$c \leq 0$), the bromo complexes are characterized by a predominance of the mono- and subsequently the dibromo complex. However, whatever the range of concentrations considered, in whichever of the two systems, there is always the simultaneous presence of at least two complexes.

Structure. The tetracoordinated copper ion has been widely studied in the solid state, and a comparison can be drawn between the spectra in solid state and in solution. The tetrachlorocuprate has been found to exist as a flattened tetrahedron (symmetry D_{2d}) or in a square-planar structure (symmetry D_{4h}). Both of these structures have different spectra, and the differences are more pronounced in the d–d transition band region.[37] The form of symmetry D_{4h} presents two absorption bands in the near-IR region:

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one at about 700–800 nm and another at about 950 nm. The form of symmetry D_{2d}, on the other hand, presents several d–d transition bands between 1100 and 2200 nm.

The tetrachlorocuprate, having an absorption maximum in the near-IR region at 1000 nm, has by analogy a square-planar structure in methanol. The similarity between the two solvents methanol and water has already been referred to, and these are the only two solvents in which $CuCl_4^{2-}$ has D_{4h} symmetry. In all other solvents studied, by they protic or aprotic,[30–32] its symmetry is D_{2d}.

The tetrabromocuprate has never been observed in a square-planar structure, and the results of all previous studies concerning solutions or solid state converge to attribute a D_{2d} symmetry for this ion. In methanol its absorption maximum has been calculated at 1060 nm, which is very near 1100 nm, and therefore it has a D_{2d} symmetry in conformity with all other studies.

Ruthenium(II) Complexes of 3,6-Bis(2-pyridyl)pyridazine: Synthesis, Characterization, and Effect of the Nonchromophoric Ligands on the Photophysical and Photochemical Properties

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The synthesis and characterization of a series of novel Ru(II) heteroleptic complexes containing the ligand 3,6-bis(2-pyridyl)-pyridazine (dppi) are reported. The absorption spectra (including their solvent dependence), luminescence spectra, luminescence decay, and photochemical reactivity of four of these complexes, containing the same chromophoric (dppi) ligand and different nonchromophoric ligands, are reported. The complexes studied are $Ru(dppi)(CO)_2Cl_2$, $Ru(dppi)(CO)_3Cl^+$, $Ru(dppi)(CO)_2$-$(COOC_2H_5)Cl^+$, and $Ru(dppi)(\eta^6\text{-}C_6H_6)Cl^+$. For comparison purposes, the properties of the free ligand have also been investigated. The absorption spectra of the complexes show intense ligand-centered (LC) bands in the UV region and moderately intense, broad metal-to-ligand charge-transfer (MLCT) bands at lower energies. The first three cited complexes exhibit a red shift of the lowest energy MLCT absorption bands with decreasing solvent polarity. All the complexes are luminescent in a rigid matrix at 77 K with a relatively long luminescence lifetime (10^{-5}–10^{-4} s), and their emission spectra are structured and red-shifted about 2000 cm^{-1} with respect to that of the free ligand. On the basis of these results, emission is assigned to a ^{3}LC excited state. The $Ru(dppi)(CO)_3Cl^+$ complex exhibits a double emission in acetonitrile or dichloromethane fluid solution at room temperature, and the luminescence spectrum and lifetime indicate that the emitting levels have MLCT and LC characters. The carbonyl complexes examined are all photosensitive in fluid solution, with release of a CO ligand, and the photochemical quantum yields appear to be related to the energy gap between the lowest excited state(s) and the reactive metal-centered (MC) level.

Introduction

The synthesis[2,3] and investigations on the chemical and physical behavior[3–7] of ruthenium(II) complexes with bipyridine-like N-polydentate chelating ligands have attracted the attention of an increasing number of research groups in the last 15 years. In fact, as a consequence of their unique combination of ground- and excited-state properties,[3–7] this class of coordination complexes has played and is still playing an important role in the development of several branches of pure and applied chemistry, such as photochemistry, photophysics, photocatalysis, electrochemistry, chemiluminescence, electrochemiluminescence, and supramolecular photochemistry.[6,8–12]

A key factor in determining the photophysical and photochemical behavior of transition-metal complexes is the relative energy of the ligand-centered, charge-transfer, and metal-centered excited states.[6] This relative energy depends on the chromophoric and nonchromophoric ligands, so that, in principle, one can design complexes with the desired properties by a judicious choice and combination of the ligands.

As a part of an investigation on mono- and binuclear complexes of the above class,[13] we report here the synthesis, the charac-

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

compd	ν(CO)	ν(C=C) and ν(C=N)	ν(Ru—Cl)	other
dppi		1586, 1570, 1560, 1534		
1	2072, 2003	1604, 1591, 1563, 1551	355	
2	2063, 1987	1602, 1591, 1569, 1550		
3	2052, 1989	1603, 1590, 1571, 1550	338	1640 [ν(COOR)]; 1055 [ν(OCOR)]
4	2053, 1990	1599, 1586, 1568, 1546	330	1625 [ν(COOR)]; 1045 [ν(OCOR)]
5	2140, 2088, 2079	1602, 1583, 1566, 1547	342	
6		1600, 1585, 1568, 1550		

[a] In units of cm^{-1}; KBr pellets.
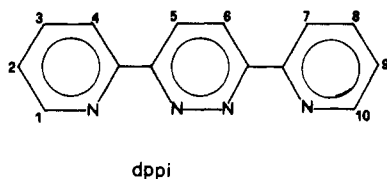
Figure 1. Structural formula of 3,6-bis(2-pyridyl)pyridazine (dppi).

terization, and the photochemical and photophysical properties of several ruthenium(II) complexes containing the chromophoric polypyridine ligand 3,6-bis(2-pyridyl)pyridazine (dppi, Figure 1), and the nonchromophoric ligands CO, Cl, COOC$_2$H$_5$, and η^6-C$_6$H$_6$.

Experimental Section

**General Information.** 3,6-Bis(2-pyridyl)pyridazine,[14] polymeric Ru-(CO)$_2$Cl$_2$,[15] [Ru(CO)$_3$Cl$_2$]$_2$,[16] and [Ru(C$_6$H$_6$)Cl$_2$]$_2$[17] were prepared according to literature methods. All reactions were carried out in the dark, under an inert atmosphere. Elemental analyses were performed on a Carlo Erba 1106 apparatus. For conductivity measurements (approximately 10^{-3} mol dm^{-3} light-protected solutions in nitromethane) a LKB 5300B Conductolyzer was employed. Infrared and ^{1}H NMR spectra were obtained with a Perkin-Elmer 1330 spectrophotometer and a Bruker AW 300 spectrometer, respectively.

Preparations. Ru(dppi)(CO)$_2$Cl$_2$ (1). A stirred suspension of [Ru-(CO)$_2$Cl$_2$]$_x$ (300 mg, 1.31 mmol) and dppi (308 mg, 1.31 mmol) in 25 mL of methanol was warmed at 50 °C for 24 h. The pale yellow microcrystalline precipitate was filtered off, washed with methanol and with diethyl ether, and vacuum-dried (574 mg, 90%).

Ru(dppi)(CO)$_2$I$_2$ (2). Complex 1 refluxed in methanol for 20 h with an excess of KI quantitatively yielded the corresponding diiodide as orange-yellow microcrystals.

Ru(dppi)(COOR)(CO)$_2$Cl (R = CH$_3$ (3), C$_2$H$_5$ (4)). A stirred suspension of [Ru(CO)$_3$Cl$_2$]$_2$ (102 mg, 0.20 mmol) and dppi (98 mg, 0.41 mmol) in 10 mL of the appropriate alcohol was warmed at 50 °C for 24 h. The orange-yellow solution was vacuum-evaporated to 2 mL and then allowed to stand overnight in a light-protected open vessel. The crude crystalline product was washed with alcohol and dried (3, 155 mg, 80%; 4, 190 mg, 95%).

[Ru(dppi)(CO)$_3$Cl]PF$_6$ (5). To a solution of [Ru(CO)$_3$Cl$_2$]$_2$ (106 mg, 0.21 mmol, in 5 mL of THF) was added a solution of dppi (97 mg, 0.54 mmol, in 7 mL of THF) and the mixture refluxed for 3 h. The resulting orange-pink solution was evaporated to dryness, the residue dissolved in
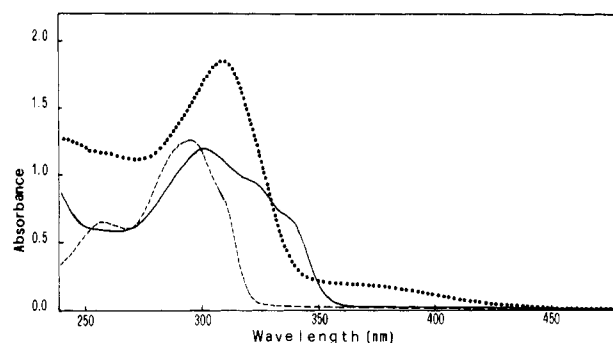
Figure 2. Absorption spectra of Ru(dppi)(CO)$_3$Cl$^+$ (—), Ru(dppi)-(CO)$_2$(COOC$_2$H$_5$)Cl$^+$ (∞), and dppi free ligand (- - -) in AN solution. $c = 4 \times 10^{-5}$ M for both complexes and ligand.
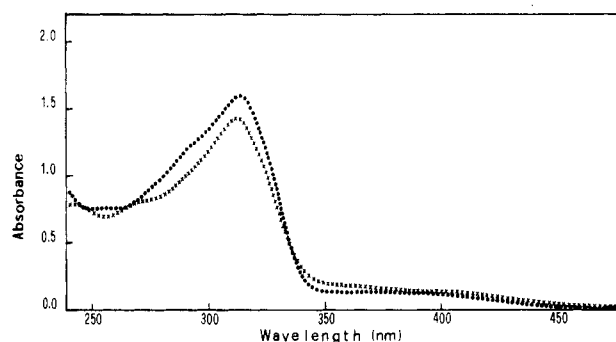
Figure 3. Absorption spectra of Ru(dppi)(CO)$_2$Cl$_2$ (∞) and Ru-(dppi)(η^6-C$_6$H$_6$)Cl$^+$ (×××) in AN solution. $c = 4 \times 10^{-5}$ M in each case.

methanol, and an excess of NH$_4$PF$_6$ added. The pale yellow microcrystalline precipitate was washed with alkaline water, methanol, and diethyl ether and dried (227 mg, 94%). $\Lambda = 96.9$ Ω^{-1} cm^2 mol^{-1}.

[Ru(dppi)(η^6-C$_6$H$_6$)Cl]PF$_6$ (6). [Ru(C$_6$H$_6$)Cl$_2$]$_2$ (50 mg, 0.10 mmol) was treated with dppi (94 mg, 0.40 mmol) in 5 mL of methanol at room temperature for 1 h. The mixture was filtered, and NH$_4$PF$_6$ (150 mg, 0.92 mmol) was added to the dark red solution. The yellow microcrystalline solid that formed was washed with methanol and diethyl ether and vacuum-dried (107 mg, 90%). $\Lambda = 88.7$ Ω^{-1} cm^2 mol^{-1}.

All new compounds gave satisfactory elemental analyses.

Photophysical and Photochemical Apparatus and Methods. The following solvents of the best commercial grade were used as supplied: acetonitrile (AN), methanol (MeOH), dichloromethane (CH$_2$Cl$_2$), butyronitrile (BN), tetrahydrofuran (THF), dimethylformamide (DMF), chloroform (CHCl$_3$), tetrachloromethane (CCl$_4$), ethanol (EtOH), and toluene.

The absorption spectra in the UV and visible regions were recorded with a Varian Cary 219 spectrophotometer and a Hewlett-Packard 8452A diode array spectrophotometer. Uncorrected luminescence spectra were obtained with a Perkin-Elmer LS-5B spectrofluorimeter equipped with a Thorn Emi 9781RO3 tube. Emission lifetime measurements were carried out with a JK System 2000 neodymium YAG DPLY 4 laser and a Tektronix 7612 digitizer for data acquisition. Emission quantum yields were measured at room temperature (298 K) by the optically dilute method,[18] the spectrofluorimeter being calibrated with a standard lamp. Ru(bpy)$_3$$^{2+}$ in aqueous solution was used as a quantum yield standard, assuming a value of 0.028.[19]

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Table II. 300-MHz ^{1}H NMR Spectra (δ, ppm) of the New Complexes

compd	$H_1/H_{10}{}^a$	H_2/H_9	H_3/H_8	H_4/H_7	H_5/H_6	other
dppi[b]	8.80 d	8.07 m	7.60 m	8.65 d	8.68 s	
1[b]	9.37 d/8.88 d	7.98 m/7.70 m	8.47 m/8.20 m	9.92 d/8.60 d	9.26 d/9.07 d	
2[b]	9.32 d/8.89 d	7.90 m/7.71 m	8.42 m/8.20 m	8.93 d/8.55 d	9.25 d/9.00 d	
3[c]	9.32 d/8.89 d	7.90 m/7.71 m	8.42 m/8.20 m	8.93 d/8.55 d	9.25 d/9.00 d	
4[c]	9.06 d/8.72 d	7.60 m/7.49 m	8.02 m/7.96 m	8.72 d/8.24 d	8.85 d/8.46 d	3.49 s (CH$_3$)
5[d]	9.10 d/8.84 d	7.94 m/7.64 m	8.48 m/8.08 m	8.65 d/8.61 d	9.14 d/8.87 d	1.06 t (CH$_3$), 3.87 q (CH$_2$)
6[d]	9.15 d/8.83 d	7.78 m/7.64 m	8.25 m/8.10 m	8.81 d/8.40 d	8.96 d/8.63 d	6.10 s (C$_6$H$_6$)

[a] Hydrogen numbers refer to positions quoted in Figure 1. Hydrogen 1 is the one nearest the metal-ligating pyridyl nitrogen. [b] In DMSO-d_6. [c] In CDCl$_3$. [d] In CD$_3$CN.

Table III. Spectroscopic Data and Photochemical Quantum Yields

complex or ligand	abs^a E, cm^{-1} (ϵ, M^{-1} cm^{-1})	lumin^b E, cm^{-1} (τ, μs)	photochem Φ^c
dppi	33 800 (31 500)	23 200 (476)	
Ru(dppi)(CO)$_2$Cl$_2$	26 500 (2700)	21 200 (77)	0.71
Ru(dppi)(CO)$_2$-(COOC$_2$H$_5$)Cl$^+$	27 500 (4100)	21 200 (112)	0.35
Ru(dppi)(CO)$_3$Cl$^{+\,d}$	29 500 (15 400)^e	21 300 (83)	0.11
Ru(dppi)(η^6-C$_6$H$_6$)Cl$^+$	24 700 (2900)	21 200 (83)	

^{a} Lowest energy maximum or shoulder; AN solution, 298 K. For the entire spectra, see Figures 2 and 3. ^{b} Energy of the highest energy feature of the emission band; MeOH/EtOH 4:1 mixture, 77 K. Estimated error in emission lifetime $\leq$10%. ^{c} Quantum yields of the photoreaction; MeOH solution, λ_{exc} = 365 nm. Estimated error ±10%. ^{d} Luminescence was also observed at room temperature (see text). ^{e} The anomalous higher extinction coefficient for this complex compared with the others is attributed to overlap of the lowest energy MLCT band with the LC band at higher energy.

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 centered at 365 nm. The light intensity incident in the reaction cell (5.1 × 10^{-7} einstein/min) was measured with a ferrioxalate actinometer.[20]

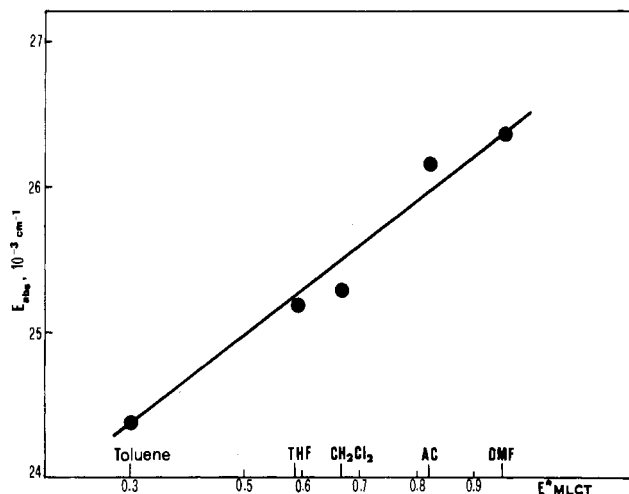When necessary, the solutions were deareated by bubbling nitrogen.

Results

Halogen-bridged polynuclear Ru(II) species, namely polymeric Ru(CO)$_2$Cl$_2$, [Ru(CO)$_3$Cl$_2$]$_2$, and [Ru(C$_6$H$_6$)Cl$_2$]$_2$, react easily with dppi, giving rise to the complexes whose IR and NMR data are reported in Tables I and II, respectively. [Ru(CO)$_2$Cl$_2$]$_x$ originates the unique product **1**, structurally characterized[13c] as the cis-dicarbonyl–trans-dichloro isomer. The diiodo analogue **2** was prepared in order to obtain useful information for the NMR assignments. The reaction products of [Ru(CO)$_3$Cl$_2$]$_2$ with dppi depend on the solvent: while in methanol and ethanol the corresponding carboalkoxy species **3** and **4** are produced, in THF the cationic fac-tricarbonyl complex **5** is formed. Treatment of [Ru(C$_6$H$_6$)Cl$_2$]$_2$ with dppi gives rise to the product **6**, a cationic complex arising from bridge breaking and the displacement of a chloride ion from the coordination sphere of the metal.

As indicated by the lack of change in their absorption spectra, all the complexes were thermally stable in the solvents used for at least 12 h.

The absorption spectra of the examined complexes and free ligand in AN solution are shown in Figures 2 and 3, and the wavelengths and extinction coefficients of the lowest energy absorption maxima or shoulders are gathered in Table III. The spectra of all the complexes containing carbonyl ligands exhibit a solvent dependence, particularly noticeable for the lowest energy absorption feature. Figure 4 shows the plot of the energy of the lowest absorption maximum of Ru(dppi)(CO)$_2$Cl$_2$ vs the E^*_{MLCT} solvent parameter.[21] For the other carbonyl complexes the same behavior is observed, but there is a large overlap of the solvent-sensitive band with the more intense absorptions at higher energies (see Figures 2 and 3).

At 77 K in a rigid alcoholic matrix (MeOH/EtOH 4:1 mixture) all the complexes exhibit similar structured emission spectra (e.g.,

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Figure 4. Plot of the energy of the lowest MLCT band vs the E^*_{MLCT} solvent parameter for Ru(dppi)(CO)$_2$Cl$_2$.
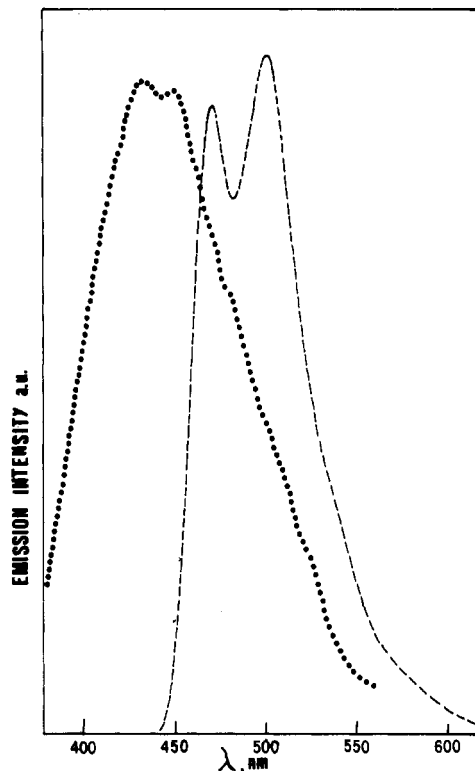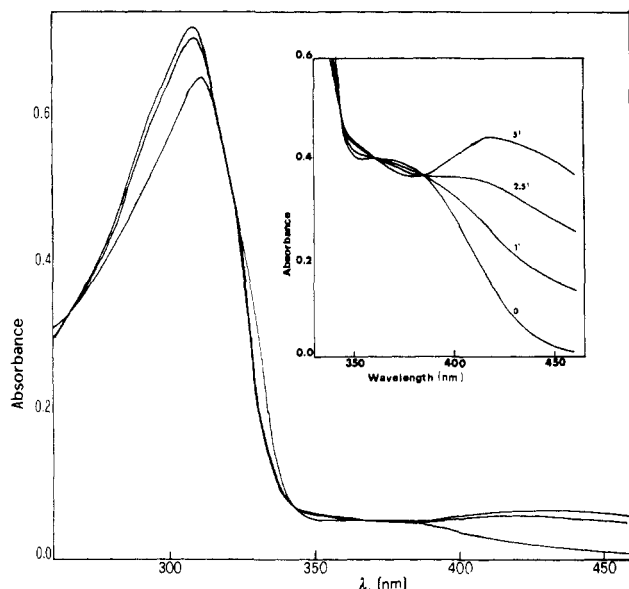

Figure 5. Emission spectra of Ru(dppi)(CO)$_3$Cl$^+$ (- - -) and dppi free ligand (ooo) in an MeOH/EtOH 4:1 mixture at 77 K.

see Figure 5 for the low-temperature emission spectrum of Ru-(dppi)(CO)$_3$Cl$^+$), which present the highest energy feature at about 21 200 cm^{-1} (Table III), vibrational progressions of about 1300 cm^{-1}, and lifetimes in the range 10^{-4}–10^{-5} s (see Table III). The free chelating ligand shows a structured luminescence band (Figure 5), with the highest energy feature at 23 200 cm^{-1}, and a lifetime of 476 μs. Such a value is slightly lower with respect

Figure 6. Spectra changes in the visible and UV regions on irradiation of Ru(dppi)(CO)₂Cl₂ in MeOH solution (excitation wavelength 360 nm). The irradiation times (in minutes) are indicated on the figure. In the entire figure only three curves are reported for clarity reasons.

to the lowest triplet excited-state emission lifetime of poly-pyridine-type molecules,[6,22,23] most likely because of acid–base interactions between the alcoholic solvent and the four nitrogen atoms; actually, in a rigid nitrile matrix (butyronitrile/propionitrile 5:4) at 77 K, the lifetime increases up to 1.4 ms, and the highest energy feature of the emission spectrum moves slightly to the red (22 900 cm⁻¹). In fluid solution at room temperature, only Ru-(dppi)(CO)₃Cl⁺ was luminescent (Figure 6), and its emission was observed to be strongly dependent on the solvent used: in alcohols no emission was noted.

All the carbonyl complexes examined were photosensitive. The changes in the UV–visible absorption spectrum for the complex Ru(dppi)(CO)₂Cl₂ in methanol solution upon irradiation are shown in Figure 7. A similar behavior was observed in each solvent employed. The quantum yields of the photoreactions in deaerated methanol solutions, measured from the increase in absorbance at 450 nm, are reported in Table III. The photochemical products on prolonged irradiation showed a slight photosensitivity, which was not further investigated.

Discussion

The photophysical and photochemical properties of transition-metal complexes are commonly discussed with the assumption that the states involved can be described in a sufficiently approximate way by localized molecular orbital configurations.[24] With such an assumption, the electronic transitions and excited states are classified as metal centered (MC), ligand centered (LC), and charge transfer (either metal to ligand, MLCT, or ligand to metal, LMCT). This approach is appropriate and useful in most cases[6,25] but is no longer strictly applicable when there is a large covalence in the metal–ligand bond in the ground state and if excited states of different nature are sufficiently close in energy to be intermixed.[26,27]

Absorption Spectra. By comparison between the spectra of the complexes and of the free ligand (Figures 2 and 3) one can assign the intense bands at about 300 nm in the complexes to metal-
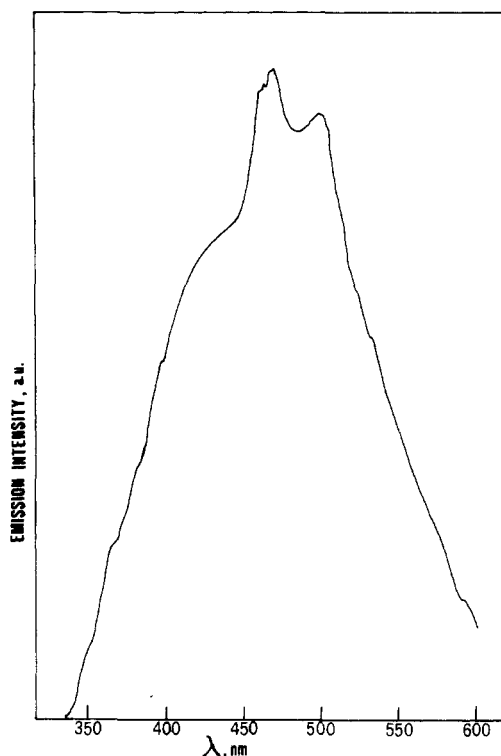
Figure 7. Emission spectrum of Ru(dppi)(CO)₃Cl⁺ in AN solution at room temperature (λ_exc = 340 nm).

perturbed ligand-centered transitions. Each complex also exhibits a broad, moderately intense absorption above 340 nm that can be assigned to charge-transfer (MLCT) transitions from Ru to dppi. The observations that lead to such an assignment as follows: (i) aside from the Ru(dppi)(η⁶-C₆H₆)Cl⁺ complex (vide infra), the bands are sensitive to solvent polarity;[6,21,28,29] (ii) the extinction coefficients are in the expected range for CT bands; (iii) the energies of the bands move to the blue with the increasing ligand field strength of the ligands, as expected for MLCT transitions in these complexes. Actually, one can observe that when a Cl ligand is replaced with a CO ligand, which has a stronger ligand field, the band moves to the blue; an intermediate effect is obtained for COOC₂H₅, whereas the π-coordination of the C₆H₆ group instead of two CO and one Cl ligand shifts the band to the red.

The strong solvatochromism of the MLCT bands of metal polypyridine carbonyl complexes has been explained in terms of differences between ground and excited states in both electric dipole moment and solvent polarizability.[21,28] Several solvent parameters can be used to correlate the solvatochromic effects.[30-33] The solvent parameter E*_MLCT, introduced recently by Manuta and Lees,[21] seems to be most appropriate to correlate the solvent sensitivity of metal polypyridine carbonyl complexes.[21,24,28,29] Our results confirm the expected trend (see Figure 4). The approximate value for the solvent sensitivity B[21] for the Ru(dppi)(CO)₂Cl₂ complex was 2000, an expected value for polypyridine complexes containing two carbonyl ligands.[28,34] The lowest energy absorption band of the Ru(dppi)(η⁶-C₆H₆)Cl⁺ complex was practically unaffected on varying the solvent, suggesting a small MLCT

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character of the related transition.

Luminescence. In principle, the luminescence of metal complexes can be due to metal-centered (MC), ligand-centered (LC), or charge-transfer (CT) excited states. The presence in the emission spectra of a vibrational structure with a progression of 1300 cm^{-1} (Figure 5), typical of the aromatic ligands,[6,23] indicates that a ^{3}MC nature can be excluded. Because of the constancy of the emission energy on changes of nonchromophoric ligands and, as a consequence, MLCT energy, a ^{3}CT assignment is excluded as well. Assignment of the emissions to dppi ^{3}LC, metal-perturbed transitions is quite plausible also because of (i) the small red shift compared with the emission of the free ligand and (ii) the relatively long lifetime.[6,22,23,27,34,35]

In fluid solution at room temperature, ^{3}LC emission can seldom be observed because of the occurrence of faster, thermally promoted deactivation processes often caused by surface crossing to distorted ^{3}MC states.[6] Such a behavior is likely the reason that for Ru(dppi)(CO)$_2$Cl$_2$, Ru(dppi)(CO)$_2$(COOC$_2$H$_5$)Cl$^+$, and Ru(dppi)(η^6-C$_6$H$_6$)Cl$^+$ emission is no longer observed at room temperature. In the Ru(dppi)(CO)$_3$Cl$^+$ complex, the presence of three CO ligands pushes the ^{3}MC level to higher energy, making difficult the ^{3}LC → ^{3}MC activated crossing. This is likely the reason the complex exhibits luminescence also in AN or CH$_2$Cl$_2$ fluid solution at room temperature (Figure 6). Its emission spectrum is structured, slightly blue-shifted with respect to the low-temperature emission (see Figure 5), and relatively long-lived (0.8 μs, emission quantum yield 0.006 in deaerated AN solution). Any attempt to time resolve two components in the emission spectrum has been unsuccessful. We believe that in this complex the room-temperature luminescence could be due to two different emitting levels, thermally equilibrated, of MLCT and LC character. The ^{3}MLCT excited state would be responsible for the (unstructured) emission band centered at about 23 200 cm^{-1}, whereas the ^{3}LC excited state could account for the structured emission corresponding to the low-temperature spectrum. This hypothesis also accounts for the blue shift in the emission spectrum

on increasing temperature, a quite unusual behavior for transition-metal complexes.[6] The lack of emission for this complex at room temperature in alcohol solvents is probably an expected behavior in view of the acid-base interactions involving the solvent and the peripheral nitrogens, in particular in the excited states. Strong acid-base interactions are reported to be responsible for introducing important channels for nonradiative decay in ruthenium pyrazine complexes.[36]

Photochemical Behavior. Photoinduced CO release is a common phenomenon for metal carbonyl complexes and is attributed to ^{3}MC excited states.[37] The changes observed in the electronic absorption spectra of the ruthenium(II) carbonyl complexes studied here (i.e., the displacement of the MLCT absorption band to the red, see Figure 7) are consistent with carbonyl release.[34,38] We believe that in our complexes CO release occurs via an activated surface crossing from the lowest excited state, LC in nature, to a closely lying ^{3}MC level. The photochemical quantum yields for the photoreaction (Table I) decrease in the series on going from Ru(dppi)(CO)$_2$Cl$_2$ to Ru(dppi)(CO)$_2$(COOEt)Cl$^+$ to Ru-(dppi)(CO)$_3$Cl$^+$, as the energy gap between the lowest excited state and the ^{3}MC level increases, according to the proposed mechanism.

Conclusions

The constancy of the chromophoric polypyridine ligand has offered us the possibility of studying the effect of the nonchromophoric ligands. The results show the key role of the relative energy position of the MC, MLCT, and LC excited states in determining photochemical behavior and luminescence properties of transition-metal compounds.

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