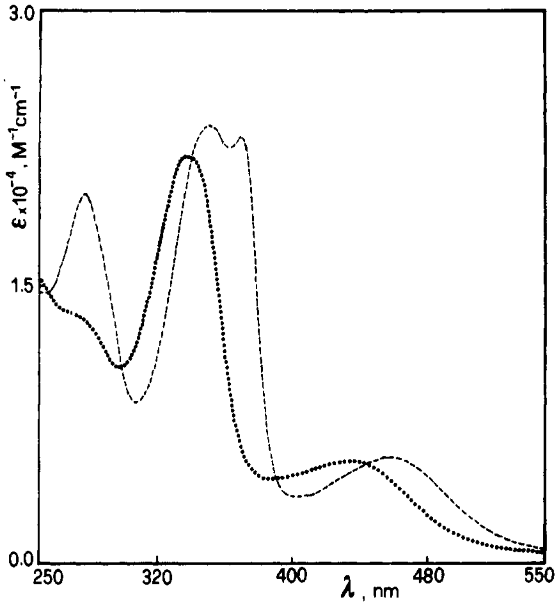


Figure 2. Absorption spectra of $Cl_2(CO)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ (···) and $Cl_2(CO)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ (- - -) in AN.

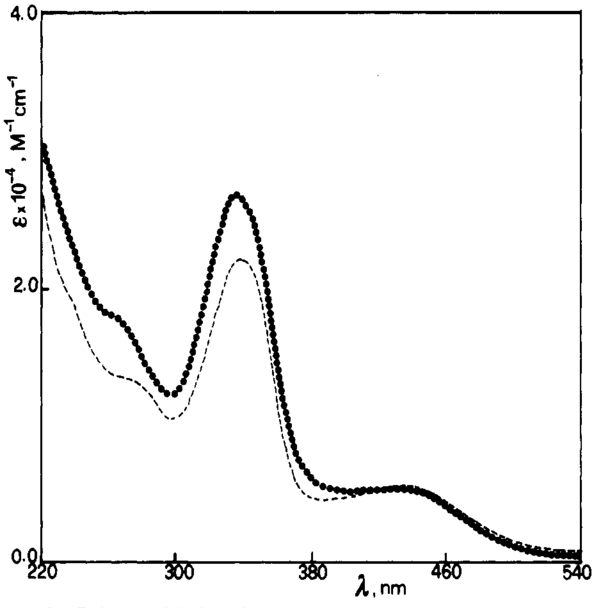


Figure 3. Calculated (···) and experimental (- - -) absorption spectra of $Cl_2(CO)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ in AN (see text).

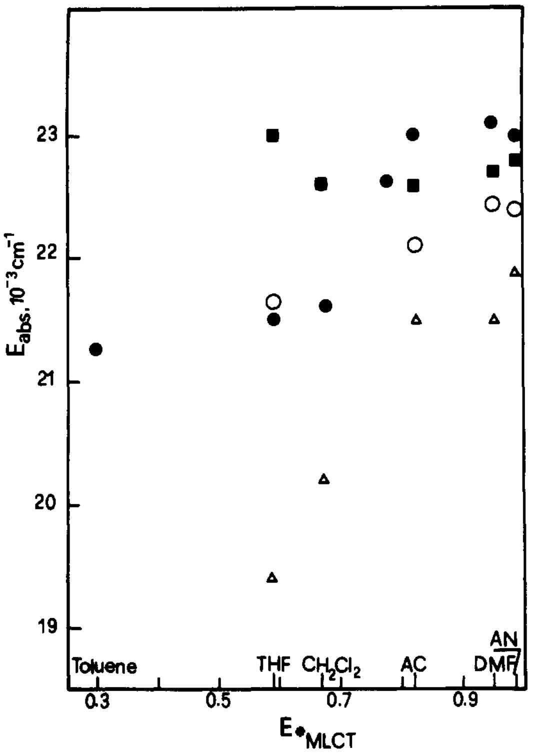


Figure 4. Plot of the energy of the MLCT bands vs the $E_{\bullet MLCT}$ solvent parameter[26] for $Cl_2(CO)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ (●), $Cl_2(CO)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ (△), $(\mu\text{-}2,3\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2^{2+}$ (□), and $(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]$ (○).

For the complexes that do not contain carbonyl ligands, the energy of the visible band is practically unaffected by changing solvent, whereas for **5** and **6** a slight red shift is observed on decreasing solvent polarity. A plot of the energy of the visible band vs the solvent parameter $E_{\bullet MLCT}$[29] is shown in Figure 4.

No luminescence was observed in the region 480–800 nm for all the complexes both in AN fluid solution at room temperature and in a BN rigid matrix at 77 K.

The monometallic and symmetric bimetallic complexes containing only $Ru(C_6H_6)Cl$ moieties are not photosensitive even on prolonged irradiation. By contrast, the bimetallic complexes containing $Ru(CO)_2Cl_2$ moieties are strongly photosensitive; their AN solutions are rapidly decomposed even on exposure to laboratory light. The changes in absorption spectrum caused by the photoreaction are shown in Figure 5 for the heteroligated Ru dimer containing 2,3-dpp. The quantum yields for reactant disappearance (measured spectrophotochemically) are independent of the excitation energy in the wavelength range used for irradiation (405–505 nm) and are reported in Table III.

Discussion

The photophysical and photochemical properties of transition-metal complexes are usually discussed by assuming that each spectroscopic state can be described by a localized electronic configuration.[30] Within this approach, the electronic transitions and excited states of coordination compounds can be classified as metal centered (MC), charge transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT), and ligand centered (LC). Extensive studies in the last 20 years have shown that such an approximate treatment is appropriate in most cases.[4,31,32]

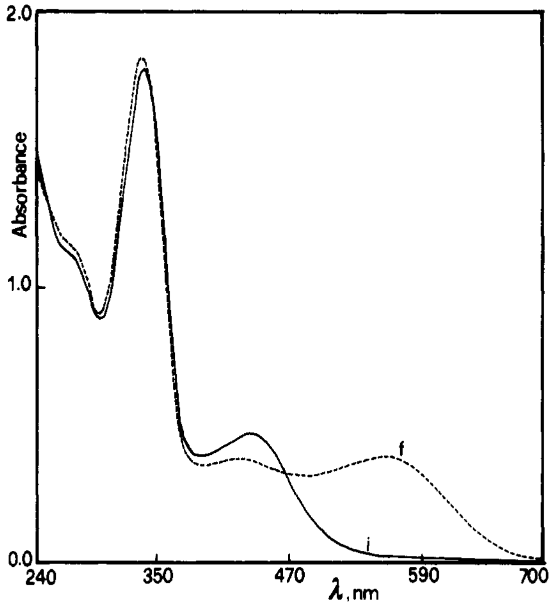


Figure 5. Spectral changes on irradiation of $Cl_2(CO)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(\eta^6\text{-}C_6H_6)Cl^+$ in AN solution with 405-nm light: i = initial spectrum; f = constant spectrum at the end of the irradiation ($t \geq 20$ min).

Absorption Spectra. The similarity of the intense bands at about 350 nm with the bands of the free ligands[17] allows us to assign such bands to metal-perturbed LC transitions. A red shift of the energy maximum of the LC bands of the complexes compared to those of the free ligands is a common behavior.[30]

The bands in the visible region can be attributed to Ru → dpp charge-transfer transitions for the following reasons: (i) their extinction coefficients are moderately high[4,33] (Table III); (ii) the bands of the complexes containing 2,5-dpp lie at lower energy than the corresponding bands of the complexes containing 2,3-dpp, as expected on the basis of the different oxidizing properties of the two isomeric ligands;[34] (iii) the bands move to the red on passing from the mono- to the dinuclear complexes, as expected for MLCT bands involving bridging ligands.[4,6,8,9,17,18,35]

In the parent homoligated dinuclear complexes **3**, **4**, **9**, and **10**, the (two equivalent) Ru → dpp CT transitions lie at high energy for **9** and **10** compared to **3** and **4** because of the presence in **9** and **10** of the two (strongly electronic withdrawing) carbonyl ligands (see Table III). In the heteroligated dinuclear complexes **5** and **6**, the two fragments are not equivalent, so that in each case two distinct Ru → dpp CT transitions are expected, with that which involves the $Ru(CO)_2$ fragment at higher energy. The absorption spectra of **5** and **6**, however, could not be the mere superimposition of the two $Cl_2(CO)_2Ru(dpp)$ and $Cl(\eta^6\text{-}C_6H_6)Ru(dpp)$ moieties, because the "chromophoric" units are bound to (and therefore perturbed by) different metal fragments. Similar results have been recently obtained by Zulu and Lees on the absorption properties of a ligand-bridged heterodinuclear complex.[36] In our case, unfortunately, the parent CT bands are not sufficiently separated to allow any speculation in this regard. The difference in extinction coefficients of the LC transition between the calculated and experimental spectra of **5** and **6** (Figure 3) can be attributed to the reduced symmetry of the bridging ligands in the heteroligated Ru dimers, which can reduce the overlap between the π and π* orbitals of the ligands.

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(27) A similar method was used for the analysis of ligand–ligand interactions in tris-heteroleptic (polypyridine)ruthenium(II) complexes.[28]

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(34) For each couple of isomeric complexes, the bands in the visible region are observed at higher energies for the 2,3-dpp complexes with respect to the 2,5-dpp isomers, as expected for MLCT transitions involving such ligands: in fact, although electrochemical measurements on the new complexes are not available, reduction potentials of $Ru(2,3\text{-dpp})(CO)_2Cl_2$, $Ru(2,5\text{-dpp})(CO)_2Cl_2$, and their symmetric dimers[17] have shown that 2,5-dpp is easier to reduce than 2,3-dpp in analogous complexes.

(35) On the contrary, MLCT bands involving peripheral ligands are usually blue-shifted on passing from mono- to dinuclear complexes.[11,13,18]

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The energies of MLCT bands of metal complexes containing both polypyridine and carbonyl ligands are known to be strongly dependent on the solvent.[20,29,37,38] Several solvent parameters have been used to correlate the energy displacement of such bands.[39] One of the most useful is the $E_{\cdot\mathrm{MLCT}}$ parameter introduced by Manuta and Lees,[29] based on changes in dipole moment and molecular polarizability between ground and excited states. The ruthenium(II) complexes in which no carbonyl ligand is present do not show any solvatochromic effect (Figure 4), as expected because of the small polar character of the CT transition,[40] whereas a linear dependence on solvent polarity is found for the energies of the bands of $Ru(dpp)(CO_2)Cl_2$ and related complexes.[17] In light of such results, it could be expected that only one of the two MLCT bands that are present in **5** and **6** might be sensitive to the $E_{\cdot\mathrm{MLCT}}$ parameter. The observed behavior of **5** and **6** (Figure 4) would be consistent with such an expectation. For high-polarity solvents, the observed band maxima can be due to the non-solvent-sensitive $Cl(C_6H_6)Ru \rightarrow$ dpp CT transition, whereas, in low-polarity solvents, the $Cl_2(CO)_2Ru \rightarrow$ dpp CT transition is displaced at lower energies and the band maxima become solvent sensitive.

Photochemical Behavior. Photochemical reactivity is a well-known property of ruthenium(II) polypyridine carbonyl complexes.[17,40-43] The photoreaction originates from an MC excited state, populated by thermal activation from the lowest lying excited state, and leads to the release of a carbonyl ligand with formation of solvated species. Complexes **5** and **6** are strongly photoreactive, and the changes in their electronic absorption spectra upon irradiation are in agreement with such a reaction. The MLCT bands are displaced toward lower energies because the metal becomes easier to reduce, and the LC absorption bands move slightly to the blue, as previously observed for similar complexes[17,41] (see Figure 5). However, the quantum yields for the photoreaction are noticeably different between **5** and **6**. To account for such a difference, one can consider that in polynuclear complexes coupling between excited states involving different metal centers is common. For example, luminescence in polynuclear complexes can be quenched by intramolecular energy- or electron-transfer processes between metal fragments.[7,12-14] This is the case for the luminescence from $Ru(bpy)_2(CN)_2$, which is completely quenched via intramolecular energy transfer from the triplet Ru → bpy CT excited state to the doublet state of $Cr(CN)_6{}^{3-}$ in the dinuclear complex $(CN)Ru(bpy)_2(NC)Cr(CN)_5{}^{4-}$ and via intramolecular electron transfer in $(CN)Ru(bpy)_2(CN)Ru(NH_3)_5{}^{2+}$.[13] An important role in controlling the efficiency of the intramolecular energy- and/or electron-transfer quenching is played by the bridging ligands.[11,13,16,44,45] Another useful probe for intramolecular deactivation is the quenching of the photochemical reactivity exhibited by a (free) moiety.

The ligand field strength of CO is much higher than that of η^6-C_6H_6; therefore, in **5** and **6** two different MC excited states are present: one, presumably higher in energy, centered on the Ru ion of the $Ru(CO)_2Cl_2$ moiety (hereafter called Ru_a) and the other centered on the Ru ion of the $Ru(\eta^6\text{-}C_6H_6)Cl$ moiety (Ru_b). Apparently, the MC excited state of Ru_a, M_aC, is photoreactive, whereas the other one is not, and deactivation of the reactive excited state can thus occur by energy transfer (see Figure 6). Actually, the photoreactivity of the heteroligated 2,5-dpp-containing dimer (Φ = 0.01) is reduced of about 20 times with respect to the previously reported photoreactivity of the homoligated dinuclear complex $[Ru(CO)_2Cl_2]_2(\mu\text{-}2,5\text{-dpp})$ (Φ = 0.2),[17] whereas the photoreactivity of the dinuclear heteroligated 2,3-dpp derivative is practically unchanged with respect to its corresponding carbonyl homoligated complex (Φ = 0.2 for both the complexes).[17,46] Such different behaviors can be explained by considering that in these dinuclear systems electron exchange is the only mechanism available for intramolecular energy transfer,[47] and such a mechanism needs an effective orbital overlap.[47,48] In 2,5-dpp complexes the two ruthenium atoms are in the same plane with the bridging ligand, and the overlap between the orbitals involved in the intramolecular energy transfer could be enhanced by delocalization of metal orbitals on the bridging ligand orbitals. This delocalization is reduced in the complexes of 2,3-dpp, a ligand whose geometry is known to be nonplanar.[8] Therefore, intramolecular energy transfer could be a competitive deactivation process in the 2,5-dpp complex, whereas this could be prevented for the 2,3-dpp analogue. Inefficiency of the electronic factors would be the reason for the inefficiency of the process. Lack of intramolecular electron transfer in dinuclear metal complexes containing 2,3-dpp as bridging ligand was also found by Petersen for $Ru(bpy)_2(2,3\text{-dpp})Fe(CN)_4{}^+$,[49] in which the Ru → dpp MLCT luminescence is not quenched by the $Fe(CN)_4{}^-$ moiety, in spite of the fact that iron complexes are good quenchers of ruthenium polypyridine emission by bimolecular electron-transfer processes.[50]

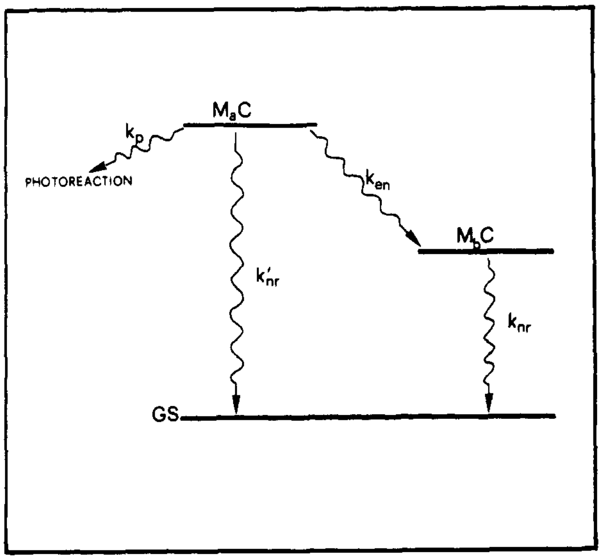

Figure 6. Qualitative schematic picture of the excited-state energy levels for the heteroligated dinuclear complexes. For clarity, only the states (and the transitions) necessary to the discussion of the photochemical results are shown. k_{en} and k_p are the rate constant for intramolecular energy transfer and photochemical reaction, respectively. M_aC refers to the metal-centered excited state involving the $Ru(CO)_2Cl_2$ fragment, and M_bC refers to the metal-centered excited state involving $Ru(\eta^6\text{-}C_6H_6)Cl$. GS is the ground state.

Conclusions

The heteroligated Ru(II) dinuclear N-heterocyclic complexes studied in this paper show some quite interesting properties. The presence of two different Ru(II) moieties bound together by polypyridine-like bridging ligands offers the possibility of two types

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(46) Actually, the photoreaction quantum yields for the homoligated dinuclear complexes were calculated in MeOH, whereas the solvent used for the heteroligated ones was AN. However, this does not affect the discussion on the differences between photochemical behavior of the two isomeric heteroligated complexes.

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of MLCT transitions with different properties (e.g., one of them is sensitive to solvent polarity, and the other one is practically insensitive) in the same complex.

The asymmetry in the bridging ligands induced by the different metal fragments affects some properties of the electronic transitions related to the dpp ligands (e.g., extinction coefficients of the LC bands).

The different geometry of the bridges appears to be a key factor for the communication between the metal moieties in the dinuclear complexes. Intramolecular energy transfer from the photoreactive Ru fragment containing carbonyls to the $Ru(\eta^6\text{-}C_6H_6)Cl$ fragment is apparently an effective deactivation process for the 2,5-dpp complex, whereas this is not the case for the 2,3-dpp isomer. As a consequence, complex **5** maintains a strong photoreactivity in solution, typical of ruthenium(II) polypyridine carbonyl complexes, whereas complex **6** exhibits a 20 times lower photoreactivity.

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Magnetic Circular Dichroism Spectra for the $Au_9(PPh_3)_8^{3+}$ Ion

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Electronic absorption and magnetic circular dichroism (MCD) spectra in the vis–UV range 1.66–3.60 μm^{-1} are reported for $[Au_9(PPh_3)_8]X_3$ ($X = NO_3^-, ClO_4^-$) salts in acetonitrile solution at room temperature. The MCD spectra consist of *B* terms, are generally better resolved, and show more distinct spectroscopic features than the absorption spectra. The spectra are interpreted in terms of D_{2h} skeletal geometry and MO's that are approximated by 6s orbitals on the Au atoms. The lowest energy excited configurations and states are assumed to be σ framework localized. MCD *B* term signs are determined from two-centered σ-orbital overlaps within the cluster complex ion.

Introduction

An interesting aspect of gold chemistry is the formation of homonuclear cluster complexes by gold in low valence states (between 0 and 1).[1] The best characterized examples are complexes that range in nuclearity from Au_4 to Au_{13} and contain tertiary phosphine ligands. These cluster complexes are unique in that they are held together by unsupported Au–Au interactions and feature centered and noncentered structures. The nature of the electronic structure and the Au–Au bonding in these complexes has been the subject of several studies ranging from simple Hückel MO schemes to more elaborate Dirac scattered-wave calculations that include relativistic effects.[2-5] However, there has been a notable lack of experimental corroboration for these electronic structural models. There have been some electronic spectra reported for several cluster complexes both from solution measurements and from diffuse reflectance on solid compounds,[1,4a] but these spectra have not yet been interpreted in detail. The lack of interpretation may be partly due to the large number of possible excited states that can be visualized as the nuclearity of the complex increases. This situation is unfortunate because electronic spectroscopic data have value in providing an experimental basis for electronic structure and in providing information about low-energy excited states and the empty MO's of the complex under study. In order to address this problem of spectral interpretation, we have undertaken a study of the electronic absorption spectra of representative gold cluster complexes aided by magnetic circular dichroism (MCD) spectra. In this paper the absorption and MCD spectra for the $Au_9(PPh_3)_8^{3+}$ ion in acetonitrile solution are reported and are interpreted within an MO framework that is limited to σ cluster framework orbitals.

Experimental Section

Octakis(triphenylphosphine)enneagold trinitrate, $[Au_9(PPh_3)_8](NO_3)_3$, was prepared from $Au(PPh_3)(NO_3)$[6] by reduction with $NaBH_4$ in ethanol solution according to the literature method.[7] The dark green solid, which was recrystallized from CH_3CN, gave satisfactory elemental analysis and had a UV-vis spectrum in ethanol that compared favorably with the published spectrum.[1,4a] The perchlorate salt was prepared by dissolving the nitrate salt in ethanol and adding a concentrated solution of $LiClO_4$.[7] The green precipitate gave satisfactory analysis for $[Au_9(PPh_3)_8](ClO_4)_3$. *Caution: potential perchlorate hazard!*

Table I. Spectral data for $[Au_9(PPh_3)_8](NO_3)_3$ in Acetonitrile

	absorption			MCD	
band no.	$\bar{\nu}$, μm^{-1}	λ, nm	ϵ, $M^{-1}\,cm^{-1}$	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, $(M\,cm\,T)^{-1}$
				1.83	−0.12
				2.10	+0.91
I	2.26	443	16200	2.21	+0.62[a]
				2.37	−0.76[a]
II	2.64	379	26000[a]	2.60	−4.17
III	2.90	345	39000[a]	2.86	−0.93
IV	3.19	314	62000	3.25	−7.84
				3.40	−3.84[a]

[a] Shoulder.

Absorption spectra were measured for acetonitrile solutions by means of a Cary 1501 spectrophotometer. Absorption and MCD spectra were recorded simultaneously and synchronously along the same light path by means of a spectrometer described previously.[8] A magnetic field of 7.0 T was obtained from a superconducting magnet system (Oxford Instruments SM2-7, fitted with a room-temperature bore tube). Spectral grade acetonitrile was used throughout, and all spectra were corrected for solvent blank. Because of the strong absorption due to the phenyl substituents and, in the case of the nitrate salt, the nitrate ion, spectral measurements were limited to energies below 3.6 μm^{-1}. Below this energy the ClO_4^- and NO_3^- salts gave virtually identical absorption and MCD spectra and obeyed Beer's law to within experimental error in the concentration range 10^{-4}–10^{-5} M. The solutions neither were light sensitive nor exhibited any changes during the time required to make the spectral measurements (typically 1.5 h).

Results and Discussion

The electronic absorption and MCD spectra for $[Au_9(PPh_3)_8](NO_3)_3$ in acetonitrile solution at room temperature are presented in Figure 1, while quantitative spectral data are collected in Table I. The MCD spectrum is generally better resolved and reveals more features than the absorption spectrum. For example,

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