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Syntheses, Absorption Spectra, Luminescence Properties, and Electrochemical Behavior of Mono- and Binuclear Ruthenium(II) Complexes of Isomeric Bis(2-pyridyl)pyrazines

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The complexes Ru(2,3-dpp)$(CO)_2Cl_2$, Ru(2,5-dpp)$(CO)_2Cl_2$, (μ-2,3-dpp)$[Ru(CO)_2Cl_2]_2$, and (μ-2,5-dpp)$[Ru(CO)_2Cl_2]_2$, where dpp is bis(2-pyridyl)pyrazine, have been synthesized and characterized. The absorption spectra (including their solvent dependence), luminescence spectra, luminescence decay, electrochemical behavior, and photochemical reactivity of the cited complexes have been investigated. For comparison purposes, the properties of the free ligands have also been studied. The absorption spectra of the complexes show ligand-centered (LC) bands in the UV region and broad metal-to-ligand (Ru → dpp) charge-transfer (MLCT) bands in the visible region. The latter bands are red-shifted in passing from the mono- to the bimetallic complexes and on decreasing solvent polarity. The luminescence spectrum exhibited by each complex in rigid matrix at 77 K is similar in energy and shape to that exhibited by the correspondent free ligand. No correlation is observed between the energies of the MLCT absorption bands and the energies of the luminescence bands. On the basis of these results and of the relatively long luminescence lifetimes (10^{-4}–10^{-5} s in butyronitrile at 77 K), emission is assigned to a ^{3}LC excited state. The Ru(2,5-dpp)$(CO)_2Cl_2$ complex is luminescent also in fluid solution at room temperature. Under such conditions, the emission appears to be CT in nature. Each complex undergoes irreversible oxidation near +2 V, not occurring for the free ligand, and a reversible one-electron reduction at potentials less negative than those of the free ligand reduction. The reduction potentials of the bimetallic complexes (–0.620 and –0.380 V for the 2,3- and 2,5-dpp complexes, respectively) are less negative than those of the corresponding monometallic species (–1.040 and –0.930 V), in good correlation with the energies of the MLCT absorption bands. All the complexes examined are strongly photosensitive in fluid solution, with release of a CO ligand per metal unit.

Introduction

Ruthenium(II)–polypyridine complexes have been the object of many investigations in the last 10 years because they exhibit a unique combination of chemical and spectroscopic properties. Such complexes are extensively used as (i) photoluminescent compounds, (ii) excited-state reactants in energy- and electron-transfer processes, (iii) excited-state products in chemiluminescent and electrochemiluminescent reactions, and (iv) mediators in the interconversion of light and chemical energy.[2-4] In the frame of the growing interest in the photochemistry and luminescence of supramolecular systems,[5,6] several binuclear and polynuclear ruthenium complexes have also been prepared and studied.[7-24]

In this paper we report the results of an investigation on mono- and binuclear Ru(II) complexes that contain the $Ru(CO)_2Cl_2$ moiety and the 2,3- or 2,5-isomers of the bridging ligand bis(2-pyridyl)pyrazine (Figure 1). We have examined the absorption spectra (including their solvent dependence), luminescence spectra, luminescence decay, electrochemical behavior, and photochemical reactivity. For comparison purposes, some properties of the free ligands have also been investigated.

Experimental Section

Materials and Methods. The bridging ligands 2,3-bis(2-pyridyl)pyrazine (2,3-dpp)[25] and 2,5-bis(2-pyridyl)pyrazine (2,5-dpp)[26] and the precursor complex $[Ru(CO)_2Cl_2]_x$[27] were prepared according to literature methods. The following solvents of the best commercial grade were used as supplied: acetonitrile (AN), tetrahydrofuran (THF), acetone (AC), dimethylformamide (DMF), methanol (CH_3OH), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrachloromethane (CCl_4). Freshly distilled butyronitrile (BN) was used for the low-temperature luminescence studies, and purified and dried AN (polarographic grade) was used for the electrochemical measurements.

The absorption spectra in the UV and visible regions were recorded with a Kontron Uvicon 860 spectrophotometer. For infrared spectra, Perkin-Elmer 682 and 1330 spectrometers were used. ^{1}H NMR spectra were obtained by using a Bruker AW 300 spectrometer. Elemental analyses were performed on a Carlo Erba 1106 apparatus. Uncorrected

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Table I. Selected IR Absorption Maxima[a]

complex	ν(CO)	ν(C═C) and ν(C═N)	ν(Ru—Cl)
$Ru(2,3\text{-dpp})(CO)_2Cl_2$	2060, 1995	1608, 1590, 1576, 1554	354
$(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]_2$	2065, 2010	1596	357
$Ru(2,5\text{-dpp})(CO)_2Cl_2$	2087, 2023	1608, 1590, 1570, 1562	340
$(\mu\text{-}2,5\text{-dpp})[Ru(CO)_2Cl_2]_2$	2085, 2025	1610	342
Ru(dppi)-*cis*-$(CO)_2$-*trans*-Cl_2[b]	2072, 2003	1604, 1591, 1563, 1551	355
Ru(dppi)-*cis*-$(CO)_2$-*cis*-Cl_2[b]	2062, 1995	1600, 1586, 1566, 1546	339, 310

[a] cm^{-1}; KBr pellets. [b] From ref 8a; dppi indicates 3,6-bis(2-pyridyl)pyridazine.

Table II. 300-MHz NMR Spectral Data (δ, ppm) Taken in DMSO-d_6[a]

complex or ligand	$H_{6'}/H_{6''}$[b]	$H_{5'}/H_{5''}$	$H_{4'}/H_{4''}$	$H_{3'}/H_{3''}$	H_x/H_6[c]
2,3-dpp	8.26 d	7.31 m	7.90 m	7.87 d	8.79 s
$Ru(2,3\text{-dpp})(CO)_2Cl_2$	9.26 d/8.62 m	7.77 m/7.67 m	8.18 m/7.98 m	8.09 m/7.12 m	9.42 d/9.26 d
$(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]_2$	9.45 s	7.99 m	8.24 m	8.44 d	9.60 s
2,5-dpp	8.78 d	7.55 m	8.03 m	8.42 d	9.62 s
$Ru(2,5\text{-dpp})(CO)_2Cl_2$	9.32 d/8.89 d	7.94 m/7.68 m	8.47 m/8.13 m	9.10 d/8.51 d	10.14 d/9.94 d

[a] $(\mu\text{-}2,5\text{-dpp})[Ru(CO)_2Cl_2]_2$ is unstable in DMSO. [b] Hydrogen numbers refer to positions quoted in Figure 1. In mononuclear complexes H_6 is the one near to the metal-ligating pyridyl nitrogen. [c] $x \equiv 3$ for 2,5-dpp; $x \equiv 5$ for 2,3-dpp.

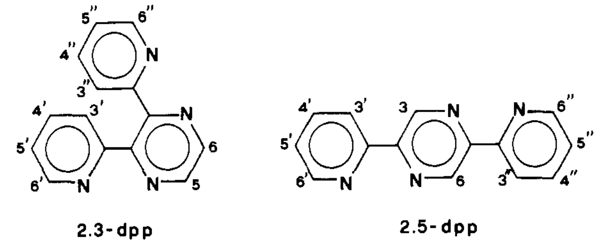

Figure 1. Structural formulas of the 2,3- and 2,5-bis(2-pyridyl)pyrazine bridging ligands.

luminescence spectra were obtained with a Perkin-Elmer LS-5 spectrofluorometer equipped with a Hamamatsu R 928 tube. Emission lifetime measurements were carried out by using a JK System 2000 neodynium YAG DPLY 4 laser as excitation source and a Tektronic 7612 digitizer for data acquisition.

The photochemical behavior was studied by irradiating the solutions with a tungsten lamp equipped with an interference filter centered at 410 nm. The light intensity incident to the reaction cell (1.5×10^{-7} einstein/min) was measured with a ferrioxalate actinometer.[28]

Electrochemical measurements were carried out with an Amel 448/XA oscillographic polarograph. The electrodes used were a Pt electrode and a hanging mercury electrode. Tetraethylammonium perchlorate (polarographic grade) was used as supporting electrolyte. For reversible processes, half-wave potentials (vs SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks (~60 mV) and the equal intensity of the cathodic and anodic currents.

When necessary, the solutions were deaerated by bubbling nitrogen.

Synthesis of Mononuclear Complexes. The procedure was similar to that followed for the analogous 3,6-bis(2-pyridyl)pyridazine derivatives.[8c] In a typical preparation, a *light-protected* suspension of polymeric $Ru(CO)_2Cl_2$ (300 mg, 1.31 mmol) and the appropriate ligand (molar ratio 1:1) in 25 mL of methanol were stirred at 50 °C for 24 h in inert atmosphere. The yellow microcrystalline precipitate was filtered off, washed with methanol and diethyl ether, and vacuum-dried. Yields ranged from 80 to 70%. In the case of 2,5-dpp, the crude precipitate contained some amount of the binuclear species that was removed by continuous extraction with dichloromethane. Anal. Calcd for $Ru(2,n\text{-dpp})(CO)_2Cl_2$ ($C_{16}H_{10}Cl_2N_4O_2Ru$): C, 41.57; H, 2.18; N, 12.12. Found for $n = 3$: C, 41.24; H, 2.03; N, 11.81. Found for $n = 5$: C, 40.90; H, 2.20; N, 11.90.

Synthesis of Binuclear Complexes. The starting material was produced by refluxing the polymeric precursor in acetonitrile for 30 min under nitrogen and then drying the solution; it was isolated, after several washings with diethyl ether, as a yellow powder having an IR spectrum and an elemental composition consistent with a species containing 2–3 equiv of acetonitrile (depending on runnings)/equiv of metal. When this material was reacted with the monometallic complexes (1:1) in methanol, with the same procedure as above, the binuclear species were obtained (≥90%) and isolated as red-brown (2,3-dpp) or yellow (2,5-dpp) powders.

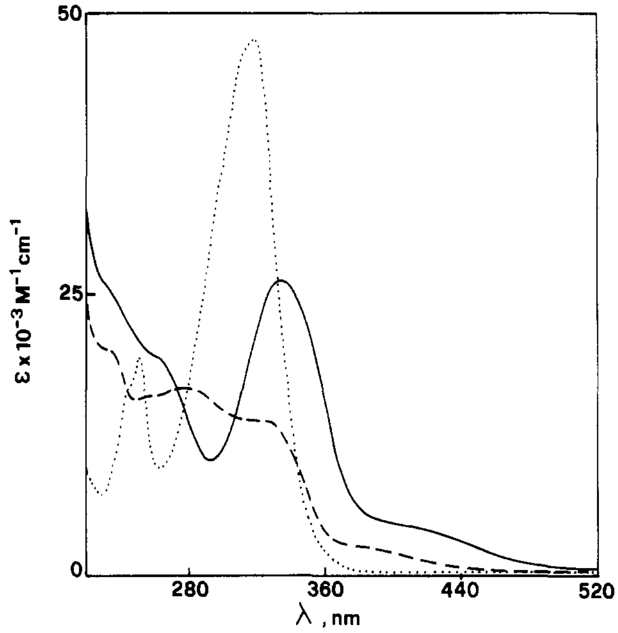

Figure 2. Absorption spectra of 2,3-dpp (···), $Ru(2,3\text{-dpp})(CO)_2Cl_2$ (- - -), and $(\mu\text{-}2,3\text{-dpp})[Ru(CO)_2Cl_2]_2$ (—) in AN solution.

Anal. Calcd for $(\mu\text{-}2,n\text{-dpp})[Ru(CO)_2Cl_2]_2$ ($C_{18}H_{10}Cl_4N_4O_4Ru_2$): C, 31.32; H, 1.46; N, 8.12. Found for $n = 3$: C, 31.32; H, 1.39; N, 7.81. Found for $n = 5$: C, 30.42; H, 1.41; N, 7.80.

Results

The reactions between the bridging ligands and polymeric $Ru(CO)_2Cl_2$, carried on with a procedure similar to that reported for the analogous complexes of 3,6-bis(2-pyridyl)pyridazine,[8a] easily afforded monometallic derivatives. The same reactions repeated using a half equiv of ligand with respect to the metallic precursor led to poor yields in bimetallic species. These were much better synthesized by reacting, in the same conditions, the mononuclear products with an adduct of dicarbonyldichlororuthenium with acetonitrile. The IR (Table I) and NMR (Table II) absorption frequencies, compared with those of the structurally characterized[8c] *cis*-dicarbonyl-*trans*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II) and *cis*-dicarbonyl-*cis*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II), seem to account for a *cis*-dicarbonyl–*trans*-dichloro arrangement around the six-coordinated metal both in the mono- and in the binuclear derivatives.

The absorption spectra in AN solution of the 2,3-dpp ligand and its monometallic and dimetallic complexes are shown in Figure 2, and those of 2,5-dpp and its complexes are shown in Figure 3. The absorption spectra of the free ligands are strongly influenced by protonation. Addition of H_2SO_4 to AN solutions

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Table III. Absorption, Luminescence, Photochemical, and Electrochemical Data

complex or ligand	abs[a] E, cm^{-1} (ϵ, M^{-1} cm^{-1})	lumin E, cm^{-1} [b] (τ, ms)[c]	electrochem[d] E_{ox}, V	electrochem[d] E_{red}, V	photochem Φ[e]
2,3-dpp	31 400 (48 000)	20 000 (77)		−1.630	
Ru(2,3-dpp)(CO)$_2$Cl$_2$	26 000 (2500)	19 600 (0.158)	+1.90	−1.040	0.65
(μ-2,3-dpp)[Ru(CO)$_2$Cl$_2$]$_2$	24 400 (4500)	18 000 (0.146)	+2.00	−0.620	0.20
2,5-dpp	31 400 (37 000)	20 050 (102)		−1.680	
Ru(2,5-dpp)(CO)$_2$Cl$_2$[f]	24 700 (1600)	19 300 (0.166)	+1.86	−0.930	0.60
(μ-2,5-dpp)[Ru(CO)$_2$Cl$_2$]$_2$	22 300 (4600)	18 550 (0.080)	+1.92	−0.380	0.20

[a] Lowest energy maximum or shoulder, AN solution, 293 K. For the entire spectra, see Figures 2 and 3. [b] Energy of the highest energy feature of the emission band; BN matrix; 77 K. For the entire spectra, see Figures 5 and 6. [c] Emission lifetime, BN matrix; estimated error ≤10%. [d] First oxidation (irreversible) and reduction (reversible) waves, AN solution, 293 K; other reduction waves were observed at more negative potentials; see text. Estimated error on redox potentials is 10 mV. [e] Quantum yields for disappearance of the reactants; estimated error ±10%. [f] Luminescence was also observed at room temperature, with E_{max} = 20 000 cm^{-1} and τ < 30 ns in AN solution.

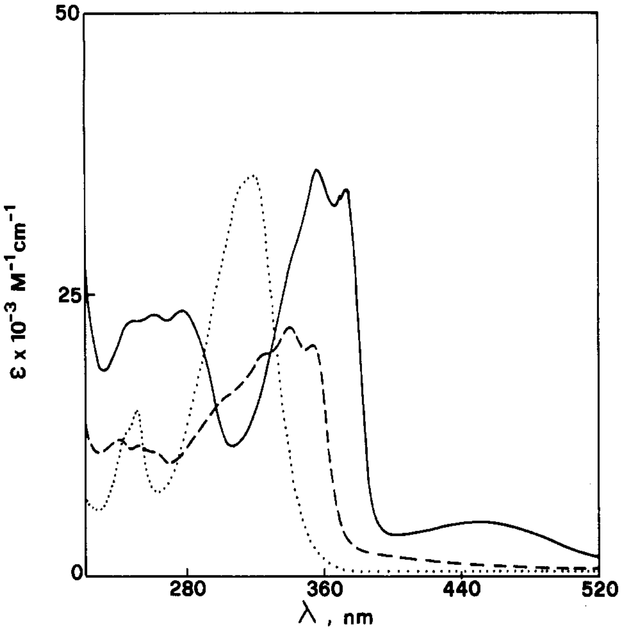

Figure 3. Absorption spectra of 2,5-dpp (···), Ru(2,5-dpp)(CO)$_2$Cl$_2$ (- - -), and (μ-2,5-dpp)[Ru(CO)$_2$Cl$_2$]$_2$ (—) in AN solution.

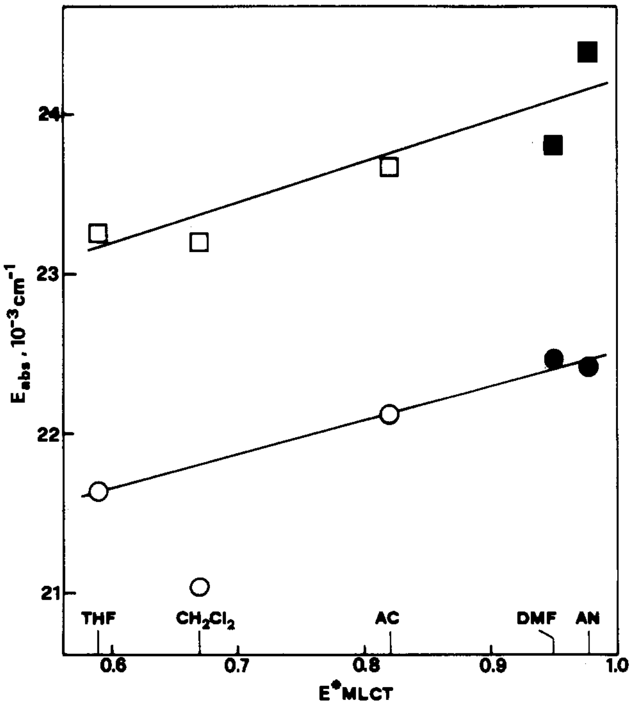

Figure 4. Plot of the energy of the MLCT band in the visible region vs the E^*_{MLCT} solvent parameter[27] for (μ-2,3-dpp)[Ru(CO)$_2$Cl$_2$]$_2$ (circles) and (μ-2,5-dpp)[Ru(CO)$_2$Cl$_2$]$_2$ (squares). Empty symbols refer to band maxima, and solid symbols, to shoulders. The solvents used are depicted in the figure (for abbreviations, see text).

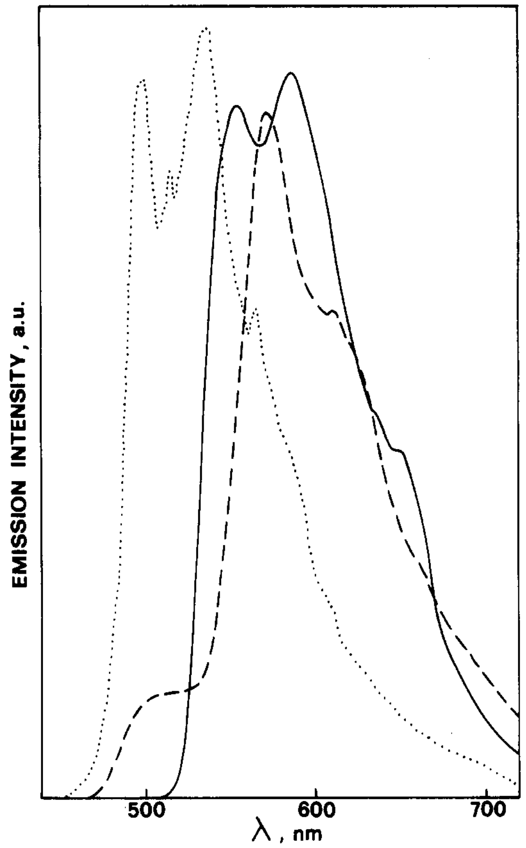

Figure 5. Emission spectra of 2,3-dpp (···), Ru(2,3-dpp)(CO)$_2$Cl$_2$ (- - -), and (μ-2,3-dpp)[Ru(CO)$_2$Cl$_2$]$_2$ (—) in BN at 77 K.

caused a red shift (~1800 cm^{-1}) of both the absorption bands and some splitting in the higher energy one. A displacement toward the red region on acidification was also observed for the bands of the monomeric complexes, whereas the spectra of the dimeric complexes were unaffected. The absorption bands of the dimeric and monomeric complexes move to the blue region with increasing solvent polarity. This effect was particularly noticeable for the visible portion of the absorption spectra, as shown in Figure 4, where the energy of the maximum (or shoulder) shown in that region by the bimetallic complexes is plotted vs the E^*_{MLCT} solvent parameter[29-31] (see Discussion). For the monometallic complexes a qualitatively similar behavior is observed, but a plot is difficult to make because the visible absorption is largely hidden by the more intense bands at higher energy (see Figures 2 and 3). The use of solvents of low E^*_{MLCT} was precluded because of solubility reasons.

The luminescence spectra of the free ligands and of their monometallic and bimetallic complexes in butyronitrile at 77 K

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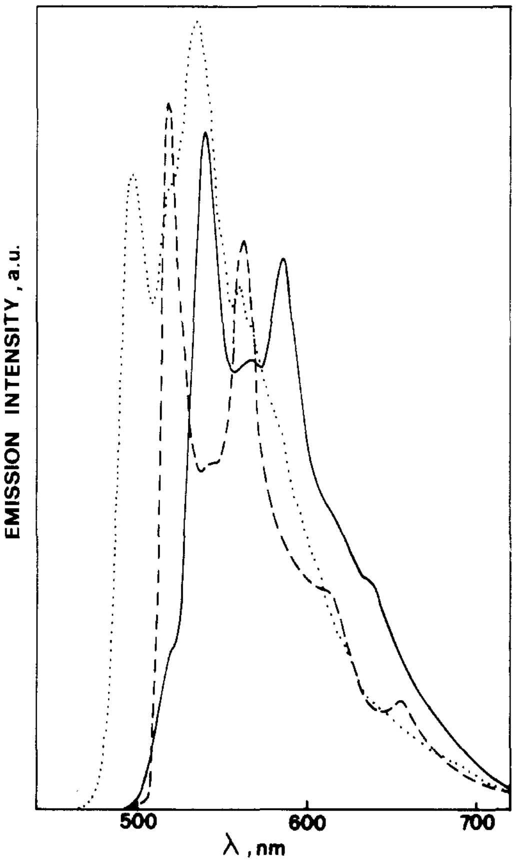

Figure 6. Emission spectra of 2,5-dpp (···), Ru(2,5-dpp)(CO)$_2$Cl$_2$ (- - -), and (μ-2,5-dpp)[Ru(CO)$_2$Cl$_2$]$_2$ (—) in BN at 77 K.

are shown in Figures 5 and 6. The emission bands of the free ligands moved to the blue region (~700 cm^{-1}) on acidification of the glassy BN solution whereas the spectra of the complexes were almost unchanged. The bands of the complexes were slightly displaced to the red region on decreasing solvent polarity (e.g., 600 cm^{-1} in going from BN to CH$_2$Cl$_2$ for Ru(2,5-dpp)(CO)$_2$Cl$_2$). In all cases, the luminescence decay was strictly exponential, with lifetimes around 10^{-1} s for the free ligands and in the 10^{-5}–10^{-4}-s range for the complexes (Table III). Some solvent dependence was also observed for the luminescence lifetimes. At room temperature, only Ru(2,5-dpp)(CO)$_2$Cl$_2$ was luminescent, with E_{max} = 20 000 cm^{-1} τ < 30 ns in deaerated AN solution. This band moves very slightly to the red region on decreasing solvent polarity (E_{max} = 19 300 cm^{-1} in CCl$_4$).

All the complexes examined were strongly photosensitive. Even exposure to laboratory light caused rapid photodecomposition. The spectral changes obtained for Ru(2,5-dpp)(CO)$_2$Cl$_2$ in CH$_3$OH solution are shown in Figure 7. A similar behavior was observed for each complex in each solvent used. Infrared spectra of irradiated solutions showed strong changes in the region of CO stretching. For example (Figure 7, inset), the intensity of the two bands at 2070 and 2010 cm^{-1} of Ru(2,5-dpp)(CO)$_2$Cl$_2$ decreased on irradiation while a new band at 1930 cm^{-1} appeared. Prolonged irradiation led to practically photostable compounds showing an absorption maximum in the visible region above 500 nm and only one band in the CO stretching region. The quantum yields of the photoreactions in deaerated methanol solutions, measured from the increase in absorbance at 510 nm, are reported in Table III.

No oxidation wave was observed for the free ligands in AN solution up to 2 V. On reduction, both ligands exhibited two reversible waves (−1.630 and −1.860 V for 2,3-dpp and −1.680 and −2.080 V for 2,5-dpp). Irreversible waves were also observed at about −2.6 V for 2,3-dpp and about −2.5 V for 2,5-dpp. The monometallic and bimetallic complexes exhibited an irreversible oxidation wave around +2 V (Table III). On reduction, each complex showed a one-electron reversible wave (Table III), followed by several irreversible waves.

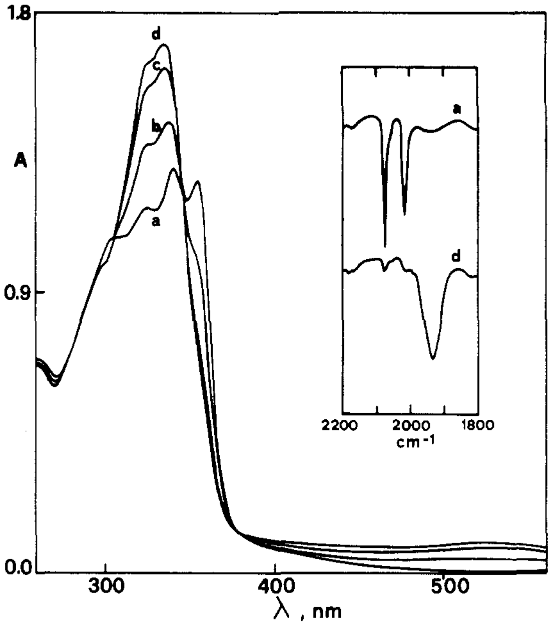

Figure 7. Spectral changes in the UV, visible, and (inset) IR regions on irradiation of Ru(2,5-dpp)(CO)$_2$Cl$_2$ solutions: (a) spectra before irradiation; (d) constant spectra at the end of the irradiation. The solvents are CH$_3$OH for the electronic spectra and CHCl$_3$ for the vibrational spectra. The excitation wavelength is 410 nm.

Discussion

Ruthenium(II)–polypyridine complexes are usually luminescent,[4] while Ru(II) complexes containing CO ligands are usually photosensitive.[4,32-35] The ruthenium complexes studied in this paper contain both polypyridine and carbonyl ligands and exhibit both luminescence and photoreactivity. The use of bridging polypyridine ligands has also allowed us to compare the behavior of monometallic and bimetallic complexes, and the study of the free ligands has provided additional information on the factors that govern the various properties.

Absorption Spectra. Besides metal-perturbed ligand-centered bands in the UV region, the complexes exhibit (Figures 2 and 3) a broad, moderately intense absorption above 390 nm that can be assigned to metal-to-ligand charge-transfer (MLCT) transitions from Ru to dpp. Such an assignment is based on the following observations: (i) there is a linear correlation between the energy of absorption maxima (or shoulders) and the first (ligand-centered; see later) reduction potential (Figure 8), as expected for MLCT transitions;[4,36,37] (ii) the bands are sensitive to solvent polarity (Figure 4);[4,29-31] (iii) on the basis of the absorption spectra of Ru(bpy)$_3$$^{2+}$ and Ru(bpy)$_2$(CO)Cl$^+$,[4,33,35] the Ru → dpp CT band of the Ru(dpp)(CO)$_2$Cl$_2$ complexes is expected to lie at an energy higher than that of Ru(dpp)$_3$$^{2+}$, whose λ_{max} is at 455 nm;[19] (iv) the energy of the band moves to the red region in going from the mono- to the binuclear complex (Table III), as it happens for the CT bands of other mono- and binuclear ruthenium(II)–polypyridine complexes;[12-14,18] (v) the extinction coefficients are in the expected range for ruthenium → polypyridine CT bands.[4]

The strong solvatochromism of the MLCT bands of metal complexes containing polypyridine and carbonyl ligands has been

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(37) Usually a better correlation is obtained between E_{max} of the MLCT bands and $\Delta E_{1/2}$, where the latter quantity is the difference between the first oxidation potential and the first reduction potential of the complex.[4,36] Since the oxidation potentials are irreversible for our complexes, we have used only the reduction potentials.

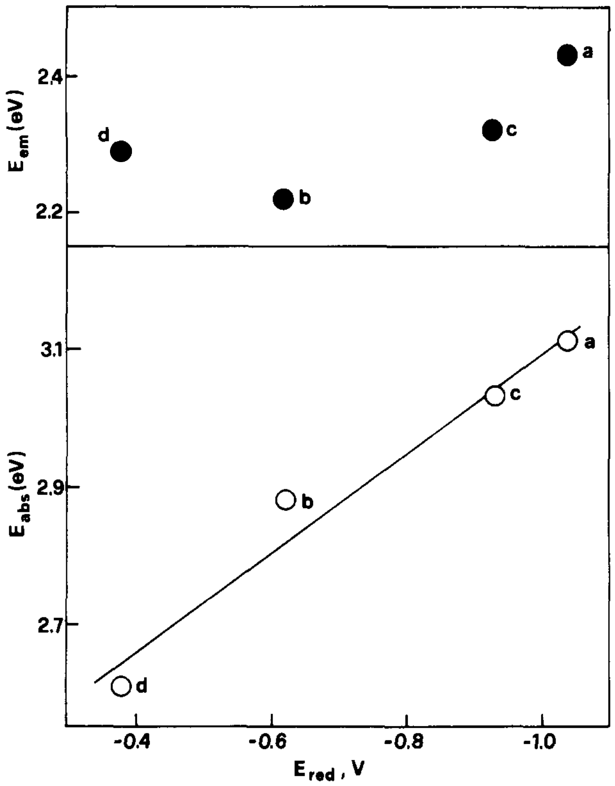

Figure 8. Correlations between absorption and emission energies with the first reduction potential E_{red}: (a) Ru(2,3-dpp)$(CO)_2Cl_2$; (b) (μ-2,3-dpp)$[Ru(CO)_2Cl_2]$; (c) Ru(2,5-dpp)$(CO)_2Cl_2$; (d) (μ-2,5-dpp)$[Ru(CO)_2Cl_2]_2$. The best fitting parameter for the linear relationship between E_{abs} and E_{red} is 0.97, and the slope is 0.75.

observed and discussed by various authors.[29-31] Several solvent parameters can be used to correlate the energy displacement of the band.[38-41] Extension of the correlation to different classes of solvents usually requires correction factors. On the basis of the results obtained for a family of M(diimine)$(CO)_4$ complexes (M = Cr, Mo, W), Manuta and Lees[29] have recently introduced a solvent parameter E^*_{MLCT}, defined between 0.00 (isooctane) and 1.00 (dimethyl sulfoxide). Kaim and Kohlmann[30] and Ruminski et al.[31] have shown that the E^*_{MLCT} parameter is fully satisfactory to correlate the solvent sensitivity of mono- and binuclear complexes containing polypyridine and carbonyl ligands. In the latter studies, however, chlorinated and protic solvents were excluded. Our results show that binuclear complexes (Figure 4) exhibit the expected trend, but (μ-2,5-dpp)$[Ru(CO)_2Cl_2]_2$ is clearly illbehaved when the solvent is CH_2Cl_2. Approximate values for the solvent sensitivity parameter B^{29} obtained from the plots (excluding CH_2Cl_2 in both cases) are 2100 and 2300, in the expected range for complexes containing only two carbonyl ligands per metal unit.[30] Solvent dependence of the MLCT absorptions is usually attributed to changes in dipole moment between ground and excited state. To explain solvent dependence in centrosymmetric complexes where excitation could not change the dipole moment, changes in molecular polarizability have been invoked by Kaim and Kohlmann.[30]

Luminescence. At 77 K, the 2,3-dpp and 2,5-dpp free ligands exhibit structured luminescence bands around 20 000 cm^{-1} with lifetimes in the range of 10^{-1} s (Table III), as expected for emission from the lowest triplet of polypyridine-type molecules.[42] The complexes examined show a structured band in the same spectral region, with a lifetime of 10^{-4}–10^{-5} s. In principle, the luminescence of metal complexes can be due to metal-centered (MC), ligand-centered (LC), or charge-transfer (CT) excited states.[4,43] Assignment of the observed bands to MC excited states can be excluded because of the presence of a vibrational structure with a progression of $\sim$1300 cm^{-1}, typical of the aromatic ligands.[4] Since the emission energies do not correlate with the reduction potentials and the CT absorption energies (Figure 8), a CT assignment can be excluded. Assignment to LC, metal-perturbed transitions is very plausible because of (i) the similar band shape and the very small red shift compared with the emission of the free ligands and (ii) the relatively long excited-state lifetime, typical of other metal-perturbed LC emissions.[42,44]

In fluid solution at room temperature Ru(2,5-dpp)$(CO)_2Cl_2$ exhibits a weak luminescence with a very short lifetime (τ < 30 ns) and the other complexes are not luminescent at all, showing that a new deactivation channel becomes available on increasing temperature. We believe that this new channel corresponds to a thermally activated crossing to a closely lying, distorted ^{3}MC excited state that undergoes fast radiationless decay to the ground state and/or chemical reaction (see below).

The weak emission band exhibited by Ru(2,5-dpp)$(CO)_2Cl_2$ is not structured and is *blue-shifted* compared with the low-temperature emission. This last feature is quite unusual for a luminescence band, since increasing temperature generally causes a red shift, more or less pronounced depending on the solvent and the nature of the band.[4] We suggest that the low-temperature and high-temperature emissions have different orbital origins. On increasing temperature (and solvent melting) a MLCT excited state may be somewhat stabilized by solvent interaction, thereby becoming accessible by thermal excitation of the lowest lying LC level. Because of the higher spin–orbit coupling, the radiative decay of such a MLCT excited state can compete with radiationless transitions, whereas this cannot be the case for the LC level at high temperature. The relatively strong solvent dependence of the luminescence band at room temperature (20 000 cm^{-1} in AN and 19 300 cm^{-1} in CCl_4, $B \sim 1000$) supports a CT assignment.

Photochemical Behavior. The complexes examined exhibit two bands in the IR spectrum around 2000 cm^{-1}, typical of cis-coordinated CO groups.[33,45] Trans-coordinated CO groups usually show only one band at intermediate energy. On irradiation, the intensity of such IR bands decreases and a new band at lower frequency appears (Figure 7, inset), indicating that the photoproduct contains only one carbonyl ligand per metal unit.[33,45] The changes observed in the electronic absorption spectra are fully consistent with carbonyl release: the MLCT absorption moves to the red region because the metal becomes less positive (and thus, easier to oxidize), and the LC absorption feature at lower energy (λ = 354 nm in AN solution for Ru(2,5-dpp)$(CO)_2Cl_2$; Figure 7), which is typical of polypyridine ligands bound to highly charged metal cations,[33] is no longer observable.

Photoinduced CO release is a common phenomenon for metal carbonyls and is attributed to ^{3}MC excited states.[32] We believe that in our complexes CO release occurs via an activated crossing from the lowest ^{3}LC excited state to a closely lying ^{3}MC level, as also suggested by the luminescence results. A more detailed photochemical investigation, especially on the Ru(2,5-dpp)$(CO)_2Cl_2$ complex, which is luminescent at room temperature, has been planned in our laboratories.

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Electrochemical Behavior. The irreversible oxidation waves observed for the complexes and not present for the free ligands can be attributed to oxidation of the metal ion. The highly positive oxidation potentials (compared, e.g., to those of polypyridine complexes[4]) are in agreement with the electron-withdrawing effect of the CO ligands. Since oxidation is irreversible, we prefer to avoid any mechanistic speculation. We would only like to note that the dimetallic complexes exhibit only one (irreversible) oxidation wave, at slightly higher potentials compared to those of the monometallic species, indicating that there is scarce communication between the two metal centers, as was previously observed for other dimetallic carbonyl compounds.[31]

The first reduction potential is reversible for all complexes, indicating that reduction occurs in the aromatic ligand. The noticeable displacement toward less negative potentials in going from the free ligand to the monometallic and dimetallic species (Table III) was expected because the electron density on the ligands decreases on coordination to the electron-poor Ru atom of the $Ru(CO)_2Cl_2$ moiety. The correlation between the reduction potentials and the energies of the MLCT absorption bands (Figure 8) has been discussed above.

Conclusions

The monometallic and bimetallic complexes examined in this paper exhibit several interesting properties. The unusual combination of polypyridine, carbonyl, and chloride ligands leads to the presence of closely lying LC, MLCT, and MC excited states. The interplay between these three types of levels on changing temperature results in the presence of a strong LC luminescence at low temperature and of a strong photosensitivity (accompanied in one case by MLCT emission) at room temperature. The properties related to the aromatic bridging ligands (e.g., the reduction potentials) are strongly affected by coordination to the metal moieties, but the two $Ru(CO)_2Cl_2$ moieties practically do not communicate in the bimetallic complexes because of the strong withdrawing effect of the CO ligands.

Note Added in Proof. After submission of this work, a paper has appeared (Thomas, N. C.; Cox, J. *Polyhedron* **1988**, *7*, 731) on Ru(2,3-dpp)$(CO)_2Cl_2$ and (μ-2,3-dpp)$[Ru(CO)_2Cl_2]_2$. Absorption maxima are given at 538 nm for the former and at 596 and 448 nm for the latter. These data are in disagreement with our results (Table III) and seem to refer to partly photolyzed solutions.

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Registry No. 2,3-dpp, 25005-96-3; 2,5-dpp, 54266-39-6; Ru(2,3-dpp)$(CO)_2Cl_2$, 117247-58-2; (μ-2,3-dpp)$[Ru(CO)_2Cl_2]_2$, 116086-31-8; Ru(2,5-dpp)$(CO)_2Cl_2$, 120362-23-4; (μ-2,5-dpp)$[Ru(CO)_2Cl_2]_2$, 120362-24-5; $Ru(CO)_2Cl_2$, 16369-40-7.

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Far-IR Spectra and Normal-Coordinate Analyses of Halogenopentaamminechromium(III) Complexes

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The infrared spectra in the 60–500-cm^{-1} region of $[Cr(NH_3)_5X]^{2+}$ salts (X = F, Cl, Br, I) and their deuterated analogues have been recorded down to 35 K temperature. Normal-coordinate analyses performed on the CrL_5X skeleton by using a modified valence force field (MVFF) as proposed by Labonville et al. are able to reproduce the measured vibrational fundamentals very well. The calculated force constants for corresponding atomic group vibrations can be transferred to a good approximation from one compound to another. Appreciable intermixing of symmetry vibrations occurs only for some vibrational modes. Deviations from C_{4v} selection rules indicate larger distortions in the crystals of heavier halogeno compounds.

Introduction

Pentaamminechromium(III) complexes are currently used as sample compounds for studying low-symmetry effects on electronic energy level schemes derived from optical spectra.[1–3] Band assignments usually face the problem of how electronic level splittings due to lower symmetry can be distinguished from vibrational fine structure. For a solution of this problem the vibrational level scheme of the complex molecule must be available together with the symmetry assignments, which are usually obtained by normal-coordinate analysis of the vibrational spectra.

Concerning chromium(III) ammine complexes, such an analysis has been reported only for $[Cr(NH_3)_6]^{3+}$.[4–6] From systems of lower symmetry, some IR spectra covering the usual frequency region have been reported.[7,8] We want to add to these results some normal-coordinate analyses that we performed on the basis of far-IR and Raman spectra of halogenochromiumpentaammines and their deuterated analogues measured at low temperature. With use of the experience obtained on the hexaammine complex, the results are taken as the starting point for the low-symmetry cases allowing comparison of high- and low-symmetry vibrational level systems. All analyses were carried out for a CrL_5X skeleton of the chromophores in which the ammonia ligands are substituted by one-center units of 17 (NH_3) or 20 (ND_3) amu. This assumption already proposed earlier for other ammonia complexes[9] turned out to be a good approximation, yielding in the case of $[Cr(NH_3)_6]^{3+}$, for frequencies lower than 500 cm^{-1}, deviations of less than 2% compared to calculations performed for the entire complex with molecular NH_3 ligands. Correspondingly, coupling between internal NH_3 and ML_5X skeleton vibrations is found to be very small. For all calculations the point symmetry was assumed as C_{4v}, which is based on an X-ray structure analysis carried out only on $[Cr(NH_3)_5Cl]Cl_2$ and its Co and Rh homologues.[10]

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